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AIR-SUSPENSION COATING OF DAIRY POWDERS: A MICRO-LEVEL PROCESS APPROACH

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ABSTRACT

Air-suspension particle coating is a process by which thin coatings are applied to powder particles. The coatings can be formulated to act as permeable barriers to increase powder shelf-life or to impart controlled release character. The ultimate objective of a coating operation is to produce individual particles, each with a well-controlled, even coating.

This project was focused on the air-suspension coating of fine powders of $\sim 100\ \mu\text{m}$ in diameter for the dairy industry. Despite the widespread use of the technology in the pharmaceutical industry, its use in the food industry has been limited. Little is known about the fundamental mechanisms, and so published work to date is product and equipment specific and is statistical in the way the experimental design and analysis has been approached. This 'black box' approach is time consuming and costly. Better methods based on an understanding of the physical and chemical mechanisms are needed to deal with the numerous products and constantly changing formulations typical of the dairy industry.

This thesis proposes a new approach to air-suspension particle coating research. The basis of this 'micro-level process approach', is to deconvolute the complex coating process into smaller manageable parts based on classical physical phenomena for which descriptions already exist. The thesis identifies and develops an understanding of the key micro-level processes controlling coated product quality and process performance. Four were selected for further study: drying, droplet impact and spreading, and stickiness which encompasses the two key micro-level processes of droplet impact and adherence and inter-particle agglomeration. They were studied separately to deconvolute the variable effects and interactions.

Kinetic data were collected for the drying droplets containing maltodextrins, whey protein isolate and gum arabic. A mathematical model, based on 'ideal shrinkage' was developed to predict the drying kinetics of single droplets with particular interest in the development of the surface glass transition temperature. The model accurately predicted the kinetics until significant morphological changes occurred in the droplet. To better predict the kinetics late in the drying process, the droplet radius was set to be constant at a time based on the surface proximity to the surface glass transition temperature (critical X concept). This was done to arrest droplet shrinkage in line with experimental observations and to more accurately depict the drying of high molecular weight, amorphous glass forming polymers. After this point, a new flexible calculation scheme was used to better predict the variation in internal droplet structure as either a dense, 'collapsed shell' structure or a 'dense skin-porous crumb' structure. Further study should focus on the surface and internal droplet structure (porosity and mechanical integrity) development during drying, particularly the conditions leading to the arresting of the droplet radius and the subsequent rate of skin thickness progression.

The critical X concept was used to make industrial-scale predictions of the optimum drying conditions that ensure maximum droplet impact and adherence efficiency and minimum inter-particle agglomeration in a Würster-style coating operation. This enabled the prediction of two key design parameters, the nozzle distance from the powder impact point and the Würster

insert height. The span in design parameters showed that there is significant opportunity for design optimisation based on the critical X concept.

A probe tack test was used to map the level of stickiness of droplets of different coating materials as they dried. As skin formation progressed, the stickiness passed through a maximum, in most cases to arrive at a point at which the droplet was no longer sticky at all (non-adhesive state). The maximum point of stickiness represents the ideal state to ensure successful droplet–substrate impact and adherence. The minimum point of stickiness represents the ideal state to prevent unwanted inter-particle agglomeration. The time interval between the onset of stickiness and the non-adhesive state was particularly dependent on the addition of plasticisers, but also on the formulation and the drying air conditions. Future work should look to establish a possible relationship between the surface glass transition temperature and the probe tack test stickiness measurements.

The impact and spreading of droplets containing maltodextrin DE5 on to solid anhydrous milkfat was studied using a high speed video camera. It was found that the final spread diameter was able to be fixed close to the maximum spread diameter by using surfactants, thus avoiding significant recoil. Because existing literature focuses on predicting the maximum spread diameter, this work defines a need for adequate prediction methods for the final spread diameter, as this is the significant parameter in coating applications.

Formulation and operating guidelines were established to independently optimise each micro-level process. These were used in a series of population based coating experiments in a pilot-scale Würster coater. This study highlighted the limited flexibility of the standard ‘off-the-shelf’ Würster coating apparatus for the coating of fine sized dairy powders. Because of this, the validation of the guidelines were inconclusive and optimisation could not be carried out. Further validation work is required on a custom-built apparatus for dairy powders.

This work has advanced the fundamental knowledge of the coating process and is independent of material, equipment and scale. This knowledge, based on physical and chemical mechanisms, can be used to develop coating formulations and identify optimum process conditions for successful coating in less time and at less expense than is current practice.

The next step is to put the guidelines into practice and craft the engineering of a continuous coating apparatus for dairy powder applications.

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I have always struggled to explain to people what I have been doing for the last three years (alright three and a half!). I almost have it now. A wise person once said, 'If it's green or wiggles it's biology, if it stinks it's chemistry, if it has numbers it's math, if it doesn't work it's technology'. I received a Bachelor in Technology (Chemical) so I know about stink and broken. I then decided to become an 'expert' in this field. Yet another wise, but not necessarily the same person defined an 'expert' as, 'someone who learns more and more about less and less, until he knows everything about nothing'. So there you have it. I am qualified for stink and broken, and what's more, I know heaps about not much. My future looks brite and there are a few people I must thank for helping me on to this bountiful path.

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CHAPTER 1

THESIS OVERVIEW

1.1 PROBLEM DEFINITION

Fonterra Co-operative Ltd, (here on Fonterra) has used spray drying microencapsulation to manufacture high intensity flavoured dairy powders for the flavours market. This is done using additives (e.g. maltodextrins) during the spray drying process that have the ability entrap/encapsulate the flavoured compounds in the particle matrix, thus functioning as a protective barrier. However, cheese powders manufactured by Fonterra can develop a noticeable oxidised flavour within weeks of the bag being opened or after 6–18 months of storage in an unopened bag.

Fonterra's encapsulation matrix was formulated as a compromise between extended shelf-life, flavour release and retention of key flavour volatiles during drying. By employing an outer post-coating to extend the shelf-life and help control flavour release, the encapsulation matrix could be optimised for volatile retention during spray drying and lead to reduced cost of manufacture.

1.2 PROPOSED SOLUTION

The loss of product quality, particularly flavour and odour, results from two major mechanisms: the volatilisation of the low concentration but intense 'top note' compounds and the oxidation of milkfat derived flavour compounds. The coating, in this instance, would provide a physical barrier to simultaneously limit the diffusion of oxygen into the lipid-flavour fraction of the particle matrix and the diffusion of volatile 'top note' compounds out of the particle matrix. Fonterra desired a method and detailed operating knowledge of air-suspension particle coating technology to compliment their knowledge on spray drying microencapsulation for the application of edible coatings to their dairy powders. Fonterra believed the technology would give them the ability to produce in the short term, longer shelf-stable powders and in the longer term, give them the ability to manufacture powders for controlled release applications.

1.3 THESIS OBJECTIVES

1.3.1 Overall thesis objective

This thesis set out to develop a method and detailed operating knowledge of coating fine (~100 μm diameter) dairy powders. However, the early literature review found that the statistical 'black box' nature of the literature was not suitable to developing a broad and

flexible technology to coat numerous potential powders under typical dairy industry operating constraints. Therefore, the overall thesis objective was narrowed to developing a phenomenological understanding of the air-suspension particle coating process to generate results that would be independent of both the substrate powder and the coating device.

1.3.2 Specific thesis objectives

At the end of Chapter 3, a plan was formulated to achieve the overall thesis objective. This resulted in the following specific thesis objectives.

1. To use a ‘micro-level process approach’ to air-suspension particle coating research.
2. To gain insight on how to control the key micro-level processes of drying, droplet impact and adherence, droplet impact and spreading, and inter-particle agglomeration.
3. To investigate chemical formulation as a means to achieving high coating quality with minimal inter-particle agglomeration.
4. Where possible, to develop phenomenological based guidelines for formulation and operation of air-suspension particle coating with application to the dairy industry.
5. To develop new characterisation techniques to study the key micro-level processes involved in the particle coating process.

1.4 THESIS SYNOPSIS

The structure of the thesis is set out as a series of chapters. Two literature reviews, a general review (Chapter 2) and a focused review (Chapter 3) were undertaken resulting in the four major experimental chapters (Chapters 5–8). Each experimental chapter contains a small but detailed literature review of the specific phenomenon the chapter investigates. A brief synopsis of the chapters is given below.

Chapter 1 is the thesis overview which defines the research problem, proposes a solution, defines the thesis scope and gives a synopsis of the thesis structure.

Chapter 2 presents a general literature review and determines the current ‘state of the art’ of air-suspension particle coating technology, with particular emphasis on the food industry. Coating technology, its principles, applications and objectives are introduced. The selection of coating materials, the equipment, key process variables and coating quality are all addressed. ‘Gaps’ in the literature are identified, and recommendations are made on how to advance the level of understanding of the mechanisms by which coating occurs and how these mechanisms can be applied in the dairy industry. Chapter 2 concludes that fundamental knowledge is limited. The current ‘state of the art’ employs experimental design and statistical analysis, which has led to results that are highly specific to material and equipment selection and have a long product development cycle. In the dairy industry, it is economically difficult to employ the current ‘state of the art’ because of low profit margins, high throughputs and ever-changing product formulations. A phenomenological study was recommended to generate results that would be independent of both the substrate powder and the coating device in order to apply them to the numerous different current dairy powders and future powders eligible for coating.

Chapter 3 is the key chapter that guided this thesis. A new ‘micro-level process approach’ to air-suspension particle coating research is proposed. The basis of the approach was to structure the large complex coating process into smaller manageable parts based on classical physical phenomena for which descriptions already exist. Deconvolution into micro-level

processes reduces the need for large experimental design and statistical differentiation of results and allows general guidelines with respect to coating formulation and operating conditions to be established. These guidelines will be more generic and less product/process specific than those obtainable from the current 'state of the art' experimental designs. The review identified ten fundamental phenomena (micro-level processes) that occur during an air-suspension particle coating process: particle motion, atomisation, droplet-particle collision, droplet impact and adherence, droplet impact and spreading, infiltration, drying, film formation, layering and inter-particle agglomeration. After consideration of their relevance with respect to their effects on the coating objectives, these ten micro-level processes were narrowed to four key micro-level processes for further study: drying, droplet impact and spreading, and stickiness which encompasses the two key micro-level processes of droplet impact and adherence and inter-particle agglomeration. They were studied separately to deconvolute the variable effects and interactions.

Chapter 4 is the materials characterisation and methods section which identifies potential coating materials suitable for dairy applications and characterises some of the physical and chemical properties used throughout the thesis.

Chapter 5 presents the drying kinetics for maltodextrins DE5, DE10 and DE18, whey protein isolate and gum arabic on a single droplet drying apparatus. Morphological observations show that skins form which affect the drying rate and subjective stickiness of the droplets as they dry. Plasticisation of the maltodextrin DE5 and whey protein isolate droplets results in faster drying rates, less severe surface warping and an increase in the subjective stickiness. A mathematical model was developed (in Appendix A2) based on the effective diffusion model and incorporating temperature discretisation. It successfully predicts the drying kinetics of maltodextrin DE5 but, late in the drying process when skin development becomes significant, the model under-predicts the evaporation rate. This can be accounted for by considering that the skin becomes thick and strong enough to arrest the droplet contraction. A critical surface condition (when the critical $X = (T - T_g) = 20\text{ }^{\circ}\text{C}$) was used to fix the droplet radius during the simulations. After this point, a new flexible calculation scheme was used to better predict the variation in internal droplet structure being able to predict a dense, 'collapsed shell' structure or a 'dense skin-porous crumb' structure. These modifications significantly improved drying kinetic predictions. The critical X concept was used to make industrial-scale predictions of the optimum drying conditions to ensure maximum droplet impact and adherence efficiency and minimum inter-particle agglomeration in a Würster-style coating operation. This enabled the prediction of the key design parameters of the nozzle distance from the powder impact point and the Würster insert height. The span in design parameters showed that there is significant opportunity for design optimisation based on the critical X concept.

Chapter 6 characterises stickiness development in potential coating formulations as they dry by using a probe tack test on individual droplets. Skin formation occurs in all the trials which resulted in profiles showing increasing stickiness during drying up to a maximum. After this point, stickiness fell away until the surface was completely non-sticky. The maximum point of stickiness represents the ideal state to ensure successful droplet-substrate impact and adherence. The minimum point of stickiness represents the ideal state to prevent unwanted inter-particle agglomeration. The time interval between the onset of stickiness and the non-adhesive state was particularly dependent on the addition of plasticisers, but also on the formulation and the drying air conditions.

Chapter 7 investigates droplet impact and spreading on an anhydrous milkfat surface to provide insight into how to achieve control of coating quality parameters such as coating

thickness and coating coverage. Of particular interest to this work was the maximisation of the final spread diameter. Formulation and operating guidelines to achieve a maximum final droplet spread diameter were established. Surfactant incorporation into the droplet, to lower the liquid–vapour interfacial tension, did not affect the maximum spread diameter but significantly limited droplet recoil and gave final spreading extents three times the initial droplet diameter. Higher impact velocities and droplets of lower viscosity also resulted in greater final spread diameters.

Chapter 8 highlights the key findings from the previous chapters with respect to controlling the micro-level processes and presents the results of a series of population based coating trials on a pilot-scale Würster coater. A spray droplet adhesion efficiency study was conducted. As expected from the formulation and operating guidelines established in Chapter 6, higher initial solids concentrations and higher drying air temperatures led to the over-drying and subsequent decrease in the time the droplet surface is sticky. This ultimately resulted in a decrease in the amount of coating mass deposited on the substrate particles. This study highlighted the limited flexibility of the standard ‘off-the-shelf’ Würster coating apparatus for the coating of fine sized dairy powders. Because of this, the validation of the guidelines were inconclusive and optimisation could not be carried out. Further validation work is required on a custom-built apparatus for dairy powders. Recommendations are made for the coating of dairy powders on an industrial-scale.

Chapter 9 presents the thesis conclusions and suggestions for future work.

Appendices are also included. Appendix A1 tabulates the nomenclature used throughout the thesis. Appendix A2 presents the single droplet drying kinetics mathematical model development. Appendix A3 discusses the single droplet drying kinetics mathematical model program source code.

A copy of the mathematical model program source code is incorporated on a CD inside the back cover of this thesis. The CD also presents selected probe tack test and droplet impact and spreading test videos.

1.5 THESIS SCOPE

The thesis represents a novel approach to air-suspension particle coating research. The proposed ‘micro-level process approach’ focuses key phenomena into manageable parts. Each micro-level process and its corresponding experimental investigation has the potential to constitute a thesis of its own. However, emphasis was placed on developing an overall picture of the key phenomena controlling air-suspension particle coating process objectives. As a result, the various literature reviews may not contain all the relevant information on each micro-level process.

Prediction of air-suspension particle coating has many practical problems; the relationships, are complex, conditions are non-ideal (e.g. chemical and physical irregularities of the substrate surface, disperse particle and droplet populations) and the micro-level processes are sensitive to small inaccuracies in the starting conditions. The objective was not to further develop the fundamentals to offer better predictions than can already be made. Rather, the approach taken here was to seek out existing phenomenological explanations and predictive tools from other research fields and to apply them in the context of the air-suspension particle coating process.

CHAPTER 2

AIR-SUSPENSION PARTICLE COATING TECHNOLOGY – ‘STATE OF THE ART’

2.1 INTRODUCTION

Microencapsulation is a broad term given to a collective of techniques that attempt to coat or entrap a material or mixture of materials within another material or system [Risch (1995)]. Spray drying is used to produce more than 90% of the encapsulated flavourings on the market [Reineccius (1994)]. Spray drying microencapsulation does not lend itself to a clearly defined core and coating; rather spray-dried products consist of a homogeneously blended matrix of the polymer entrapping the particle [Dziezak (1988)]. Air-suspension particle coating has the ability to produce (albeit with larger particle sizes to date) particles wholly contained within a thin continuous coating. Additionally, it offers the benefit of continued recycling of the powder to build up the coating layer to a desired thickness and has the ability to supply successive coatings of different materials useful for controlled release applications. As a result, air-suspension particle coating offers greater opportunities in terms of product protection and control.

This review determines the current ‘state of the art’ of air-suspension particle coating technology, with particular emphasis on the dairy industry. Coating technology, and its principles, applications and objectives are introduced. The selection of coating materials, and the equipment, key process variables and coating quality are all addressed. ‘Gaps’ in the literature are identified, and recommendations on how to advance the level of understanding of the mechanisms by which coating occurs and how these mechanisms can be applied in the dairy industry are made.

2.2 OPERATING PRINCIPLE

The basic principle of both air-suspension particle coating (also referred to as spray coating or fluid bed coating) and agglomeration operations is to atomise a fine liquid spray into a bed of fluidised particles. The spray consists of a solute which acts as a coating medium, and a solvent in which the solute is dissolved or slurried. The liquid impinges and spreads on the particles. The fluidisation air evaporates the solvent, leaving a layer of solute on the surface of the particle. Figure 2.1 shows schematically the two possible particle growth mechanisms that can occur in a fluidised bed.

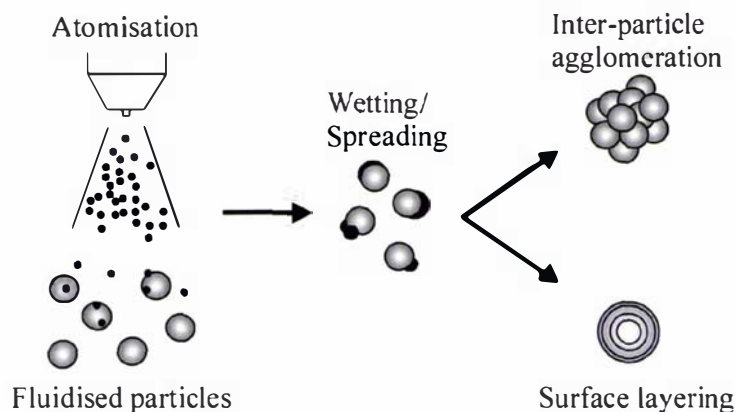


Figure 2.1: Two particle growth mechanisms (inter-particle agglomeration and surface layering) in an air-suspension particle operation [adapted from Link and Schlünder (1997)].

In the first case, particle growth takes place by coalescence of two or more particles, termed inter-particle agglomeration, or simply, agglomeration. The wetted particles are held together by liquid binding bridges which are converted to solid binding bridges when they dry [Link and Schlünder (1997)]. When agglomeration is the purpose, the process is often referred to as granulation. Granulation is essentially a size enlargement process carried out to alter key powder characteristics such as bulk density, flowability, wettability, dispersibility and dustiness.

This study concentrates on the second mechanism of particle growth, which occurs by the layering of solids on to the surface of single particles, termed surface layering or coating. In this instance, the wetted particles dry sufficiently before collision and thus are prevented from agglomerating [Link and Schlünder (1997)]. The objective of coating is to produce individual particles, each with a well-controlled, even coating [Turton *et al.* (1999)]. The operating conditions are optimised to minimise agglomeration. In general, this requires ‘dry’ or solvent-lean conditions with intensive fluidisation.

2.3 INDUSTRIAL APPLICATIONS

Solid particle coating has found specific applications in the agricultural, chemical, petroleum, cosmetic, food and pharmaceutical industries. Air-suspension particle coating is still a batch process and is expensive and time consuming, but is used in the pharmaceutical and cosmetic industries, which are able to compensate for the cost of the process by the high price of their final product [Teunou and Poncelet (2002)]. As a result, the overwhelming majority of the literature on air-suspension particle coating resides in the pharmaceutical literature.

The food industry is aware of the potential of particle coating technology and has identified numerous potential applications for its use. These include separation of ingredients from their environment (water, acid, oxygen, other food ingredients), which may be detrimental to the uncoated material or the food itself; stabilisation of the ingredient during processing (heat, pressure, moisture); to impart controlled release (during processing, storage or consumption); to change the physical characteristics of the original material by reducing the hygroscopicity, improving the flowability and compression properties, reducing dustiness or modifying density [DeZarn (1995); Reineccius (1995)].

Air-suspension particle coating has been slow to develop in the food industry [Dewettinck *et al.* (1999)]. Only limited, and application-specific, information regarding specific fluid bed processing techniques, including optimum processing conditions is available in the literature [DeZarn (1995)]. This slow development is not surprising given the limitations imposed on the food industry for the use of edible low cost ingredients and low cost processing. The food industry is typically a large volume, low cost and low profit industry where every cent of additional cost per kilogram of product is important [Reineccius (1995)].

To the author's knowledge there has not been a significant, if not a single, publication of an application of air-suspension coating of dairy powders in the public domain. Additionally, Fonterra is not aware of any competitor dairy powder on the market that is coated by an air-suspension technology, other than lecithinated powders [R. H. Archer, Massey University, personal communication, 17 March, 2004]. The work conducted here is likely to represent the first concerted effort on the air-suspension coating of dairy powders.

2.4 COATING OBJECTIVES

2.4.1 Ultimate objective

In general, the ultimate objective of a coating process is to produce individual particles, each with a well-controlled, even coating [Turton *et al.* (1999)]. Fonterra has a desire for a technology that can deliver thin coatings (less than 5% of the product weight) with near 100% coating coverage and no inter-particle agglomeration. These specifications represent a significant challenge to the air-suspension particle coating field.

2.4.2 Product quality objectives

Turton *et al.* (1999) discussed product quality with reference to air-suspension particle coating. The term 'quality' refers to one or several properties or specifications of the finished product, e.g. loading of the active ingredient, dissolution characteristics, appearance and shelf-life, to name but a few. A goal of a coating process is to obtain repeatable 'quality' standards. Quality can be measured on a macroscopic level (coater performance) or a microscopic level (coating quality). The macroscopic level is discussed below, and the microscopic level is discussed in more detail in Section 2.8.

2.4.3 Coater performance objectives

Maa *et al.* (1996) evaluated coater performance based on three criteria: product quality, product yield and production time. Teunou and Poncelet (2002) defined four coating performance criteria: material efficiency, energy efficiency, quality efficiency and productivity efficiency. Ideally, an optimum operation should produce a high quality product at a high yield, with low production cost and in a short production time. Inevitably, there is a trade-off between these performance indicators. The optimum will vary based on the product and its application. For example, the adoption by the dairy industry of air-suspension coating technology necessitates high product throughputs of the order of 2–20 tonnes of dry powder per hour. This is likely to compromise some aspects of quality.

2.5 COATING MATERIALS

The liquid in the coating solution is merely a vehicle to transport the coating material to the substrate surface and can be either aqueous (water) or an organic solvent. The dairy industry is limited to an aqueous carrier because of stringent food regulations as well as the high costs involved with solvent recovery systems. Because of the limited application of air-suspension coating in the food industry, the literature on edible films was reviewed to provide insight on potential coating materials (solutes). This literature includes the casting of free-standing films (intended for coatings on produce such as nuts, fruit and vegetables) and the assessment of permeability and mechanical strength. Three different types of coating solute were identified.

1. Aqueous soluble polymers such as proteins (milk, nut) and carbohydrates (starches, starch derivatives, gums).
2. Aqueous dispersion polymers such as latexes (e.g. Eudragits® based on acrylic copolymers) and pseudolatexes (e.g. Aquacoat ECD® based on ethyl cellulose).
3. Hot melt coatings such as lipids (fatty acids, polyglycerides and derivatives) and waxes (carnauba, beeswax, candelilla).

The choice of an appropriate coating material is influenced mainly by the specified core [Dewettinck *et al.* (1998)] and the ability of the coating material to impart the desirable characteristics to the product [King (1995)]. Although the performance of the coating material in the final application is crucial, matching of the material to the process technology and process conditions is likely to be of equal importance, and yet is almost certainly overlooked in practice. This lack of matching helps to explain why a large number of coating materials must typically be tested in order to determine their suitability when a product is developed [Kleinbach and Riede (1995)]. Therefore, there is merit in establishing guidelines for polymer selection, based not only on their performance in the final application but also on their behaviour in a coating process.

2.6 COATING EQUIPMENT

In the food industry, the processes of granulation, drying and coating are generally carried out using batch fluid bed equipment [Teunou and Poncelet (2002)] but with slight modifications to both the equipment design and the operating conditions. There are several different process arrangements for air-suspension particle coating. The liquid feed can be applied by using one of three modes: top-spray, bottom-spray and tangential-spray. Particle motion may be in a spouted bed, a vibro-bed, external recirculating beds or a Würster coater. For a comprehensive review of the operating principles, along with the advantages and disadvantages of the different coating equipment arrangements, the reader is referred to the works of Jones (1988) and Olsen (1989a,b).

The dairy industry has extensive experience with the lecithination of dairy powders in continuous vibro-beds. Although it would be desirable to extend the capabilities of these beds to coating with aqueous soluble materials, this is not advocated here. The beds are run at very high particle to air ratios, meaning that the particles are in close proximity and flow as a plug along the bed, which encourages agglomeration. Particle mixing is minimal (apart from a small amount of backflow) and vertical segregation of the larger particles towards the bottom of the bed is likely to occur. Under these operating conditions, achieving the stated quality and process objectives of coating in a vibro-bed is difficult.

The Würster-based fluid bed process is the preferred method for the application of functional coatings in the pharmaceutical industry [Cheng and Turton (2000a)] as it is more efficient with respect to the quality of the coating that is formed [Christensen and Bertelsen (1997); Teunou and Poncelet (2002)]. Figure 2.2 shows the chamber geometry and the auxiliary equipment of a typical Würster coater.

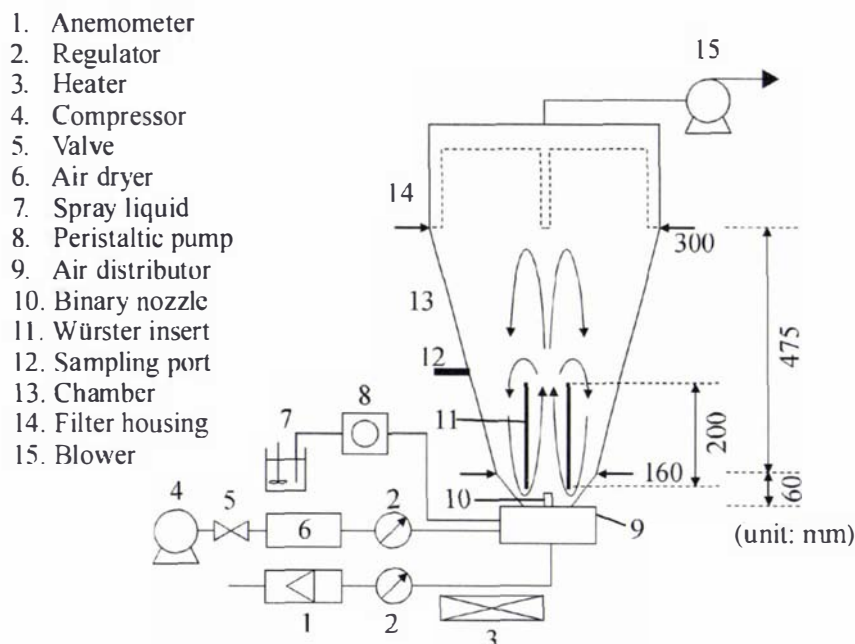


Figure 2.2: Schematic drawing of a typical laboratory-scale Würster coater showing auxiliary equipment and typical dimensions [adapted from Jono *et al.* (2000)].

The Würster coater is the most promising equipment arrangement for application in the dairy industry. All further discussion in this thesis is with respect to the Würster coating process. Section 8.4.3 discusses potential processing scenarios applicable to the dairy industry.

2.7 KEY PROCESS VARIABLES

Air-suspension particle coating is a complex process consisting of three major operations (fluidisation, atomisation and drying [Maa *et al.* (1996)]) and involves as many as 20 different variables [Knezevic *et al.* (1998)]. Table 2.1 [constructed from tables presented in Maa *et al.* (1996) and Cheng and Turton (2000a)] summarises the key parameters involved in the spray coating process. These parameters are process variables, system design variables and physical properties of the particle and the coating liquid.

Table 2.1: Key variables for air-suspension particle coating

Fluidisation	Drying air flowrate ^a Equipment type and dimensions (Würster, tangential etc.) ^b Substrate size, size distribution, density ^d Substrate surface character (charge or chemical composition, i.e. fat-containing) ^d Batch size ^{a,b}
Atomisation	Spray mode (top, bottom etc.) ^b Droplet size ^a Nozzle design (pneumatic, ultrasonic, rotary etc.) ^b Nozzle distance from bed ^a Atomising air flowrate (pneumatic) ^a Coating spray rate ^a Coating solution viscosity, surface tension, density ^c
Drying	Inlet temperature ^a Drying air flowrate ^a Outlet air relative humidity ^a Liquid coating concentration ^a Atomising air flowrate ^a

Key: ^a process variables, ^b system design, ^c coating material properties, ^d particle properties.

According to Link and Schlünder (1997), the trial and error method together with experience is still the only method for determining the optimum operating conditions for air-suspension particle coating. This is because of the complexity caused by the number of components, the fast kinetics, the differences in local conditions [Polke and Schäfer (2002)] and the feedback caused by particle and air recirculation. For example, take the complex effect of atomisation pressure [Dewettinck and Huyghebaert (1998)] applied in pneumatic nozzles on coating efficiency, as shown in Figure 2.3.

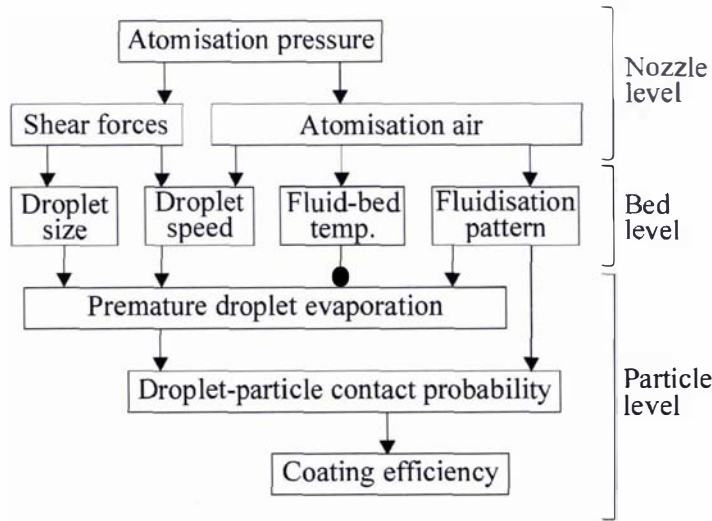


Figure 2.3: The complex effect of atomisation pressure applied in pneumatic nozzles on coating efficiency [adapted from Dewettinck and Huyghebaert (1998)]. Note: coating efficiency here is defined here as the mass of coating deposited per mass of coating material supplied.

Given that many other process variables are also important, it is easy to see that air-suspension particle coating is a complex process. In order to draw conclusions from coating investigations, it is necessary to deconvolute these complex interactions by studying a single operation at a time. Once the key variables for that operation are understood, then their effects and interactions on subsequent operations can be established and the process can be repeated until a semi-phenomenological (as opposed to statistical) picture of the entire system can be constructed.

2.8 COATING QUALITY

According to Kleinbach and Riede (1995), the process parameters necessary to achieve an optimum coating quality still tend to be found by experimental means. As a result, the product development process can become time consuming and expensive. At the microscopic level, the variation in quality can be characterised as a function of two factors, coating mass uniformity and coating morphology. Turton *et al.* (1999) discussed the important difference between these factors. Each is discussed below. Both the coating mass uniformity and the coating morphology are important when, for example, the coating is applied for a sustained release or barrier film application. However, the ‘acid test’ for coating quality is the performance in the desired application. It may well be found that an 80% coating coverage (coating morphology) is all that is required for the coating to perform adequately in the desired application.

2.8.1 Coating mass uniformity

Coating mass uniformity refers to the variation in the amount of coating material each product particle receives during a batch coating operation [Turton *et al.* (1999)]. Figure 2.4 depicts a variation in coating mass uniformity.

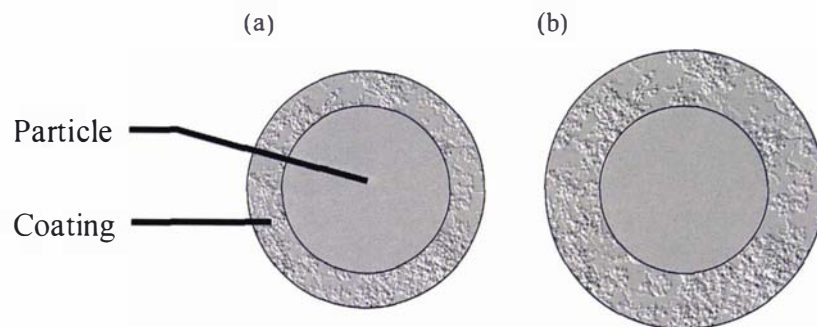


Figure 2.4: Cross-section of coated particles depicting variation in coating mass uniformity: (a) uniform, thin coated particle; (b) uniform, thick coated particle.

Here, both particles have the same characteristics of size, density, surface character and porosity but contain different masses of coating material. The mass uniformity is important when an active ingredient is applied in the coating. To date, most of the literature on air-suspension particle coating has focused on coating mass uniformity, e.g. Wesdyk *et al.* (1990), Cheng and Turton (2000b) and Sudsakorn and Turton (2000). Turton and coworkers at West Virginia University, Morgantown, USA, have made significant headway into understanding the factors affecting the variation in product coating mass uniformity in Würster coating operations. Cheng and Turton (2000a) attributed this variation to two sub-processes, namely (a) variations due to the number of particle passes through the spray zone and (b) variations due to the amount of material deposited per particle per pass through the spray zone. They found that (a) only accounted for a few percent deviation about the mean

and that (b) was far more significant. This is a key finding and suggests that the focus of investigations into coating mass uniformity should be directed towards determining how best to reduce the variation in mass deposited per pass.

Cheng and Turton (2000b) postulated that the coating mass variation per pass through the spray zone is due to the sheltering effect that particles close to the spray nozzle have on particles further away from the source of the spray. Based on geometric arguments, they presented a model for the mean and variance of the distribution of coating material on a particle in the spray zone. Analysis of the model showed that, as the voidage of the spray zone approaches unity, the variation in the product coating tends to zero, which is expected for very lean phase flow in the spray. Theoretical model predictions showed only a fair agreement (correct order of magnitude) with the experimental coefficients of variation (COV) because of the model's many simplifying assumptions. This model is the first to present a phenomenological picture of the major cause of coating variation, but still relies on experimental design and statistical analysis to yield equations describing the COV and is thus product and process specific. They concluded that, in order to accurately predict how changes in operating conditions will affect coating mass uniformity, a better understanding of the phenomena occurring in the spray zone is needed.

2.8.2 Coating morphology

Coating morphology refers to the variation of a given property between particles containing the same amount of coating material, i.e. uneven distribution of a coating material on a particle [Turton *et al.* (1999)]. Figure 2.5 illustrates variation in coating morphology.

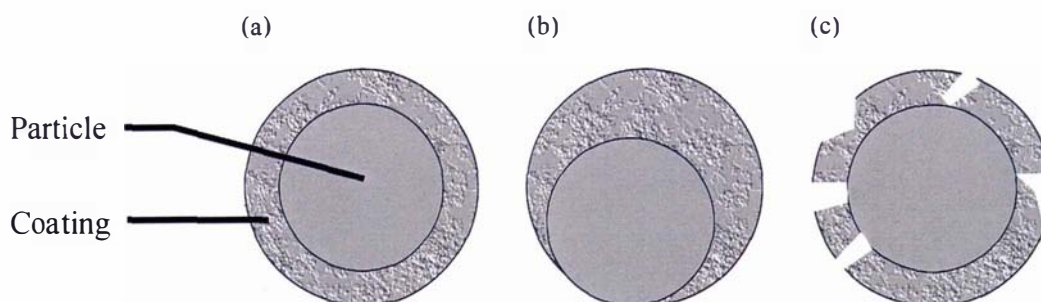


Figure 2.5: Cross-section of coated particles depicting variation in coating morphology: (a) uniformly coated particle; (b) non-uniformly coated particle; (c) coated particle with fissures.

All three particles have the same volume and have the same mass of coating material; however, in (b), this mass is unevenly distributed and is concentrated on one side of the particle, leaving an area of the particle exposed to its environment. Coating morphology also refers to the appearance or composition of the coating, which may contain amorphous and crystalline structures, porosity and fissures, as shown in (c). The coating morphology becomes an important quality determinant if there is incomplete film formation, resulting in coating imperfections such as porosity and fissures.

There is little literature on attempts to resolve issues related to achieving consistent coating morphology. Guignon *et al.* (2002) stated that it is difficult to predict the final structure as a smooth or non-continuous film. Two research groups have focused their research on coating morphology: Dewettinck and coworkers [Dewettinck (1998); Dewettinck and Huyghebaert (1998); Dewettinck *et al.* (1998); Dewettinck *et al.* (1999)] from the University of Ghent, Belgium, and Link and coworkers [e.g. Link and Schlünder (1997)] from Universität Karlsruhe, Germany. The Ghent group investigated the coating morphology and

agglomeration tendency of various food-grade coating materials with an emphasis on using the physico-chemical properties of the coating materials (hygroscopicity, viscosity, surface tension and glass transition data) to explain their results. The Karlsruhe group developed a unique apparatus in which a single, freely suspended, rotatable sphere can be coated under well-defined and constant coating and drying conditions [Link and Schlünder (1997)]. The device allows the direct observation of subsequent coating mechanisms such as droplet deposition, spreading, and drying.

Both the Ghent and Karlsruhe groups used scanning electron micrographs (SEM) to investigate coating morphology. Their key observations are discussed below with respect to key variables.

Although dried under different conditions, the polymer type will have a significant bearing on the coating morphology. Figure 2.6 shows the appearance of fine cracks in particles coated with (a) polyvinylpyrrolidone (PVP) and (b) hydrolysed gelatine. These cracks are not evident in a hydrolysed starch (maltodextrin DE18) coating (c). The cracks result from shrinkage during the drying process, which causes stress fractures in the coating. In these instances, addition of a plasticiser may help to reduce the rigidity of the coating during drying. The results illustrate the importance of understanding morphological changes during drying in order to produce thin, smooth, coherent coatings.

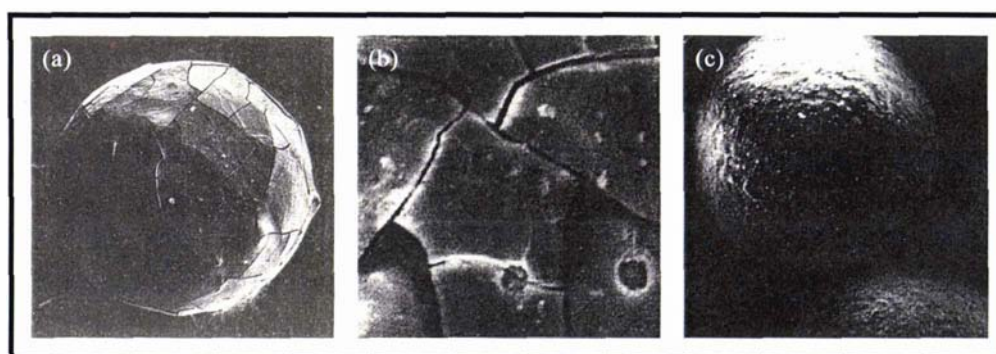


Figure 2.6: Fractures in coating surfaces: (a) PVP [taken from Link and Schlünder (1997)]; (b) hydrolysed gelatine [taken from Dewettinck *et al.* (1999)]; (c) hydrolysed starch (maltodextrin DE18) [taken from Dewettinck *et al.* (1999)].

Figure 2.7 shows a magnified image of the PVP surface coating in which the spreading and the coalescence of the PVP droplets are evident. Kleinbach and Riede (1995) gave an intuitive analysis that resulted in three key actions that can be taken to increase the quality of the coating: improving the spreading properties, diluting the coating material and using small droplets. However, no quantitative tools could be found in the literature on air-suspension particle coating on how far a droplet is likely to spread for various formulations and operating conditions. Maximising the spreading of the coating droplets should lead to greater surface coverage and better control of coating thickness.



Figure 2.7: Evidence of droplet spreading and coalescence on a PVP-coated particle [taken from Link and Schlünder (1997)].

Morphology is also affected by liquid viscosity. Figure 2.8 shows various degrees of droplet spreading and coalescence of three coating materials.

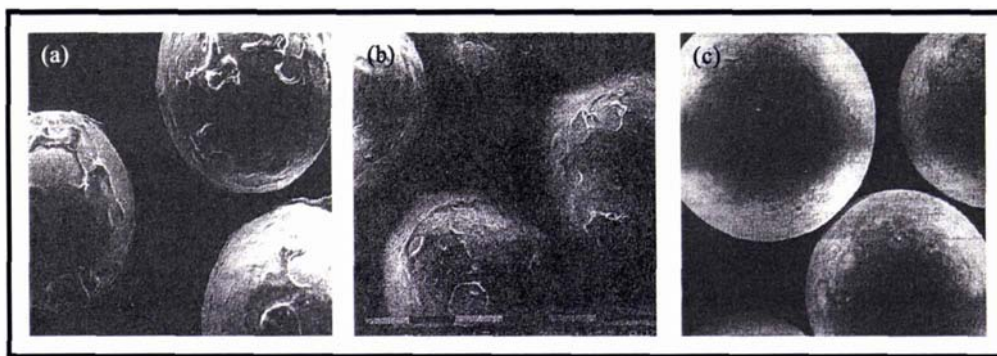


Figure 2.8: Various degrees of spreading and coalescence on coated particles: (a) a high viscosity (933 mPa.s) carboxymethylcellulose (CMC) coating solution; (b) low viscosity (8 mPa.s) CMC; (c) locust bean gum (548 mPa.s) [all from Dewettinck *et al.* (1998)].

It is obvious that viscosity alone cannot explain the difference in the extent of spreading as the locust bean gum with intermediate viscosity showed a smooth coating morphology. Dewettinck *et al.* (1998) suggested that the higher hygroscopicity of the high viscosity CMC may have been responsible for the poor coating quality. According to Dewettinck *et al.* (1998), the 'wet film properties rather than solution properties determine the agglomeration tendency'. Given that surface layering is a subset of granulation [Turton *et al.* (1999)], it is likely that the wet film properties are also important to successful coating. This is a key point, in that merely knowing the physico-chemical properties of the starting solution will not guarantee simple prediction of coating performance. Knowledge of the physico-chemical properties as coatings dry is therefore required.

A drying coating may also develop porosity. Figure 2.9 shows porosity development in a 20% w/w aqueous solution of sodium chloride.

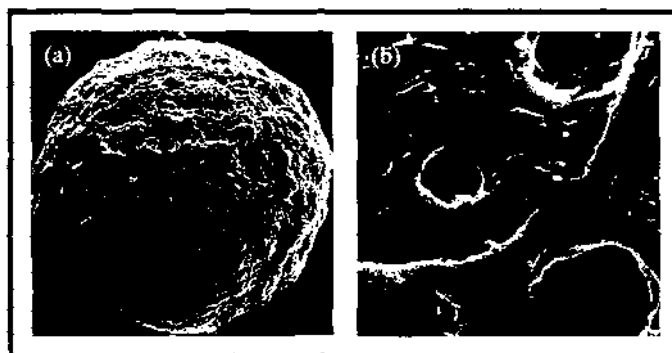


Figure 2.9: Evidence of porosity in a 20% w/w aqueous solution of sodium chloride [taken from Link and Schlünder (1997)]: (a) original particle (diameter is approximately 1.3 mm); (b) 10 times magnification.

The development of porosity in coatings will afford the particle less protection. It is uncertain how the porosity develops. It is possible that the solute forms a heterogeneous lattice structure which becomes porous when the solvent evaporates. The drying of latexes also shows similar morphologies under certain process conditions.

The drying temperature will also affect the coating morphology. Figure 2.10 shows an effect of drying air temperature on the surface morphology of lactose-coated particles.

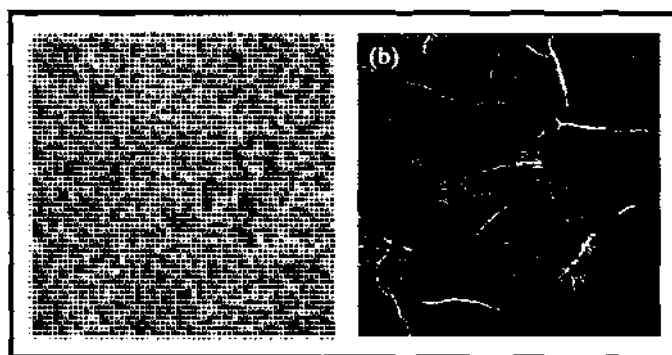


Figure 2.10: Evidence of different morphologies during the drying of lactose at different air temperatures: (a) crystallised surface morphology with drying at 70 °C; (b) amorphous surface morphology with drying at 120 °C [taken from Link and Schlünder (1997)].

Drying at the lower air temperature (70 °C) produced a crystallised surface (a) whereas drying at the higher air temperature (120 °C) produced an amorphous surface structure (b) is produced. In general, crystal structures provide better seals on products because diffusion through a crystalline matrix is slower than that through an amorphous matrix. In addition, the structure of crystallised lactose is less hygroscopic than that of its amorphous counterpart. Although not shown here, it is interesting to note that Link and Schlünder (1997) found that the same smooth amorphous surface as shown in Figure 2.10(b) could be achieved at the low air temperature condition by adding the surfactant Texapon. It is well known that surfactants can suppress crystallisation processes [Canselier (1993)]. This could have major implications with respect to reducing operating costs by using lower air temperatures if an amorphous coating is desired.

Although both groups offered qualitative explanations in relation to physico-chemical properties and phenomenological events, no quantifiable measures or guidelines to describe the behaviour of the particular coating materials under different coating conditions were put

forward. If predictive tools or guidelines could be established from similar investigations, then the microscopic phenomena (such as droplet deposition, spreading and drying) affecting coating morphology could be predicted in terms of macroscopic coating control variables. This would be a significant advance in the current level of understanding.

2.9 MODELLING THE COATING PROCESS

Given the complexity of air-suspension particle coating, it is not surprising that no integrated models of the coating process exist. Because of the large number of process parameters, coating models are usually empirical and consider the coater as a 'black box' reactor [Guignon *et al.* (2002)]. Generally, models aim to relate process and formulation parameters either to final product attributes (such as dissolution rate, flowability) or to coating process efficiencies (such as coating mass yield and agglomeration yield). Guignon *et al.* (2002) observed that other models attempt to describe in detail particular steps of the coating process, such as particle motion, and wetting/drying phenomena. Some of the macroscopic models (both phenomenological and statistical) in the literature that try to describe individual key macroscopic phenomena relevant to laboratory-scale coater investigations include models for heat transfer [Dewettinck *et al.* (1999); Freitas and Freire (2001)], hydrodynamics [Arnaldos and Casal (1996)], coating mass uniformity [Cheng and Turton (2000b)], agglomeration [Ennis *et al.* (1991); Simons *et al.* (1994); Cryer (1999); Liu *et al.* (2000)] and process control [Alden *et al.* (1988); Watano *et al.* (1991); Littman *et al.* (1997)]. There are few fundamental studies with respect to the microscopic modelling of the key processes directly applied to air-suspension particle coating applications. Only recently have a small number of researchers [Kleinbach and Riede (1995); Becher and Schlünder (1997); Link and Schlünder (1997); Panda *et al.* (2001); Zank *et al.* (2001); Guignon *et al.* (2002)] begun to undertake a deeper analysis of the underlying phenomena involved in the coating process. According to Link and Schlünder (1997), there is still a lack of understanding of the physical fundamentals and the mechanisms by which coating occurs such as droplet deposition, spreading, wetting and drying. A deeper understanding of the key microscopic phenomena can lead to prediction of the quality of coatings which can be incorporated into the existing macroscopic models.

2.10 CURRENT 'STATE OF THE ART'

2.10.1 Direction of past researchers

The coating literature has been focused on ways to produce products with high coating mass uniformity and minimal inter-particle agglomeration. There are two major research approaches to achieve this, physical and chemical. The physical approach attempts to amplify the force keeping the particles apart, whereas the chemical approach aims to curtail the force of the coating solution/binder keeping the particles together. These are discussed briefly below.

Researchers employing the physical approach change both design and operating variables to affect the key quality indicators of coating mass uniformity and agglomeration yield (percentage of particles above a cut-off size deemed to be unacceptable). This is achieved by optimising the process conditions such that the forces causing the break-up of agglomerates dominate and overwhelm the forces tending to hold particles together [Turton *et al.* (1999)]. This is evident in the many variations of fluidised bed equipment used in coating applications [e.g. Jones (1988); Olsen (1989a,b)]. Given that the coating field originated out of the granulation field, its research and development has been based upon equipment originally

designed to encourage particle–particle interaction. Thus, the advances in air-suspension particle coating technology based on this physical approach are becoming less fruitful. Evidence of this is in the several new technologies for coating particles less than 100 μm , such as rapid expansion of supercritical solutions (RESS) and spinning-disc coating. In addition, the prevention of inter-particle agglomeration is sometimes not practical by such methods because of considerable attrition, spray drying and elutriation of fine particles [Wan and Lai (1992b)].

Researchers employing the chemical approach have focused their investigations on the microscopic effect of changing formulation variables and measuring the response in the key quality indicators of coating morphology and agglomeration yield. The chemical route to preventing unwanted agglomeration in coating operations is to optimise formulation conditions to curtail the force of the coating solution/binder keeping the particles together. The drive behind the chemical route to preventing unwanted inter-particle agglomeration in coating operations relies on selecting coating formulations that exhibit good film forming but low agglomeration tendency (i.e. polymers exhibiting low tack), particularly by tailoring of the softening point of the coating material with additives such as plasticisers. The chemical approach is extensively applied by workers in the pharmaceutical coating field, in which latexes are most commonly employed as coating materials. A group of researchers led by Fukumori and Ichikawa from Kobe Gakuin University, Japan, exemplify the chemical approach stating, 'the properties of a membrane material are essential to the successful fluidised bed coating of fine particles with low inertia and a large specific surface area' [Ichikawa *et al.* (1994)]. According to Jono *et al.* (2000), their 'approach to fine particle coating have been mainly carried out through the search for new membrane materials and new formulations that can exhibit low binding strength, high process yield and the required functions of the products'.

The chemical approach appears to be promising. Paramount to adopting this approach is an understanding of the physico-chemical properties, particularly drying and tack, of the coating material during application to a fluidised bed of particles. Although evaluation of the tack properties of coating formulations is essential for solving some of the processing problems during film coating, only a limited amount of study in this area has been reported [Chopra and Tawashi (1982); Chopra and Tawashi (1984); Chopra and Tawashi (1985); Wan and Lai (1992a,b)].

2.10.2 The development and optimisation process

Process development in particle technology is often based on the traditional concepts of empirical tests and statistical methods [Polke and Schäfer (2002)]. Typically, this involves a laboratory-bench-scale unit, a larger pilot-scale plant and a still larger demonstration unit [Glicksman (1999)]. Many of the operating characteristics can change between the different size units; most notably, the gas flow patterns and hence the particle mixing patterns and the residence times (as well as particle erosion) usually increase. As a result, simple rules to predict product change with scale do not work anymore [Polke and Schäfer (2002)]. According to Pietsch (1991), expensive and extensive laboratory and pilot-scale testing of all new materials is still undertaken [as cited in Iveson *et al.* (2001)].

Optimisation of process variables usually begins with an experimental design [DeZarn (1995); Achanta *et al.* (1997)], followed by laboratory-scale trials in which key operating parameters are varied and key response variables are measured, such as the increase in particle mass (measure of coating thickness), the percentage of particles exceeding a cut-off size (measure

of agglomeration yield) and the microscopic (e.g. scanning electron microscopy) or dissolution analysis of the coated product (measure of coating coherency/coverage, i.e. coating morphology). From the ensuing analysis, multi-factorial correlations are developed [Polke and Schäfer (2002)]. Optimisation, particularly in the pharmaceutical literature, is usually conducted by response surface methodology (RSM) [Jozwiakowski *et al.* (1990); Kennedy and Niebergall (1997)]. According to Yang *et al.* (1992), 'It is essential that for controlled release coatings, the optimisation of the fluid bed process be...carried out on a case by case basis'.

According to Polke and Schäfer (2002), one of the reasons for the experimental and statistical approaches to process design could be due to the lack of suitable characterisation methods. Kleinbach and Riede (1995) stated that new laboratory methods are required which, together with theoretical models, will allow for the estimation of the fundamental process and design parameters.

Despite the numerous uses for air-suspension particle coating technology, the macroscopic 'black box' approach has essentially resulted in little understanding of the underlying physics of the process [Ennis *et al.* (1991); Tardos *et al.* (1997)]. The results of such work tend to be highly specific to material and equipment selection, and even small changes in operating conditions can lead to counter-intuitive results [Ennis *et al.* (1991); Tardos *et al.* (1997); Guignon *et al.* (2002); Polke and Schäfer (2002)]. 'Today's market requires high product quality and lower production costs, but all this must be reached in shorter development times. The traditional procedures have reached their limits' [Polke and Schäfer (2002)]. This is the 'current state of the art'.

2.10.3 Application in the dairy industry

It is not possible to employ the current 'state of the art' by adopting the same statistical based approach in the dairy industry for numerous reasons. Firstly, the profit margins that powdered dairy products receive are very low compared with those in the pharmaceutical industry. As a result, the dairy industry would not be able to tolerate the process inefficiencies that the pharmaceutical industry inevitably accepts to produce its products. Secondly, the product throughputs in the dairy industry are very large, running up to 20–24 tonnes per hour in a continuous process. A high value product targeted for coating would probably run at 1–5 tonnes per hour [R. H. Archer, Massey University, personal communication, 17 March, 2004]. Processing under the pharmaceutical industry's operating conditions (dilute particle–air volume ratio, low spray flowrates and low coating solution concentrations) requires numerous particle passes to coat the products. In the dairy industry, this would represent a significant bottleneck in the manufacturing process. Thirdly, and most importantly, many different powdered dairy products are eligible for coating and these powders have constantly changing formulations. Hence, optimisation of the coating formulation and the operating conditions of one product will not guarantee the success of another product let alone its optimisation.

2.11 CONCLUSIONS AND RECOMMENDATIONS

A number of key observations can be made about the coating literature with regard to the current 'state of the art'.

- The literature is qualitative in its treatment of coating. There are no guidelines for selecting potential coating materials or for narrowing the vast set of operating variables and operating ranges.
- The literature on air-suspension particle coating is heavily based on pharmaceutical applications, with very few reported studies on food applications. Operating conditions (dilute particle–air volume ratio, low spray flowrates) are not economically viable for most food particle coating applications.
- Literature articles are in the form of reviews, or based on small scale laboratory trials that are product and equipment specific. Optimisation takes place by statistical methods, yielding multi-factorial correlations and are thus product and process specific.
- Air-suspension particle coating is a complex process involving as many as 20 different variables and numerous process variants. Drawing direct conclusions can be difficult and there are many contradictions on optimum process conditions in the literature. Understanding relationships between key operating variables and coating quality parameters requires decoupling of the fundamental processes into smaller manageable units.
- Inspection of scanning electron micrographs of coated particles shows key phenomena related to coating morphology such as droplet deposition, droplet spreading, drying, crystallisation, porosity development and coating cracking. Because little is known about the effects of key process variables on these key phenomena, predicting coating morphology is very difficult.
- Unwanted inter-particle agglomeration is the most serious problem encountered in the spray coating process. Economically viable coating of particles smaller than 100 μm is difficult. Two approaches have been used to prevent agglomeration (physical and chemical). It is this researchers opinion that future work should concentrate on the chemical route to achieve good coating quality with minimal inter-particle agglomeration.
- There are macroscopic coating models but there is little in the way of microscopic coating quality models and linkages between the length scales.

The current 'state of the art' has been established and it is clear that the statistical based research approach is of limited use to the development of coated dairy powders. It is proposed that a new approach to investigating the coating process be developed. To be of maximum benefit, such a study should be somewhat phenomenological in character; then the results will be independent of both the substrate powder and the coating device, so that they can be applied to the numerous different current dairy powders and future powders eligible for coating. This is the basis of the following chapter.

CHAPTER 3

'MICRO-LEVEL PROCESS APPROACH' TO AIR-SUSPENSION PARTICLE COATING RESEARCH

3.1 INTRODUCTION

The 'general literature review' (Chapter 2) revealed that fundamental knowledge is limited. The current 'state of the art' is to employ experimental design and statistical analysis, which has led to results that are highly specific to material and equipment selection and has a long product development cycle. In the dairy industry, it is economically difficult to employ the current 'state of the art' because of low price margins, high throughputs and ever-changing product formulations.

An increasingly popular line of thought amongst researchers, with respect to describing chemical engineering unit operations, is that only a fundamental understanding of the micro-level scale will provide a foundation for predicting the effects and interactions between process parameters and key material properties [Kleinbach and Riede (1995); Tardos *et al.* (1997); Borho (2002); Polke and Schäfer (2002)]. The air-suspension particle coating process can be divided into subprocesses, the fundamental aspects of which should be understood if optimal operation is to be achieved [Toivakka (2003)].

This focused literature review develops a phenomenological picture of the air-suspension particle coating process by identifying key fundamental processes (micro-level processes) and their relevance with respect to coating quality and process efficiency. From this, a plan is formulated to guide the thesis research.

3.2 PROPOSED NEW APPROACH TO COATING RESEARCH BASED ON EXAMINATION OF MICRO-LEVEL PROCESSES

The basis of the micro-level process approach proposed here is to structure the very complex coating process into smaller manageable parts based on classical physical phenomena for which descriptions already exist. It is the thesis of this work that deconvolution into micro-level processes will reduce the need for large experimental design and statistical differentiation of results. It is also argued that this approach will allow general guidelines with respect to coating formulation and operating conditions to be established. These guidelines will be more generic and less product/process specific than those obtainable from the current 'state of the art' experimental designs.

It should be stressed that it is the 'practicalities' of the fundamentals that are important to this study. Prediction of air-suspension particle coating has many practical problems; the

relationships, are complex, conditions are non-ideal (e.g. chemical and physical irregularities of the substrate surface, disperse particle and droplet populations) and the micro-level processes are sensitive to small inaccuracies in the starting conditions. The objective was not to further develop the fundamentals to offer better predictions than can already be made. Rather, the approach taken here was to seek out existing phenomenological explanations and predictive tools from other research fields and to apply them in the context of the air-suspension particle coating process.

To implement the proposed micro-level process approach, four key steps are required. (1) The micro-level processes must be identified. (2) The relevance of each micro-level process must be established to determine key micro-level processes for study in step 3. (3) Development of an understanding by identifying and developing the governing equations and constitutive variables belonging to each of the key micro-level processes is required. This understanding will be used to undertake a well-designed experimental study to establish formulation and operating guidelines so that operating windows for optimal coating quality with minimal inter-particle agglomeration can be found easily and quickly with minimal experimental effort. (4) Validation of these guidelines under applicable (but idealised) conditions likely to be encountered during industrial-scale coating operations (pilot-scale coating trials). The remainder of this chapter was undertaken to realise the first two steps of the micro-level process approach: (1) micro-level process identification and (2) micro-level process relevance.

3.3 MICRO-LEVEL PROCESS IDENTIFICATION

Based on the simple operating principle given in Section 2.2 and the schematic of the Würster coating process (Figure 2.2), the life-cycles of a single coating droplet and a substrate particle can be envisaged by tracing their paths through the Würster coating apparatus. The phenomena occurring during particle coating in a Würster coater are depicted in Figure 3.1.

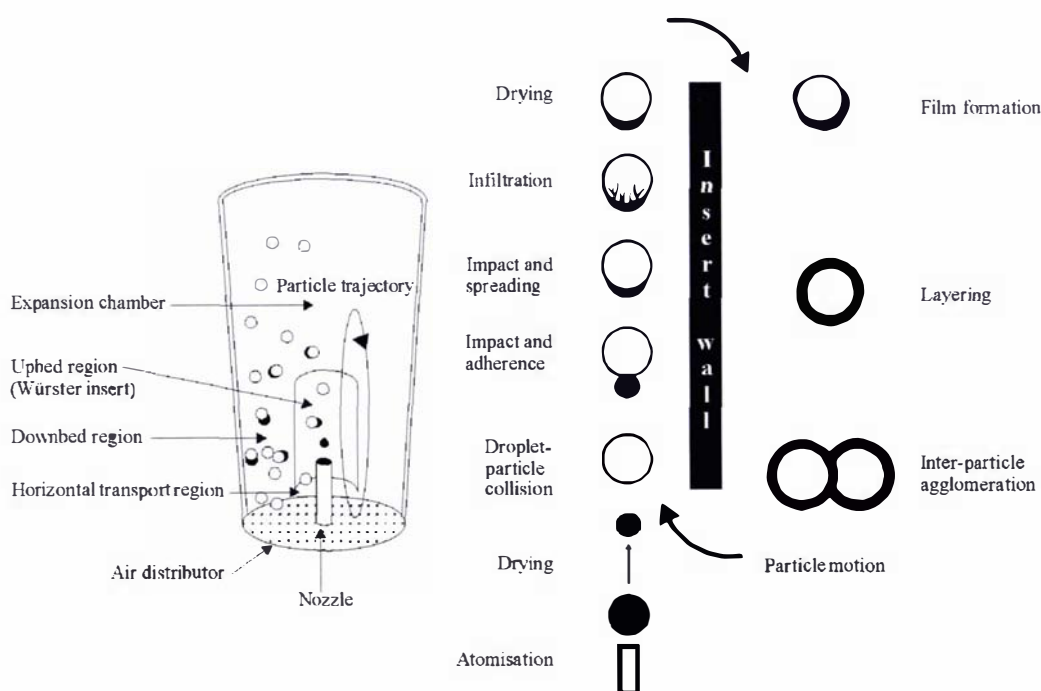


Figure 3.1: Cross-section of a Würster coater showing regions and phenomena occurring during particle coating: ○ = substrate particle; ● = atomised droplet.

As the particle passes through the partition gap (separating the air distributor plate and the Würster insert), it experiences a sudden momentum change as it passes from the low fluidisation air velocity conditions into the high velocity air stream of the Würster insert. The particle quickly approaches the superficial air velocity, typically $3\text{--}5\text{ m.s}^{-1}$ (less the slip velocity), and makes its way towards the spray zone. At the same time, coating droplets are continuously ejected from the spray nozzle. The initial velocity of the coating droplet is usually very high (approximately 100 m.s^{-1}) but the droplet quickly decelerates to take on the air velocity within the Würster insert. During this deceleration period, the atomised droplet also begins to dry. A small window of opportunity occurs when the relative velocities between the droplet and the substrate are high enough and the droplet is moist enough for droplet impingement and successful adherence. The particle may or may not 'see' the coating droplet, depending on its proximity to the nozzle and the other particles [Cheng and Turton (2000b)]. Assuming that successful impact and adherence (i.e. no droplet rebound) have occurred, the coating droplet will ideally spread on the surface of the particle (and may coalesce with previously undried deposited droplets) to begin the formation of a thin coherent coating around the particle. As the droplet spreads after impact, it may infiltrate the powder surface by flowing into its internal porous network (typical of spray-dried powders). At the same time, the impinged droplet is also drying. As it dries, the viscosity of the coating droplet increases which increases the viscous dissipation potential during the spreading process. Both infiltration and drying dampen the spreading process.

The travelling particle with the droplet 'on board' has now moved upward out of the spray zone along the length of the Würster insert. While drying, the moisture content of the coating decreases, causing an increase in viscosity. In the case of dilute coating solutions, the initial viscosity may be close to that of water, which has an associated degree of stickiness, making the particle a source of agglomeration with other powder particles. As drying progresses, the viscosity can become so great (near $10^8\text{--}10^{12}\text{ Pa.s}$) that the coating may pass through its glass transition temperature, T_g , exhibiting first a 'rubbery' character and then a 'glassy' character above 10^{12} Pa.s . Once glassy, the material will no longer exhibit stickiness if the moisture content and the temperature are maintained low enough such that the temperature of the coating surface remains below the glass transition temperature.

The now partially coated particle rises to the top and then out of the Würster insert. As it reaches the expansion zone, the particle decelerates because of the reduced superficial air velocity in the widening chamber. At this time, its gravity force exceeds the force due to air drag and it begins to fall, eventually landing on the annular bed of fluidised particles. The particle must be completely non-tacky by the time it reaches the annular bed as the high concentration of particles and the low inertial forces in this region encourage agglomeration. Here the particle will make its way through the bed (probably plug flow) until it reaches the horizontal transport region once again and the entire process reoccurs. Many repetitions are needed to produce a layer of coating on the particle surface.

The following ten micro-level processes can be identified from the above 'life cycle analysis': particle motion, atomisation, droplet-particle collision, droplet impact and adherence, droplet impact and spreading, infiltration, drying, film formation, layering and inter-particle agglomeration. The following briefly reviews these micro-level processes to determine their relevance. The relative importance of each micro-level process was determined by considering the following criteria.

1. The potential contribution of each micro-level process to the ultimate coating objectives.
2. The contribution of each micro-level process to process inefficiencies.

3. The relative time scales over which the micro-level processes occur.
4. The degree to which the operator has an ability to control the micro-level process with the knowledge gained from its study.

This review is not exhaustive, but is aimed at identifying which micro-level processes are key to governing coating quality and process performance. These will then become the focus of further study in this thesis.

3.4 PARTICLE MOTION

Four different regions of particle motion within the Würster coater can be identified: the upbed region, the expansion chamber, the downbed region and the horizontal transport region [Christensen and Bertelsen (1997)]. Particle motion in each of the four zones is very different. The upbed region (draft tube) promotes the regular circulation of particles within the bed by forcing most of the fluidising gas up through the centre of the bed, thus causing the particles to be entrained upwards with the gas [Turton *et al.* (1999)]. Particle circulation is well controlled, repeatable and quite stable. The velocity of the particle is close to the pneumatic gas velocity (less the slip velocity). Kleinbach and Riede (1995) found that, by increasing the air velocity, an increase in coating quality resulted, where coating quality was defined as the release rate of the encapsulated material. This was attributed to a lower residence time of a particle in the spray zone, and hence a lower time of exposure of the particle to the higher humidity in the spray zone. Prolonged exposure in this zone led to dissolution of the substrate material, which was then incorporated into the coating.

In the expansion zone above the bed, the gas velocity decreases, and the particles consequently decelerate and ultimately fall back into the fluidised bed in the annular region surrounding the Würster insert (downbed region). Here, the particles are fluidised just above the minimum fluidisation velocity. At the bottom of this region, they move radially towards the centre (horizontal transport region) where they are pneumatically transported to the upbed region, and the entire process is repeated. Typical coating cycles are 15–60 s even for full-scale equipment such as the Glatt® GPCG 200 [Christensen and Bertelsen (1997)].

The most important region for air-suspension particle coating is the downbed region, as this is where agglomeration is most likely to occur because of the high particle concentrations and the low inertial forces keeping potentially sticky particles apart. The Geldart group classification diagram [Geldart (1973)], shown in Figure 3.2 has been of great value in allowing easy prediction of fluidisation properties in terms of particle size and density [Seville *et al.* (2000)].

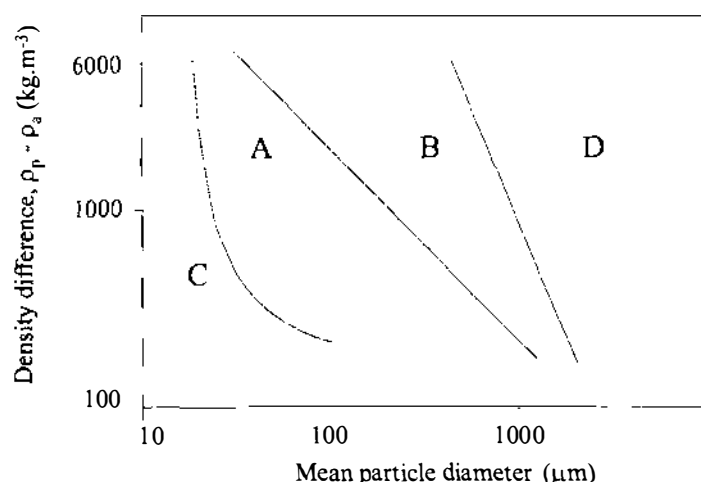


Figure 3.2: Geldart (1973) powder classification diagram for fluidisation [adapted from Guignon *et al.* (2002)].

Whole milk powder (WMP) of 100 μm in diameter should be able to be fluidised (Group A) given its difference in density from air (approximately 1300 kg.m^{-3}). In practice, it is not this simple, as the chart does not take into account the surface character of the particles. In the case of many fat-containing dairy powders (such as some high intensity flavoured powders), this surface can be a layer of fat (up to 95% of the particle surface area [Kim *et al.* (2002)]), which is known to cause stickiness problems during processing in the continuous vibro-beds. Exploratory trials (Section 8.3.3) found that it was possible to fluidise/circulate WMP in a laboratory-scale Glatt® (UniGlatt D7852, Glatt® Process Technology GmbH, Binzen, Germany) Würster coater at air temperatures below 50 °C. However, a natural cheddar cheese powder (CH5510) and a natural butter flavoured powder (LC1000) were much more difficult to fluidise/circulate showing strong Group C character. Geldart Group C particles are characterised by highly cohesive forces and are hard to fluidise. Face powder, flour and starch are typical of these particles [Kunii and Levenspiel (1991)]. Geldart (1973) stated that such a powder lifts as a plug in small diameter tubes and channels badly. The efficient fluidisation/circulation of dairy powders is possible but requires more work. It was not studied further here.

3.5 ATOMISATION

Rekhi *et al.* (1989) [as cited in Cheng and Turton (2000a)] concluded that obtaining uniformly coated particles depends to a great extent on the liquid delivery system in the fluid bed process. This can be achieved by numerous atomiser methods such as pneumatic, dual-fluid, ultrasonic and rotary disc. The most common type of atomising nozzle used in coating operations is the dual-fluid nozzle, which uses the kinetic energy of a high pressure gas (usually air externally or internally mixed with the liquid coating stream) to break up the liquid into a fine spray [Turton *et al.* (1999)]. The fundamentals of droplet production and atomiser operation can be found in the standard texts of Masters (1991) and Liu (2000). It would appear that further advances in ultrasonic atomisers (to be able to atomise higher viscosity solutions than currently) will allow the very small droplet sizes and narrow size distributions required for the coating of particles below 100 μm in diameter.

The challenge in producing uniformly small droplets is the main reason for the difficulty in coating particles with diameters less than 100 μm [Turton *et al.* (1999)]. The first consideration is the size of the droplets relative to the substrate to be coated [Maa *et al.*

(1996)]; Simons and Fairbrother (2000)]. According to Iveson *et al.* (2001), several researchers have found a strong correlation between the droplet size and nuclei size distributions in fluid bed granulators. According to Maa *et al.* (1996), the higher the particle/droplet size ratio, the lower is the agglomeration. For coating, the particle/droplet size ratio must be at least 10 [Guignon *et al.* (2002)]. Thus, for the coating of 100 μm diameter dairy powders, the liquid droplets should be in the range 5–10 μm .

Generally, small droplets (with a narrow size distribution) will also enhance wetting and favour a homogeneous final coating [Turton *et al.* (1999); Guignon *et al.* (2002)]. Hence, small droplet sizes are crucial to enhance spreading and minimise agglomeration, both of which have direct influences on the coating objectives.

Numerous atomiser correlations to describe spray droplet size as a function of atomiser operating variables are available in the literature. However, these correlations apply to particular nozzle designs, operating over restricted working ranges [Masters (1991)]. Dewettinck and Huyghebaert (1998) used the following correlation (Equation (3.1)) to predict the Sauter mean droplet diameter, $D(3,2)$ [m], for a pneumatic nozzle as a function of the properties of the coating fluid.

$$D(3,2) = \frac{585 \times 10^3 \sqrt[3]{\gamma_{lv}}}{v_{rel} \sqrt{\rho_d}} + 597 \left(\frac{(\mu_d / 1000)}{\sqrt{\gamma_{lv} \rho_d}} \right)^{0.45} \left(\frac{1000 U_{sol}}{U_{at}} \right)^{1.5} \quad (3.1)$$

where γ_{lv} , v_{rel} , μ_d , ρ_d , U_{sol} and U_{at} are the droplet surface tension (liquid-vapour) [N.m^{-1}], the relative outlet air velocity [m.s^{-1}], the droplet viscosity [Pa.s], the droplet density [kg.m^{-3}], the fluid volumetric flowrate [$\text{m}^3.\text{s}^{-1}$] and the air volumetric flowrate [$\text{m}^3.\text{s}^{-1}$] respectively. Atomisation is critical to coating quality; and as it is nozzle dependent, it is best characterised (droplet size and size distribution, spray angle) prior to any coating development process.

3.6 DROPLET–PARTICLE COLLISION

The fundamental initiation step of the coating and granulation process is always the same, the successful collision between a coating droplet and a substrate particle [Link and Schlünder (1997)]. The fundamentals of this process, described by Link and Schlünder (1997), are analogous to dust deposition on collector particles, which occurs in two steps: particle transport to the surface and particle adhesion on the surface. The first step is characterised by an impingement efficiency and the second is characterised by an adhesion efficiency. The collection efficiency is thus a product of the efficiencies of these two steps. Step one, impingement, is considered here and step two, adhesion, is considered in the following section. As shown in Figure 3.3, transport to the surface occurs by one of three mechanisms: interception, inertia and diffusion.

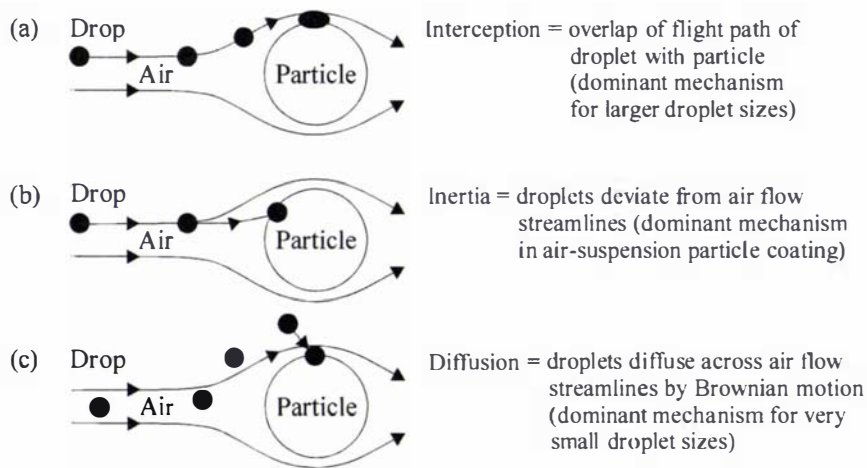


Figure 3.3: Droplet-particle collision mechanisms: (a) interception; (b) inertia; (c) diffusion [adapted from Guignon *et al.* (2002)]. ○ = substrate particle; ● = atomised droplet.

Depending on particle-droplet sizes and relative velocities, one of the above mechanisms will dominate. In the case of air-suspension particle coating, collection caused by inertia is the most important mechanism [Link and Schlünder (1997)]. This requires the ‘collector’ or substrate particle surface to be on the trajectory of the droplet from the nozzle [Guignon *et al.* (2002)]. Hence, nozzle positioning, spray angle, number of droplets and droplet velocity relative to the circulating particles are of crucial importance.

The impingement efficiency, which determines the number of droplets reaching the surface of particles, depends on the droplet density, size and shape and their rate of production compared with those of the particles [Link and Schlünder (1997); Guignon *et al.* (2002)]. The relationships between these properties of the droplets and the particles are not known. According to Link and Schlünder (1997), impingement efficiency can be determined by the ratio of the area surrounded by the critical trajectory (the droplets will impinge inside this area) to the projected area of the particle. However, Cheng and Turton (2000b) (Section 2.8.1) pointed out that the droplet may or may not ‘see’ the substrate because of a particle sheltering effect.

Coating under dilute particle-air volume conditions will increase the impingement efficiency but at the expense of increased coating time. One would naturally increase the rate of droplet production through higher coating flowrates; however, this will lead to increased coalescence of atomised droplets en route to the substrate, producing larger drops as well as raising the relative humidity in this part of the coater, both of which serve to increase the potential for inter-particle agglomeration. There is much work to be done on increasing the likelihood that a droplet will ‘see’ the substrate in the spray zone. This pursuit is left to Turton and coworkers. This thesis will consider the case in which a droplet does ‘see’ the substrate in an effort to establish the conditions conducive to successful droplet adherence.

3.7 DROPLET IMPACT AND ADHERENCE

Droplets that do not successfully adhere upon impingement represent a coating process inefficiency as coating material is lost. The material either is carried away to dilute the final bagged product or needs to be recaptured and reprocessed, and the required coating time must be extended to make up for the adhesion inefficiency. In addition, finely spray-dried droplets can agglomerate together and alter the bulk density of the powdered product, which is a key quality specification used by the dairy industry.

The adhesion probability is a function of the momentum of the droplet and the physical properties of the liquid, and also of the surface characteristics of the droplet and the particle at the moment of collision [Link and Schlünder (1997); Guignon *et al.* (2002)]. The adhesion of fluids to dissimilar surfaces is not possible unless they have good wettability (and subsequent spreadability) to the substrate [Adhikari *et al.* (2001)]. Adhesion of drops onto the particle surface is considered optimal for a normal angle of incidence of the droplet [Guignon *et al.* (2002)].

Coating efficiency is influenced by premature droplet evaporation as a result of the size and the velocity of the coating droplets and the air temperature [Dewettinck and Huyghebaert (1998)] as well as the time of flight between droplet formation and impingement. Adhesion is also affected by the dynamics of wetting and spreading, and drying during wetting and spreading, as they affect characteristics of the droplets and the particles such as moisture content and surface morphology [Link and Schlünder (1997)]. Hence adhesion, drying and wetting/spreading are interrelated and, because of this complex interplay, the current 'state of the art' can determine adhesion probabilities only experimentally [Link and Schlünder (1997)].

Given the strong impact on process economics (particularly through losses from droplet over-drying, explained later in Section 3.10) it would be useful to develop a deeper understanding of the stickiness or tack character of the coating formulation as it dries.

3.8 DROPLET IMPACT AND SPREADING

After the impingement and adhesion of the droplet to the particle surface, the success of the coating operation depends on how well the droplet spreads on the particle surface [Teunou and Poncelet (2002)]. The phenomenon of droplet impact and spreading has received attention for a variety of technical applications such as thin film coating, pesticide application, spray painting, spray combustion, spray cooling of hot surfaces, deposition of solder bumps on printed circuit boards and inkjet printing [Link and Schlünder (1997); Aziz and Chandra (2000); Liu (2000)], although no study in direct relation to air-suspension particle coating has been performed. Some possible outcomes of the impact of a droplet on a surface in relation to spray coating applications are shown in Figure 3.4.

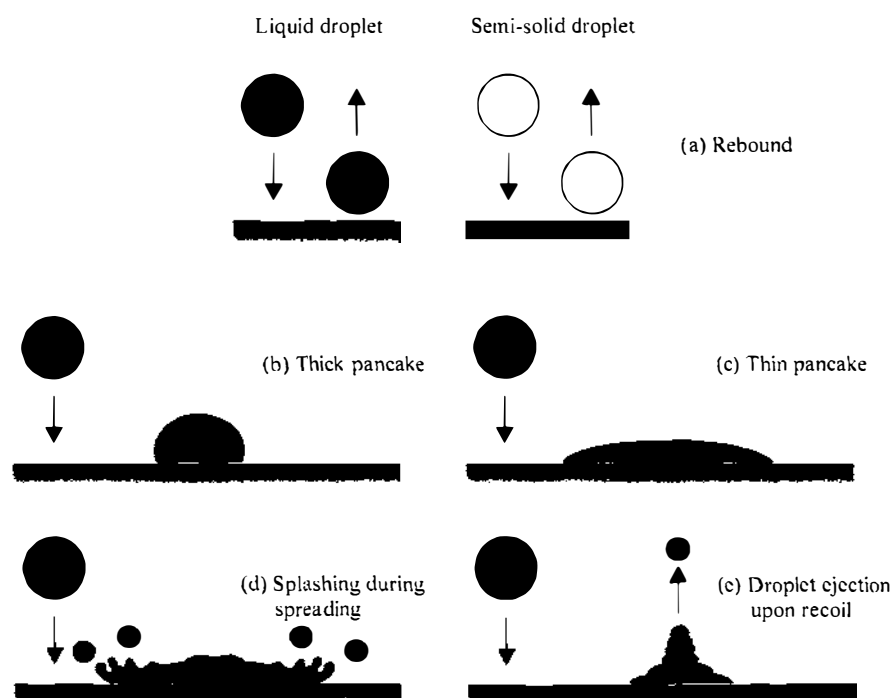


Figure 3.4: Possible outcomes of the impact of a droplet on a flat, dry surface in relation to air-suspension particle coating applications: (a) liquid and solid droplet rebound; (b) thick pancake; (c) thin pancake; (d) splashing during spreading; (e) droplet ejection upon recoil.

Figure 3.4(a) illustrates the case in which either the droplet velocity is too high or significant droplet drying has occurred, both resulting in droplet rebound. Figure 3.4(b) is the case of limited spreading after impact and adherence. From a coating perspective, two problems arise if the droplet adheres successfully but does not spread: (1) operational control of the coating thickness is lost because a large hemispherical deposit will result (thick pancake); (2) extended processing time and a greater quantity of coating material will be required to cover the surface of the particle. Alternatively, Figure 3.4(d) shows that if the droplet impact velocity is too high during impingement, splashing may occur or, if the droplet recoil velocity is too high, Figure 3.4(e) shows that droplet ejection may occur. Rebound, splashing and droplet ejection may leave voids in the spread deposit, which will reduce the protective barrier the coating provides for the particle in its specific application. In air-suspension particle coating, it is desirable to optimise the formulation and the process conditions such that the maximum spread diameter is achieved and retained without splashing or droplet rebound. This is likely to be a thin pancake as shown in Figure 3.4(c). It is believed that 'thin pancake' droplet spreading will lead to tighter control of the film thickness and more coherent coatings through increased surface coverage.

Prior knowledge about the affinity of the coating formulation for the product surface is crucial in order for a thin coherent coating to form. Numerous studies have been aimed at determining the wettability of powders in relation to powder processing applications. Such methods include sessile and infiltrating droplets on packed powder compacts, capillary rise methods and dynamic contact angle analysis [Link and Schlünder (1996); Pepin *et al.* (1998); Popovich *et al.* (1999)]. In the granulation field, investigations have set out to relate wettability parameters such as equilibrium contact angle and surface tension to granulated product attributes such as granule size, strength and porosity. However, many of these studies do not include the effect of the conditions at impact upon spreading. The impact will cause a lower equilibrium contact angle as the film recedes from its maximum spread diameter after inertial spreading to a static state.

Pasandideh-Fard *et al.* (1996) developed a relationship (Equation (3.2)) that predicts the maximum spread factor, ξ_{max} [–], (ratio of the maximum spread diameter during impact and spreading to the initial droplet size).

$$\xi_{max} = \frac{d_{max}}{d_0} = \sqrt{\frac{We + 12}{\frac{3}{8}We s^* + 3(1 - \cos \theta_a) + 4\left(\frac{We}{\sqrt{Re}}\right)}} \quad (3.2)$$

where d_0 , d_{max} , Re , We , θ_a and s^* are the initial droplet diameter [m], the maximum spread diameter [m], the Reynolds number [–], the Weber number [–], the advancing liquid–solid contact angle [°] and the dimensionless thickness [–] of the solidified layer ($= s/d_0$) respectively. The solidified layer, s [m], is defined as the solidified bottom layer of a hot molten droplet landing on a cold surface. Re and We are given by:

$$Re = \frac{\rho_d v_0 d_0}{\mu_d} \quad (3.3)$$

$$We = \frac{\rho_d v_0^2 d_0}{\gamma_{lv}} \quad (3.4)$$

where ρ_d , v_0 , d_0 , μ_d and γ_{lv} are the droplet density [kg.m^{-3}], the initial droplet impact velocity [m.s^{-1}], the initial droplet diameter [m], the droplet viscosity [Pa.s] and the droplet surface tension (liquid–vapour) [N.m^{-1}] respectively.

Equation (3.2) was developed from an energy balance between the droplet before impact and its state at the maximum extent of spreading. Although it is subject to some crucial assumptions and constraints, it does give an insight into how to control the spreading behaviour of the droplet. The three terms in the denominator of the right-hand side of Equation (3.2) represent the three effects that restrain droplet spreading, i.e. solidification, surface tension and viscous dissipation respectively. The model is simple in application, requiring knowledge of the materials properties of the liquid–substrate advancing contact angle, surface tension, density and viscosity. The process parameters of droplet size and impact velocity are also required. According to Toivakka (2003), improved droplet spreading and coating coverage can be achieved with small droplet sizes, high impact velocity and low viscosity. The author also stated that impact and spreading are typically microsecond events with reference to inkjet droplet spreading on paper.

The impact and spreading behaviour is of crucial importance to understanding how a thin coherent coating can be formed. It is desirable to control the coating thickness and to maximise the spread diameter of the droplets. The impact and spreading is to be the subject of further study in this thesis.

3.9 INFILTRATION

At the same time as the coating spreads over the particle surface, it can infiltrate the porous network of the particle. For 50 μm diameter inkjet droplets impacting a powder bed, Holman *et al.* (2002) noted that the spreading and infiltration time scales were similar, precluding their treatment as separate phenomena. Figure 3.5 depicts the process of surface spreading and infiltration.

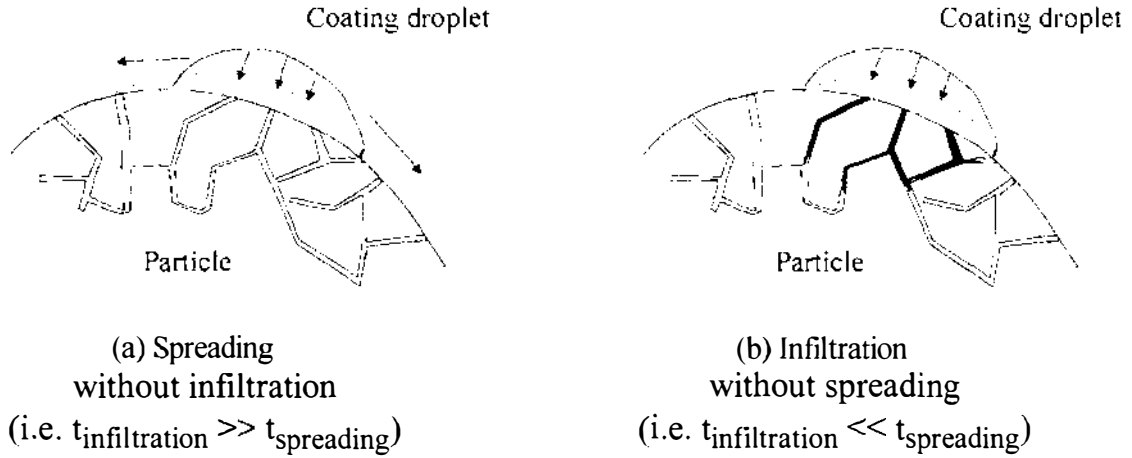


Figure 3.5: Spreading and infiltration of a coating droplet on a porous, wettable particle surface: (a) spreading without infiltration; (b) infiltration without spreading [adapted from Turton *et al.* (1999)].

Simultaneous infiltration during the spreading process represents a loss of coating material because it is not used to coat the surface of the product. Infiltration is expected to occur on a spray-dried powder particle, given the high degree of surface irregularities (yet almost spherical) and the internal pore network. Kennedy and Niebergall (1996) found that infiltration significantly reduced coating yields, with the degree of porosity and the pore size having major effects. Measurements of the contact angle on powdery materials have revealed that the spreading of a droplet is also strongly influenced by the rate of penetration [Link and Schlünder (1996)]. Both Link and Schlünder (1997) and Turton *et al.* (1999) acknowledged increased wettability as penetration is improved. However, there is probably an upper limit to this positive effect. Therefore, the relative rates of spreading and infiltration will determine the extent to which infiltration will affect the coating process.

Although there are many different mathematical descriptions of the infiltration process, they all contain the same key variables. The simplest equation for calculating the dynamics of flow at the pore scale is attributed to Washburn [Cerepi *et al.* (2002)]. It is usually considered to be rigorous for the case of capillary penetration into a uniform capillary tube or a bundle of uniform capillary tubes. The infiltration velocity at which a pore will fill, v_i [m.s^{-1}], is given by Equation (3.5).

$$v_i \equiv \frac{dh}{dt} = \frac{\Delta P}{8\mu_d h} R_c^2 = \frac{1}{8\mu_d h} \left[\frac{2\gamma_{lv} |\cos \theta|}{R_c} - \rho_d g h \right] R_c^2 \quad (3.5)$$

where h , ΔP , R_c , μ_d , γ_{lv} , θ , ρ_d and g are the length of fluid penetration [m], the pressure drop between the meniscus and the bulk liquid [Pa], the average pore-throat radius [m], the droplet viscosity [Pa.s], the droplet surface tension (liquid–vapour) [N.m^{-1}], the angle between the fluid meniscus and pore wall [$^\circ$], the droplet density [kg.m^{-3}] and the acceleration due to gravity [9.81 m.s^{-2}].

Equation (3.5) for the infiltration rate can be compared qualitatively with Equation (3.2) for maximum spreading extent, ξ_{max} . The same properties of the droplet formulation are important to both. Increasing the solids concentration in the droplet will simultaneously increase the droplet viscosity and density, both of which serve to reduce the infiltration rate. A ‘ball park’ calculation can shed some light on how best to control this phenomenon. A 40% w/w maltodextrin DE5 solution at 20 °C ($\mu_d = 242.7 \text{ mPa.s}$; $\rho_d = 1185 \text{ kg.m}^{-3}$; $\gamma_{lv} =$

68.7 mN.m^{-1} ; $\theta = 67^\circ$) is used in the analysis. Using Equation (3.5) with the solution properties given above, a pore-throat radius of $1 \text{ }\mu\text{m}$ and a length of fluid penetration of $10 \text{ }\mu\text{m}$ takes 21 s to fill a single pore at a velocity of $0.5 \text{ }\mu\text{m.s}^{-1}$. Reducing the droplet viscosity to 11.9 mPa.s (20% w/w maltodextrin DE5) decreases the time to 1 s. This is in agreement with Turton *et al.* (1999), who stated that decreases in binder viscosity enhance the rate of both coating droplet spreading and infiltration. Lowering the surface tension will decrease the infiltration rate while lowering the droplet recoil extent [Pasandideh-Fard *et al.* (1996)], which will lead to decreased droplet splashing and further final spreading extents. For example, reducing the surface tension to 30 mN.m^{-1} increases the droplet infiltration time to 42 s. An alternative to manipulating the properties of the droplet formulation is to alter the surface porosity of the particle. For example, decreasing the pore-throat size by half doubles the infiltration time. In the dairy industry, this could be effected by a pre-processing step such as pre-coating or particle rounding and compaction in a roller drum. The latter would require another unit operation, making it a less desirable option. The pharmaceutical industry often employs a pre-coat to reduce product variations attributed to substrate porosity. This undercoat is typically made using a less expensive material. These calculations illustrate the importance of key formulation and operating parameters for control of the infiltration micro-level process. At this stage, infiltration is accepted and excess coating material and time is required to account for the pore uptake during coating of dairy powders.

3.10 DRYING

Atomised droplets must strike the substrate surface before they become too dry. If they dry too quickly, their low surface moisture content means that they are no longer tacky or deformable and will probably bounce off (refer Figure 3.4(a)). This represents a coating process inefficiency. Numerous researchers have observed this problem [Yang *et al.* (1992); Aronson and Tsaur (1993); Fukumori (1994); Link and Schlünder (1997)]. Aronson and Tsaur (1993) noted that their coating levels were significantly lower than the amount of coating material supplied to the system and attributed this to the over-drying (typically referred to as spray drying in the coating literature) of the coating droplets. This problem is particularly prevalent in top-spray arrangements where droplets travel counter-current to the air flow.

Similarly, in a study on a single nucleus, Link and Schlünder (1997) found that the coating growth rate of the nucleus increased with decreasing surface tension of the coating solution. However, the maximum growth rate did not coincide with the critical micellar concentration (CMC¹). This was attributed to the significant amount of spray drying the droplets experienced prior to impingement, which increased the surface tension of the droplets to values above the CMC. This further reinforces the importance of understanding the surface moisture content of the droplet at the point of impact.

To achieve successful coating, it is important to optimise the drying conditions, particularly to avoid over-drying of the droplets. According to Genskow (1990), optimisation of the drying process by statistical methods is usually a tedious process involving many pilot trials [as cited in Achanta and Okos (1995)], which is only made more onerous when there are many potential coating materials to trial.

¹ Critical micellar concentration (CMC) is the surfactant concentration above which micelle (aggregate) formation of surfactant molecules to protect their hydrophobic tails from the aqueous environment becomes appreciable [Shaw (1985)]. The CMC concentration usually corresponds to the lowest surface tension value.

A predictive tool for drying could reduce the commercialisation time in three ways. Firstly, it would enable prediction of the surface moisture content at which a droplet impinges the particle surface, which could be used to optimise both the proximity of the spray nozzle to the powder flow and the drying air conditions. Secondly, it would enable prediction of the drying time required for the coating layer on the particles to dry before they leave the top of the Würster insert. This would avoid surface wetness/tackiness causing inter-particle agglomeration in the downbed region. Thirdly, it could be used to understand the complex interplay between droplet drying and droplet spreading. As drying occurs simultaneously with spreading, according to Turton *et al.* (1999), drying can substantially modify the expected impact of a given operating variable and this should not be overlooked. Droplet impact and spreading are strongly influenced by viscosity, which usually increases with increasing solute concentration and decreases with increasing temperature. In general, however, the dominant observed effect is that lowering the drying air temperature lowers the binder viscosity and enhances wetting. This is due to the overriding effects of drying, which serve to increase the solute concentration and hence the viscosity as drying progresses. This illustrates the complex coupling of the droplet drying and droplet spreading micro-level processes.

Drying will also determine the surface morphology, particularly the rate of film formation and the appearance of surface imperfections such as coating cracking as shown in Figure 2.6. Understanding how formulation and operating conditions affect coating morphology should also be carried out in a drying study.

The drying time for impinged droplets in the upbed region can be controlled by manipulating the drying air conditions (velocity, temperature and outlet relative humidity) as well as the particle circulation time (air velocity, Würster height and partition gap). For the atomised droplets, the extent of drying can be controlled, in part, by conditions mentioned above, the proximity of the nozzle to particle flow, the atomiser variables (e.g. orifice size, atomiser air velocity) and the initial droplet viscosity. Given the large number of control parameters, a 'ball park' calculation to determine the time frame in which drying occurs is presented below.

Assuming constant rate drying, the time to evaporate a pure liquid droplet in a quiescent gas stream, t_{evap} [s], (a valid assumption for small droplets at low terminal velocities) can be estimated with Equation (3.6) proposed by Marshall Jr (1954).

$$t_{evap} = \frac{\rho_d \Delta H_v d_d^2}{8 \lambda_a \Delta T} \quad (3.6)$$

where ρ_d , ΔH_v , d_d , λ_a and ΔT are the droplet density [kg.m^{-3}], the latent heat of water vapourisation [J.kg^{-1}], the droplet diameter [m], the thermal conductivity of air [$\text{W.m}^{-1}.\text{°C}^{-1}$] and the difference between the temperatures of the droplet surface and air [°C]. With a droplet diameter of 10 μm , a droplet surface temperature of 40 °C and an air temperature of 70 °C , the time to dry is calculated to be 0.04 s. However, the equation assumes evaporation into dry air (i.e. RH = 0) and does not contain a term to describe mass transfer. These both limit the applicability of this equation to industrial drying situations.

Foodstuffs rarely show constant rate drying, especially in concentrated products [Cheong *et al.* (1986); Zogzas and Maroulis (1996); Dolinsky (2001); Räderer (2001); Farid (2003)]. Instead the falling rate period is usually observed from the outset of drying because insufficient water transport to the surface occurs such that a constant evaporation rate cannot

be maintained. The transport of water to the surface of the drying substance is described in terms of diffusion, which can be regarded as the controlling mechanism in many drying processes [Ferrari *et al.* (1989)]. Therefore, the time for a single droplet to dry was estimated using Crank's (1956) equation [taken from Räderer (2001)] for diffusion in a solid, non-porous sphere. Although it is limited by numerous assumptions (non-shrinking system, uniform initial moisture distribution, negligible external resistance to moisture transfer, constant surface moisture content, constant diffusion coefficient, unidirectional moisture movement and isothermal process conditions), it can provide a 'ball park' estimate of the drying time.

$$\frac{C_t - C_e}{C_0 - C_e} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-\frac{n^2 \pi^2 D_w t}{R^2}\right] \quad (3.7)$$

where C_t , C_0 , C_e , R , D_w and t are the averaged moisture contents at time t , zero and equilibrium [(kg water).(kg⁻¹ dry solid)] respectively, the droplet radius [m], the binary moisture diffusion coefficient [m².s⁻¹] and time [s] respectively. According to Sano and Keey (1982), the moisture diffusion coefficient for skim milk varies by seven orders of magnitude as it dries from 90% w/w to fully dry (assumed w/w as basis not given). A typical moisture diffusivity of 1×10^{-10} m².s⁻¹ at 0.6 (kg water).(kg⁻¹ dry solid) [Adhikari (2002)] was used for maltodextrin DE11 in the calculation. The droplet was assumed to dry from 80% w/w water to 6.1% w/w with an equilibrium moisture content of 6% w/w. The 'ball park' calculation showed that, for a 10 µm diameter droplet, the drying time, under internal mass transfer controlled conditions, was 0.17 s, i.e. four times slower than that for a pure water droplet. This implies that internal moisture transfer is the controlling mechanism during drying, a result that has been confirmed by many researchers who state that the moisture diffusivity is the most crucial property in drying calculations [Zogzas and Maroulis (1996); Yamamoto (1999)]. Knowledge of concentration-dependent moisture diffusivities is clearly important in designing drying processes. Unfortunately, few experimental data are available on the concentration-dependent diffusivities for liquid foods and their variation can be significant [Schoeber (1976); Wijnhuizen *et al.* (1979); Yamamoto (1999)].

The benefits of understanding the drying micro-level process and the amount of control the operator is afforded make drying an ideal candidate for further review in this thesis.

3.11 FILM FORMATION

Furuta *et al.* (1984) and Krochta *et al.* (1994) provide some insight into the mechanisms of film formation for aqueous soluble polymer solutions. Film formation from aqueous polymer dispersions (such as latexes) has been examined by several researchers [refer to Fukumori (1994)]. The essential differences in film formation mechanisms between solution and dispersion polymers can be appreciated by considering Figure 3.6.

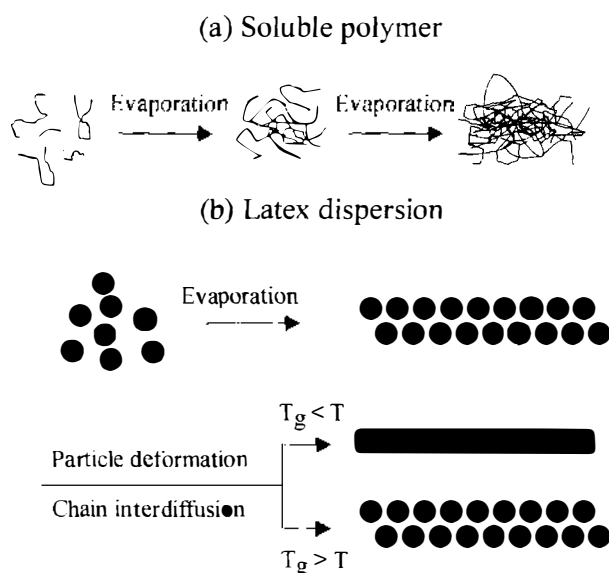


Figure 3.6: Film formation mechanisms from solution: (a) aqueous soluble polymer; (b) insoluble polymer dispersion (latex) [adapted from Aronson and Tsaur (1993)].

Aqueous soluble polymer solutions form films by chain entanglement. If the polymer has appreciable solubility in the solvent, it forms a continuous film over a broad molecular weight range. In contrast, a latex or colloidal dispersion of polymer particles forms films through a capillary-driven coalescence and curing mechanism. This work focuses on soluble polymer solutions. As such, it is accepted that polymer entanglement will result as the drying proceeds and as solubility limits are exceeded.

No literature related to film formation of aqueous soluble polymers on a powder surface could be found. Film formation will result from all the micro-level processes discussed above. The rate and the extent of the spreading, drying and coalescence of droplets will be the major determinants of the final coating morphology. Unhindered spreading and coalescence will lead to thin, coherent coatings, whereas over-drying of the droplets on a particle surface will lead to the formation of agglomerated ‘raspberry-type’ coatings. These structures may be porous and brittle, affording little protection to the substrate. According to Weidner *et al.* (1996), coalescence is accelerated by differences in surface tension between droplets, but is unfavoured by high viscosity. It is clear that high droplet moisture contents at impact and low drying rates will lead to more coherent coatings by promoting spreading and coalescence.

In addition to these micro-level processes, the plasticity of the film as it dries will also determine important morphological features, particularly, the development of wrinkles and cracks. These can drastically affect the coating drying rate and the final barrier properties. If the water is removed from the surface by evaporation fast enough, so that it is not replenished from within by diffusion, there may be a rubbery-glassy transition and the surface of the product can turn glassy while the core remains rubbery, leading to skin formation. The appearance of skin formation or crusts has been observed by numerous researchers [Achanta and Okos (1995); Räderer (2001)]. Morphological development associated with the rubbery to glass transition will be important to the final coating quality and stickiness.

3.12 LAYERING

As the processes of droplet impingement, adherence, spreading and drying are repeated an onion skin structure is built up layer by layer. The physical mechanisms of layering are not

yet fully understood [Panda *et al.* (2001)]. The rate at which the successive layering of coating material occurs is likely to be a complex function of the above micro-level processes. Ideally, the rate of layering should be maximised, but achieving this is first dependent on optimising the key micro-level processes. Once optimised, further research would best be carried out along the lines of that undertaken by Cheng and Turton (2000b) to maximise the rate of layering.

3.13 INTER-PARTICLE AGGLOMERATION

Unwanted inter-particle agglomeration is the most serious problem that is encountered in the spray coating process [Fukumori *et al.* 1987, 1988, 1991a, 1991b, 1992; Maa *et al.* (1996)], particularly for coating particles smaller than 100 μm [Jono *et al.* (2000); Kage *et al.* (2001)] as required in applications to which this project applies. Agglomeration can cause rapid defluidisation, resulting in process shut-down and product loss. A specification for the flavoured dairy powders is that the average particle diameter does not exceed 150 μm [R. H. Archer, Massey University, personal communication, 17 March, 2004]. Given that the average uncoated particle diameter is 100 μm , there is little room for agglomeration in the final product.

The mechanisms involved in agglomeration and coating are very similar; they are addressed in the granulation literature. According to Iveson *et al.* (2001), there are three sets of rate processes: wetting and nucleation, consolidation and growth, attrition and breakage. Wetting is common to coating and agglomeration. Nucleation is defined as the sticking together of primary particles because of the presence of a liquid bridge [Tardos *et al.* (1997)] and must be avoided in coating. This means that wetted particles must have sufficiently high inertial energy so that, upon impact, the energy is unable to be absorbed in viscous dissipation. If nucleation is avoided, the other rate processes of agglomeration are also avoided. However, if two wetted particles have agglomerated, then some shearing force is necessary to overcome the hydrostatic pressure (caused by surface tension) and viscous dissipation necessary to tear them apart. Two major opposing forces on agglomerates exist: one due to the coating/binder holding the particles together and the other due to the continual movement and collision of particles causing the break-up of the agglomerates [Turton *et al.* (1999); Jono *et al.* (2000)]. The growth and the ultimate size of the agglomerates produced are thus a function of the magnitude of the two major opposing forces on agglomerates [Turton *et al.* (1999)]. However, once two sticky powder particles come together, it is almost too late to prevent agglomeration because the relative particle velocities will generally be low. Only by introducing a shearing or turbulent force will it be possible to 'rip' apart initially bonded particles. In practice, the introduction of a shearing force is difficult, instead the use of impact baffles have been found to be more effective. However, if the agglomerates are too sticky, excessive build-up of sticky agglomerates can occur on the baffle exacerbating the problem. It is likely to be of more benefit to optimise the formulation conditions such that nucleation does not occur in the first instance.

Kage *et al.* (2001) stated that the coating efficiency (defined in this case as the rate of mass increase on the substrate per rate of coating supplied) is determined by the moisture content in the coating layer. They proposed the *R* index – ratio of inlet to outlet air humidity – as a macroscopic control indicator that relates well to coating efficiency and inter-particle agglomeration [Kage *et al.* (1996); Kage *et al.* (2001)]; coating efficiency increases with increasing *R*, indicating that better coating occurs on to films of higher moisture content. However, this also leads to increased agglomeration. Conversely, when coating is done under

poor film-forming conditions, the agglomeration of core particles can be kept to 1% w/w or less, even when coating particles smaller than 100 μm [Ichikawa *et al.* (1993)]. Hence, a trade-off between fast film-forming conditions and increased agglomeration potential must be sought; that is, to find and work close to the boundary between coating and agglomeration.

The boundary between coating and agglomeration has not been reported in the literature, but considerable advances to define the boundaries of successful coalescence have been made in the granulation literature. By considering the energy dissipation in the coming together of the liquid coating/binder layers and the subsequent formation of a dynamic pendular bridge, Ennis *et al.* (1991) developed expressions for the minimum velocity required for two identical particles to rebound. When simplified to cases in which the viscous force or capillary force is dominant, Ennis *et al.* (1991) were able to formulate analytical expressions for the critical Stokes number, St^* [–], which must be exceeded for rebound to occur. Taking the ratio of the Stokes numbers showed that the viscous Stokes number criterion is more restrictive than the capillary Stokes number, in that more initial kinetic energy is required for rebound.

The viscous critical Stokes number for coalescence, St_v^* [–], is given by Equation (3.8).

$$St_v^* = \left[1 + \frac{1}{e} \right] \ln \left[\frac{h_c}{h_a} \right] \quad (3.8)$$

where e is the particle coefficient of restitution [–], h_c is the thickness of the coating/binder layer [μm] and h_a is the characteristic length scale of surface asperities [μm]. The viscous Stokes number for coalescence, St_v [–], can be expressed analytically via Equation (3.9).

$$St_v = \frac{2m_p v_{r0}}{3\pi\mu a^2} = \frac{8\rho_p v_{r0} a}{9\mu} \quad (3.9)$$

where m_p , v_{r0} , μ , a and ρ_p are the particle mass [kg], the initial relative particle collisional velocity [m.s^{-1}], the coating layer/liquid bridge viscosity [Pa.s], the particle radius [m] and the particle density [kg.m^{-3}] respectively.

It is important in any coating apparatus that the inter-particle collisions exceed the critical Stokes number so that coating rather than agglomeration is achieved. In a coater, there is a range of particle velocities and possibly a maldistribution of the coating solution leading to a distribution of operating Stokes numbers. Turton *et al.* (1999) illustrated this by defining granulation regimes in terms of the distribution of Stokes numbers, as shown in Figure 3.7.

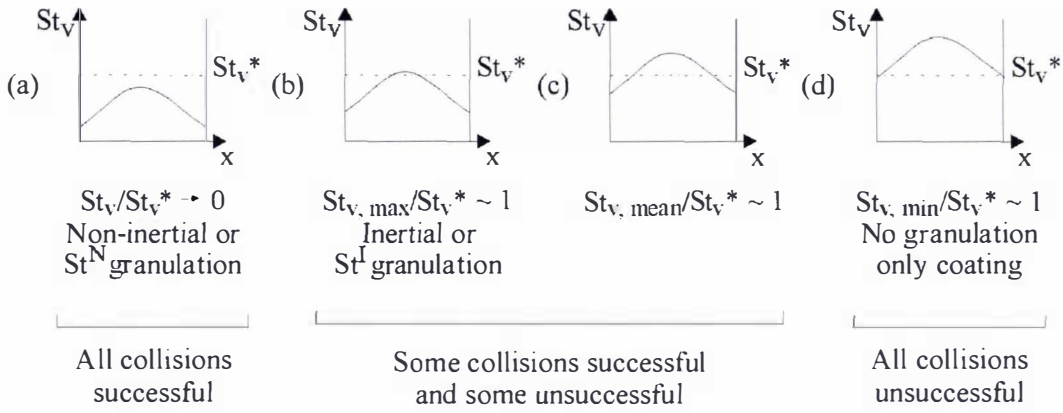


Figure 3.7: Regimes of granulation [adapted from Turton *et al.* (1999)]. St_v = viscous Stokes number, St_v^* = critical viscous Stokes number, $St_{v,max}$ = maximum viscous Stokes number, $St_{v,mean}$ = mean viscous Stokes number, $St_{v,min}$ = minimum viscous Stokes number, x = distribution of viscous Stokes numbers.

Figure 3.7(d) is the regime of interest to coating without agglomeration and supports the statement of Link and Schlünder (1997) ‘that to achieve particle growth by surface layering only, the process should be run at ‘dry’ conditions and intensive fluidisation which inhibits the building up of liquid bridges between the particles’. Equations (3.8) and (3.9) illustrate the importance of high impact velocity, low viscosity and small coating layer thickness in reducing the amount of agglomeration. The equations also show that smaller particles agglomerate more easily, which is consistent with findings to date.

Simons *et al.* (1994) took a different approach, developing a model to provide an approximate value of the rupture energy of pendular liquid bridges. They stated that the viscous forces do not always dominate and that the crucial stage of binder bridge formation had been neglected. This, they argued, is dependent on the wetting behaviour of the liquid on the solids, governed by the surface tension and the contact angle. A simple expression for the energy required to rupture a pendular liquid bridge was derived for the case of perfect wetting (i.e. zero contact angle).

$$W^* = cV_b^{*0.5} \quad (3.10)$$

where W^* , c and V_b^* are the dimensionless rupture energy [–], a constant [1.8] and the dimensionless bridge volume [–]. The expression was shown to be in close agreement with the limited amount of data available at the time. Hence, the approximation of the rupture energy of a liquid bridge can be made with a knowledge of bridge volume, the particle size and the surface tension of the coating solution. Simons *et al.* (1993) found a direct relationship between the extra kinetic energy required for fluidisation because of the presence of free liquid and the energy required to rupture liquid bridges.

The qualitative effect of the above-mentioned variables is well known; however, additionally important is the change in viscosity as the coating layer dries, which increases viscous dissipation upon particle–particle impact, leading to a greater chance of agglomeration. It is with respect to this last statement where potential gains can be made; effective control of agglomeration may lie in the control of the coating surface moisture content, and therefore viscosity and stickiness, of the coating layer as it dries. A study of droplet stickiness development during drying has the potential to link the droplet impact and adherence, the

drying and the inter-particle agglomeration micro-level processes. Droplet stickiness development will be the subject of further study.

3.14 CONCLUSIONS AND RECOMMENDATIONS

In this chapter, a new 'micro-level process approach' to air-suspension particle coating research was proposed. Ten fundamental micro-level processes were identified to occur: particle motion, atomisation, droplet-particle collision, droplet impact and adherence, droplet impact and spreading, infiltration, drying, film formation, layering and inter-particle agglomeration. The relevance of each micro-level process to the coating objectives was discussed. Four were selected for further study: drying, droplet impact and spreading, and stickiness which encompasses the two micro-level processes of droplet impact and adherence, and inter-particle agglomeration.

From a commercial viewpoint, drying represents a significant cost to the process. Drying also strongly influences coating morphology and hence the effectiveness of barrier protection.

To minimise product cost and flavour dilution, Fonterra stipulated that coatings be less than 5% of the product weight. To achieve tight control of the coating layer thickness and obtain coherent coatings it is desirable to maximise the droplet spread diameter. For this reason, droplet impact and spreading have been selected for further study.

Stickiness is important for two reasons. Firstly, unwanted inter-particle agglomeration is a universal problem in the coating fine particles, which can be related to the stickiness of the coating formulation as drying proceeds. Secondly, over-drying of the spray droplets reduces the adhesion probability upon impact because the droplet surface has dried to a non-sticky state. The three chapters addressing drying, droplet impact and spreading, and stickiness attempt to achieve step 3 of the 'micro-level process approach', that is, to develop an understanding of each of the key micro-level processes. Each chapter contains a brief review then determines the key formulation and operating control variables with respect to coating in a Würster coater. Appropriate test methods are developed, conclusions are drawn and guidelines are established to enhance each micro-level process.

The remaining chapters undertake the final two steps to implement the 'micro-level process approach': (3) development of an understanding by identifying and developing the governing equations and constitutive variables belonging to each of the key micro-level processes, and (4) the validation of formulation and operating guidelines.

CHAPTER 4

MATERIALS CHARACTERISATION AND METHODS

4.1 INTRODUCTION

The project is specifically targeted to coating of dairy-based powders with food-grade coatings. This limits the materials that can be selected, but also affects the micro-level rate processes that form the coatings. This chapter identifies potential coating materials for dairy-based powder coating applications. Some of the major physico-chemical properties involved in the key micro-level processes are also measured and the experimental methods for their collection are discussed. In the absence of experimental data, literature data were used, and in some cases, predictive correlations are given.

4.2 MATERIALS SELECTION

4.2.1 Introduction

Selection of coating materials in the public domain literature has been focused on the desired product application. This thesis proposes to additionally select coating materials, and their formulations, based on their performance during the actual coating process. The materials selected here are also made based on their product applications, with particular reference to their diffusive barrier properties and use in food grade applications. Because of the lack of food grade coating applications, the materials are selected from the spray drying microencapsulation and edible films literature.

4.2.2 Potential applications

For the dairy applications of interest to Fonterra, the coating material must provide good diffusion resistance to 'lock in' the 'top note' flavours and to reduce moisture and oxygen diffusion into the particle during storage. Good solubility in water is also important because the majority of powdered dairy products are used in water-soluble applications. However, there is also a desire to develop controlled release applications with products showing limited water solubility, i.e. bake stable applications in which the coated powder must survive the kneading process.

Labelling requirements are also of concern to Fonterra. Therefore, the most acceptable coating materials are dairy derived ingredients or additives already used by the dairy industry. Any new material must be perceived as 'natural'.

According to Lent *et al.* (1998), coating formulations consist of three primary components: a high molecular weight polymer, a plasticiser and a solvent. It has already been established

that the dairy industry is limited to aqueous systems, hence the following reviews potential high molecular weight polymers and potential plasticisers.

4.2.3 Maltodextrins and corn syrup solids

Maltodextrins and corn syrup solids are hydrolysis products of starch. They are prepared as white powders or concentrated solutions by partial hydrolysis of corn starch with safe and suitable acids and/or enzymes [Kenyon and Anderson (1988)]. Starch hydrolysates are characterised on the basis of a dextrose equivalent value (DE, the amount of measured reducing power relative to glucose as 100), which is usually between 2 and 50 [Manoj *et al.* (1996)]. Thus, a preparation with a DE of 5 corresponds to a polymeric species of 20 glucose molecules (degree of polymerisation, DP). A preparation with a DE of 0 is the native starch and a preparation with a DE of 50 is maltose [Hogan *et al.* (2001b)]. Maltodextrins are produced both in the United States and in other countries by several suppliers, so they are readily available.

The Food and Drug Administration (FDA) defines maltodextrins $(C_6H_{12}O_5)_nH_2O$ as nonsweet, nutritive saccharide polymers that consist of D-glucose units linked primarily by alpha-1–4 bonds and that have dextrose equivalence less than 20. Corn syrup solids $(C_6H_{12}O_5)_nH_2O$ are defined by the FDA as dried glucose syrups in which the reducing sugar content (DE) is 20 or higher [Kenyon and Anderson (1988)]. A number of dairy-based products are already formulated with low DE maltodextrin. If such a product also contains a maltodextrin of DE20 or higher, an additional label declaration may be required, which is a disadvantage for the producer [R. H. Archer, Massey University, personal communication, 20 August, 2004].

Maltodextrins are widely used as food components to increase viscosity, to retard crystallisation, to improve drying characteristics and to decrease stickiness and hygroscopicity of dried materials [Roos and Karel (1991a)]. Fonterra has used maltodextrins as bulking agents and as an additive to reduce stickiness during drying. In the production of some microencapsulated spray-dried powders, the maltodextrin can constitute between 50 to 85% of a powdered product's weight [R. H. Archer, Massey University, personal communication, 20 August, 2004].

Hydrolysed starches offer the advantages of being relatively inexpensive, bland in flavour (generally get sweeter with increasing DE), highly soluble (up to 75% w/w) while still exhibiting low viscosity, and afford good protection against oxidation. The major shortcomings are a lack of emulsifying capacity and marginal retention of volatiles during drying. For this reason, they are usually combined with other true emulsifying matrix materials such as gum arabic, modified starches or proteins to achieve the necessary emulsion stability [Kenyon and Anderson (1988)].

Maltodextrins and corn syrup solids have been found to have poor retention of volatile compounds during spray drying [Reineccius (1991)]. Two reasons are generally cited: poor film-forming properties and poor emulsion-stabilising properties [Reineccius (1991)]. Retentions generally range from 70 to 85%, depending on the drying conditions. However, the retention does increase with decreasing DE value [Bangs and Reineccius (1981)], which has been attributed to a better film-forming ability. Rosenberg *et al.* (1985) employed scanning electron microscopy (SEM) to study the structure of spray-dried microcapsules. They found that the maltodextrin DE20 microcapsules were dented, porous, brittle and contained surface cracks, whereas the maltodextrin DE10 microcapsules showed the same

indentations but were free of pores and cracks. Coating with maltodextrin DE18, Link and Schlünder (1997) found a smooth and non-porous coating. These differences in observations of the maltodextrin morphological character are likely to arise from differences in drying conditions.

After drying, the barrier performance during storage is important, but maltodextrins and corn syrup solids have been found to vary greatly in protecting encapsulated flavours from oxidation [Reineccius (1991)]. Anandaraman and Reineccius (1986) found that simple hydrolysed starches can give excellent protection to the oxidative storage of spray-dried orange oils, and that the degree of protection is directly related to the DE of the hydrolysed starch. Higher DE maltodextrins are considered to be less permeable to oxygen and therefore offer better protection [Reineccius (1991)]. Reineccius (1988) stated that the higher DE products also have a greater number of free reducing groups and suggested that it is possible that some of the stability observed by Anandaraman and Reineccius (1986) is due to the high reducing environment provided by the matrix. This is interesting, as the matrix itself might be considered to be acting as an antioxidant [Reineccius (1988)]. Hence, low molecular weight materials appear to be more desirable to act as a gas-permeable barrier during storage.

Another important trait for successful coating, although not commonly reported for food products, is their adhesive properties. Felton and McGinity (1996) [as cited in Felton and McGinity (1999)] compared the adhesive properties of two complete hydroxypropylmethylcellulose (HPMC) film coating systems, Opadry® and Opadry® II, commercially available from Colorcon (West Point, PA, USA). The latter material contained maltodextrins formulated to achieve better adhesion, especially to hydrophobic substrates. The results revealed that having maltodextrin in the formulation enhanced polymer adhesion to both hydrophobic and hydrophilic tablet compacts. Hence, maltodextrins should aid coating adhesion to the spray-dried particle regardless of surface hydrophobicity.

Considering the information, maltodextrins represent a good coating material for dairy applications. They are particularly useful for stability during storage to moisture and resistance to oxygen and have excellent solubility in water. In addition, many of these attributes have potential to be tailored by using mixtures of various DE values.

The starch hydrolysis products and their suppliers to the dairy industry are numerous and constantly changing. The Maltrin® carbohydrate product range supplied by Salkat NZ Limited (Auckland, New Zealand) (sourced from Grain Processing Corporation, Muscatine, IO, USA) were selected for their wide range of characteristics. In particular, the low DE products have low hygroscopicity (good storage stability) and minimal reducing sugar levels for low browning tendency (good for bake stability applications). The higher DE products have higher solubilities and lower viscosities but usually at the expense of higher hygroscopicity. Three products were selected for use in this work: maltrin M040 (DE5), maltrin M100 (DE10) and maltrin M180 (DE18). The average molecular weights of these products are 3600, 1800 and 1000 g.mole⁻¹ respectively.

4.2.4 Gum arabic

Acacia gums, commonly known as gum arabic is a natural exudate from the trunk and branches of leguminous plants of the family Acacia [Thevenet (1988)]. There are several hundred species of Acacia, however, only a few are able to produce gum and these are mainly concentrated in the sub-Sahara desert region of Africa: the Sahel [Thevenet (1988)]. In the early 1970's and mid 1980's gum arabic suffered from supply shortages due to drought

conditions in the major producing regions (i.e. Sudan) [Trubiano and Lacourse (1988)] which resulted in poorer quality and higher costs, however, the product quality and stability in supply are becoming more consistent [Reineccius (1989)].

The gum acacias vary greatly in functional properties [Reineccius (1994)]. Gum arabic is a neutral or slightly acidic salt of a complex polysaccharide containing calcium, magnesium and potassium ions [Nisperos-Carriedo (1994)] and is made up primarily of D-glucuronic acid, L-rhamnose, D-galactose, and L-arabinose, having a molecular mass of approximately 250–1000 kDa [Whistler and Daniel (1985)]. It also contains between 2–5% w/w protein, which is responsible for its emulsification properties [Thevenet (1988); Nisperos-Carriedo (1994)].

The major user of gum arabic is the food industry and it also finds use in the pharmaceutical and the printing industries. The flavour industry uses the gum as a flavour-fixative, protecting the flavour from evaporation, oxidation, and absorption of moisture from the air. Gum arabic has been the standard of excellence as a flavour encapsulating material because it is an outstanding natural emulsifier, is bland in flavour, and provides good retention of volatiles during spray drying [Leahy *et al.* (1983); Reineccius (1988); Trubiano and Lacourse (1988); Kim and Morr (1996)]. Gum arabic has also been used as a binder in fluid bed granulation [Rohera and Zahir (1993)]. They are generally slightly more expensive than the modified food starches and somewhat inferior in emulsification properties and flavour retention. They can however, offer excellent protection against oxidation, and therefore can be an excellent overall choice as an edible film for the encapsulation of flavours. The gum acacias have the additional advantage of being regarded as ‘natural’ [Reineccius (1994)] and are now being marketed as a prebiotic both of which are likely to be held in high regard with the consumer.

Gum arabic dissolves readily in hot or cold water and is the least viscous and most soluble of the common food hydrocolloids. Nisperos-Carriedo (1994) reports the following properties of gum arabic:

- Aqueous solutions up to 50% w/w can be prepared. A 40% w/w solution produces an excellent mucilage for adhesiveness.
- It is insoluble in alcohol and most organic solvents.
- It is compatible with other plant hydrocolloids, proteins and starches.
- It produces stable emulsions with most oils over a wide pH range.
- Electrolytes generally reduce the viscosity of gum arabic solutions. Many salts particularly trivalent metal salts, give precipitates.

SEM studies by Rosenberg *et al.* (1985) and Rosenberg *et al.* (1990), revealed spray-dried gum arabic microcapsules to be essentially free of pores and cracks suggesting it provides a good protective barrier for coated products.

Gum arabic (Type 4639-A, batch 48, Willy Benecke GmbH, Hamburg, Germany) was sourced from Bronson and Jacobs Pty, Ltd, Auckland.

4.2.5 Whey protein isolate

Milk contains about 33 g.l⁻¹ total protein [Dalglish (1989) as cited in Gennadios *et al.* (1994)] comprising two principal fractions, casein and whey proteins. Whey protein which is approximately 20% of total milk proteins, is protein that has been separated from whey fluid by chemical (precipitation with salts, others and/or heat) and/or physical methods (membrane separation or ultracentrifugation). Whey protein contains five principal protein types; α -

lactalbumin, β -lactoglobulin, bovine serum albumin, immunoglobulins, and proteose-peptones of which β -lactoglobulin is the major protein (3.7 g.l^{-1} in milk) [Gennadios *et al.* (1994)]. Subject to the way casein is coagulated, by enzymatic rennet coagulation or by acid coagulation, whey is distinguished as sweet whey (rennet whey) and acid whey (quark whey), respectively. Another type of whey is industrial-grade whey, which results from protein coagulation with acids other than lactic acid, e.g. hydrochloric, sulphuric or acetic acids. Due to the numerous separation techniques the properties of whey protein products vary significantly. The physico-chemical properties of whey proteins have been studied extensively [refer to Young *et al.* (1993a)]. Being dairy derived, whey proteins are a natural choice for a coating material and they have been investigated as edible films for about a decade [Chen and Zutara (2001)].

Whey protein films provide excellent barrier properties. Whey protein isolate provided an effective oxidation barrier for microencapsulation of orange oil [Kim and Morr (1996)]. Microencapsulation of anhydrous milkfat in whey protein based wall systems were found to provide effective protection against oxidation even under extreme storage conditions [Moreau and Rosenberg (1996)]. Bangs and Reineccius (1981) found that the addition of whey protein improved volatile retention over maltodextrin DE10 alone.

Whey proteins have the ability to adsorb at the oil/water interface and stabilise emulsions [Fäldt and Bergenståhl (1996b)]. This property was exploited by Lee and Rosenberg (2000) who produced water insoluble, whey protein-based microcapsules which exploited the heat gelation and chemical cross-linking ability (with glutaraldehyde) of the whey proteins employing a double emulsification technique to encapsulate anhydrous milkfat.

Transglutaminase has also been used to catalyse the covalent polymerisation of whey proteins to give water-insoluble character, but its high cost has limited its use in edible films [McHugh and Krochta (1994)]. On the other hand, simple heat gelation of the whey protein microcapsules produced by Lee and Rosenberg (2000) showed minimal water solubility (as low as 1.3% w/w of the total protein content at 30°C after 14 days in solution). Lent *et al.* (1998) explains that heat facilitates the formation of intermolecular disulphide bonds by thiol-disulphide and thiol oxidation reactions, which results in water-insoluble films, where the minimum heat treatment required for formation of intact whey protein films is 75°C for 30 min. This is very near the denaturation temperature (78°C) for β -lactoglobulin, the major component. It is likely that the gelation process forms a rigid protein network around the fat globule via disulphide linkages enabling the protein to remain on the globule surface. In addition, Moreau and Rosenberg (1995) state that, the presence of free $-\text{SH}$ groups in the whey protein structure may protect the encapsulated fat from oxidative deterioration [as cited in El-Salam *et al.* (2000)]. This would provide a stable moisture barrier in dough mixtures prior to baking.

Films produced from whey proteins have been found to be brittle and the addition of plasticisers is needed to impart film flexibility [Gennadios *et al.* (1994)]. Properties of whey protein films, such as plasticity or permeability, can vary with small variations in chemical content [Lent *et al.* (1998)]. This sensitivity can be exploited to provide optimum controlled release properties.

Whey protein isolate (WPI) is the most concentrated form of the whey protein products manufactured by Fonterra (by ultrafiltration or ion exchange) which contains at least 90% w/w whey protein [R. H. Archer, Massey University, personal communication, 17 March, 2004]. An ion exchange manufactured product was selected here as it contained less

denatured protein (1–2% as opposed to 10% for products made by ultrafiltration) [M. Pritchard, Fonterra Palmerston North, personal communication, 17 June, 2003]. WPI (low fat LGC, U8314) was sourced from NZMP, New Zealand. The high cost of WPI would make it less likely to be used in a product application, however, its film forming ability was of interest. Similar studies with lower grade products such as the whey protein concentrate (WPC) (30% to 75% w/w whey protein) may also be warranted. WPC is approximately half the price of WPI but contains more fat and less β -lactoglobulin.

4.2.6 Plasticisers

Both the maltodextrins and whey proteins produce coatings with cracks despite showing good resistance to oxidation and flavour loss in the spray drying microencapsulation literature. To correct this, plasticisers are commonly employed in the formulation to make the films softer and more pliable during drying resulting in less chance of fracture. Plasticisers are relatively low molecular weight materials which have the capacity to alter the physical properties of a polymer to render it more useful in performing its function as a film coating material [Hogan (1995)]. It is generally considered that the plasticiser molecules interpose themselves between the individual polymer strands thus preventing polymer–polymer interactions. There are often chemical similarities between a polymer and its plasticiser; for instance, glycerol and propylene glycol are plasticisers for several cellulosic systems and possess –OH groups, a feature in common with the polymer. The effectiveness of plasticisation is commonly related to the reduction in the glass transition temperature, T_g , of the polymer system. According to Entwistle and Rowe (1978), plasticisers with a high degree of interaction with the polymer will decrease the T_g of the film to a greater extent than those which interact poorly with the polymer [as cited in Felton and McGinity (1999)]. In addition, Felton and McGinity (1999) found that stronger adhesion occurred when the T_g of the film was lower.

Plasticisers can also alter characteristics such as permeability, toughness, strength and tear resistance [Mahmoud and Savello (1992)]. In addition, Aronson and Tsaur (1993) suggested that both film formation and surface tack depend on the coating material softening point, thus, an increase in polymer plasticity can lead to increased tack and subsequent agglomeration.

Plasticisers having food applications include mono-, di- and oligosaccharides (mainly glucose, or fructose-glucose syrups, honey); polyols (mainly sorbitol, glycerol, glyceryl derivatives and polyethylene glycols); lipids and derivatives (mainly fatty acids, monoglycerides and ester derivatives, phospholipids, surfactants). Films may require plasticisers at 10 to 60% w/w (dry basis) depending on the rigidity of the polymer. Two plasticisers were chosen for use in this study. The polyol, glycerol (BDH Chemicals New Zealand Ltd, Palmerston North, New Zealand) was chosen over its counterparts because of its universal acceptance as a food additive and its frequent appearance in the literature for benchmarking. The second plasticiser chosen for investigation was a high DE maltodextrin to lower the T_g of the primary coating material. In this instance, maltodextrin M180 (DE18) was chosen as the last maltodextrin DE available before it must be declared as a corn syrup solid, which is an additional labelling item.

4.2.7 Surfactants/Wetting agents

Surfactants and wetting agents are commonly employed in surface and adhesion science to increase the wettability of a surface to promote spreading. If the wetting agent is correctly selected, spreading is promoted by lowering the liquid–vapour interfacial tension, γ_{lv} [$\text{N}\cdot\text{m}^{-1}$],

and the solid–liquid interfacial tension, γ_{sl} [N.m^{-1}] [Shaw (1985)], causing a droplet to roll out as a thin film on the substrate surface.

Sodium dodecyl sulphate (SDS) (SERVA Electrophoresis GmbH, Heidelberg, Germany) and octylphenoxy polyethoxyethanol (Triton X-100) (BDH Chemicals New Zealand Ltd, Palmerston North, New Zealand) were selected to investigate the effect of using low molecular weight surfactants on the dynamics of the droplet spreading with a view to their more rapid transfer to the free expanding surface (discussed in Section 7.8.2). SDS is a small anionic surfactant molecule with a molecular weight of 289 g.mole^{-1} . Triton X-100 (TX) is a non-ionic polymer with a molecular weight of 628 g.mole^{-1} . The diffusion coefficient of SDS is about an order of magnitude larger than that of TX, which means that SDS can repopulate the dilating surface of a spreading droplet more rapidly than TX [Zhang and Basaran (1997)].

Three lecithin-based wetting agents (produced by ADM, Decatur, IL, USA) were supplied by Hawkins Watts Ltd (Auckland, New Zealand). The exact compositions of these lecithins are not known. However, lecithins are mixtures of four principal phospholipid components: phosphatidylcholine (774 g.mole^{-1}), phosphatidylethanolamine (730 g.mole^{-1}), phosphatidylinositol (749 g.mole^{-1}) and phosphatidic acid (687 g.mole^{-1}), which are the active ingredients responsible for the observed wetting behaviour. Performix E (PE) comes in fluid form and is a highly hydroxylated lecithin, making it the most hydrophilic of the wetting agents trialled, having an approximate hydrophilic to lipophilic balance (HLB²) value of 12. It is not permitted for use in New Zealand foodstuffs [P. Harrison, Hawkins Watts Ltd, personal email, 03 March, 2004]. Ultralec P (UP) is a de-oiled lecithin that is considered to be a ‘natural emulsifier’, has an intermediate HLB value of 7 and comes in dry powder form. Yelkin Gold (YG) has been used for whole milk powder lecithination and is predominantly hydrophobic in character with an HLB value of 4.

4.2.8 Anti-tack agents

Recognition of the problem of tackiness has led to the use of a variety of pharmaceutical additives, such as, talc, silicon dioxide, kaolin, magnesium stearate, cholesterol [Wan and Lai (1992b)] and salt. It is the intention of this work to understand tackiness development such that the use of anti-tack additives is not necessary to minimise formulation costs and labelling requirements.

4.2.9 Conclusions

Maltodextrins (DE5, DE10 and DE18), whey protein isolate and gum arabic were materials selected as potential water-soluble coating materials. Maltodextrin DE5 was selected as a potential coating material due to its common use as a bulking agent and stickiness reducing agent in spray-dried dairy powders. Maltodextrin DE10 represents an alternative material to the currently used maltodextrin DE5. Maltodextrin DE10 is almost twice as soluble as DE5 at 27°C and has only one-third of the viscosity at 40% w/w solids concentration [Grain Processing Corporation, Maltrin® brochure, 1999]. However, maltodextrin DE10 has a lower T_g and therefore would be more susceptible to caking on storage. On its own maltodextrin DE18 is not a likely candidate as a material coating film because of its low glass transition temperature, which will cause stickiness during drying and storage. It was investigated as a means to plasticise maltodextrin DE5.

² The HLB value is the hydrophilic to lipophilic balance value and is an index of the predicted preference of an emulsifier/wetting agent for oil or water. The higher the HLB value, the more polar, or hydrophilic, is the molecule [ADM, Emulsifying brochure, 2001].

Although there are few data on the drying kinetics or stickiness of whey protein isolate in the literature, whey protein isolate is unique as a potential coating material because it can provide both water-soluble and water-insoluble barriers depending on the drying air temperature.

Gum arabic is considered to be the standard of excellence for the spray drying microencapsulation of volatile flavour compounds. Its 2–5% w/w protein content imparts good emulsification properties, making it easily dispersible in an aqueous system. No drying kinetic data for gum arabic could be found in the literature.

The remainder of this chapter determines the key physico-chemical properties for some of the selected materials required in this thesis.

4.3 OXYGEN DEPLETION STUDIES

Before further investigation was made, it was important to justify that an edible diffusion barrier is necessary to limit mass transport of oxygen into and/or volatile 'top note' out of the particle matrix.

In general, the four main causes of food powder flavour instability are: chemical interactions of flavour compounds, chemical reaction of the flavour compounds with constituents of the food matrix, selective loss of key flavour compounds by physical means, and changes induced by external factors such as oxygen, light, and packaging [McHale (1989)]. Non-enzymatic oxidation of milk lipids has been identified by Wewala (1997) and Frankel (1998) as an important cause of flavour deterioration of dairy products. Autoxidation of unsaturated fatty acids yields hydroperoxides that decompose to a broad group of carbonyl products which can contribute to 'rancid' off-flavours resulting in shorter shelf-life of milkfat containing products [Moreau and Rosenberg (1996)]. These volatile carbonyl compounds are detectable at extremely low levels (parts per billion) [Frankel (1998)], so it only takes a small amount of oxygen to cause irreparable quality loss. Flavours imparted by the carbonyl compounds are described as 'oxidised, fishy, metallic, painty and tallowy' [Frankel (1998)]. This is consistent with the flavour observations made by Fonterra.

To verify whether oxidation was occurring in the powders of interest a simple test was required. From the numerous methods available for measuring oxidation given in Frankel (1998) and Wewala (1997), the oxygen headspace consumption method was opted for due to its simplicity and the fact that it did not require an extraction step which is commonly associated with the loss of volatile components and the creation of artefacts. The methodology developed by Wewala (1997) (Fonterra, Palmerston North) was followed closely due to the high sensitivity of the test. Briefly, it involved the weighing 50.0000 g of each powder into new oxygen consumption bottles. The bottles were immediately crimped to seal the sample and the bottles wrapped in tin foil to prevent light increasing the rate of oxidation. The bottles were incubated at 30 °C for 3 weeks. Samples were taken every 3 days by taking a 400 ± 50 μl headspace sample with a gas-tight micro-syringe (Hamilton Company, Reno, NV, USA). An empty bottle containing only laboratory air was run as a blank sample. The samples were analysed for oxygen content by a Shimadzu GC-9A gas chromatograph (Shimadzu Corporation, Kyoto, Japan) fitted with a thermal conductivity detector and an Alltech CTR-1 column (Alltech Associates, Inc., Deerfield, IL, USA). The column is a packed column inside a packed column (6 ft long, 0.25 in O.D.). The flowrate of the carrier gas (helium) was $55 \text{ ml} \cdot \text{min}^{-1}$. The average of triplicate samples was reported.

Two powders were selected for trial. The natural cheddar cheese flavoured powder (CH5510) is approximately 50% w/w maltodextrin DE10 and 16.5% w/w enzymatically lipolysed milkfat. The natural butter flavoured powder (LC1000) is approximately 85% w/w maltodextrin DE10 and 13.5% w/w milkfat [R. H. Archer, Massey University, personal communication, 17 March, 2004]. The high maltodextrin contents are required to avoid stickiness problems during drying and to act as a microencapsulating matrix. The results of the oxygen consumption study for a natural cheddar cheese and natural butter flavour powders are shown in Figure 4.1.

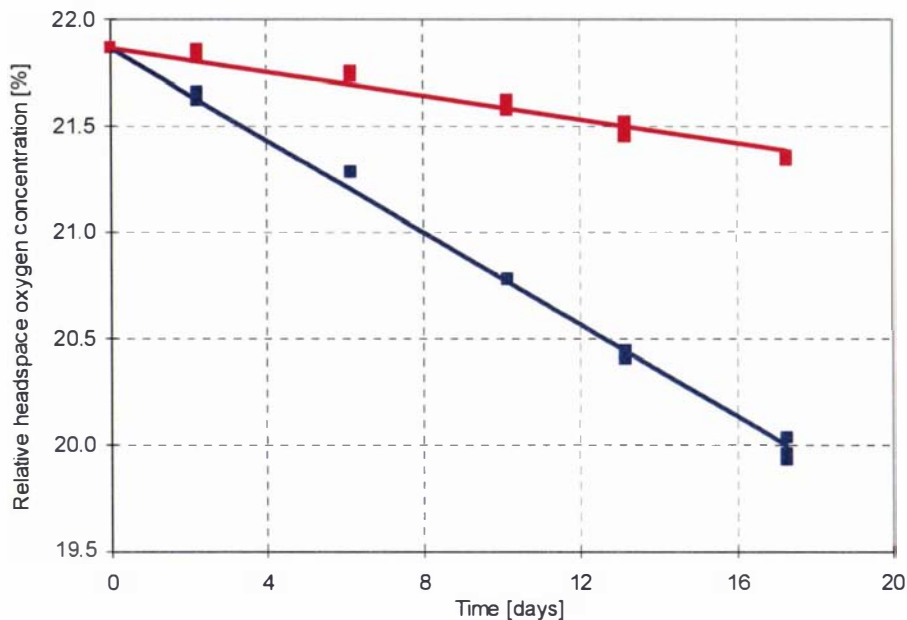


Figure 4.1: Oxygen consumption of a natural cheddar cheese flavoured and a natural butter flavoured spray-dried powder produced at Fonterra, Longburn: ■ natural cheddar cheese flavoured powder (CH5510); ■ natural butter flavoured powder (LC1000).

It is clear that the powder consumes some of the available oxygen in the sample vial headspace indicating that the products are not well protected under the current spray drying microencapsulation conditions. The trends exhibited zero order reaction kinetics, yielding a linear depletion with time. The faster rate of oxygen consumption for the natural butter flavour ($1.84 \mu\text{l O}_2$ per g powder per day compared to $0.51 \mu\text{l O}_2$ per g powder per day) is expected since it contains a higher proportion of polyunsaturated fats. From these results, the application of an edible barrier is justified.

4.4 BINARY MOISTURE DIFFUSION COEFFICIENT

According to Zogzas and Maroulis (1996), moisture diffusivity is the most crucial property in drying calculations as it can vary by several orders of magnitude over the course of drying.

The maltodextrin DE5 binary moisture diffusion coefficient, $D_w(u, T_d)$ [$\text{m}^2 \cdot \text{s}^{-1}$] was predicted using the following equation from Adhikari (2002). Its development is discussed in Appendix A2 (Section A2.3.6.4).

$$D_w(u, T_d) = D_{w, \min} + D_{0, \text{ref}} \exp\left(-\frac{16}{1+16u}\right) \exp\left[-\frac{1}{R_g} \left(\frac{100+195u}{1+10u}\right) \left(\frac{1}{T_d} - \frac{1}{T_{\text{ref}}}\right)\right] \quad (4.1)$$

where $D_{w,min}$, $D_{0,ref}$, u , R_g , T_d and T_{ref} are the minimum binary moisture diffusion coefficient [–], moisture diffusivity in dilute solution at the reference temperature (in this case 303 K) [$\text{m}^2 \cdot \text{s}^{-1}$], the droplet moisture content [(kg water)·(kg⁻¹ dry solid)], the universal gas constant [8.314 J·mole⁻¹·K⁻¹], the droplet temperature [K] and the sample reference temperature [303 K]. The predicted $D_w(u, T_d)$ for maltodextrin DE5 at 40, 60, and 80 °C as a function of moisture content is shown in Figure 4.2.

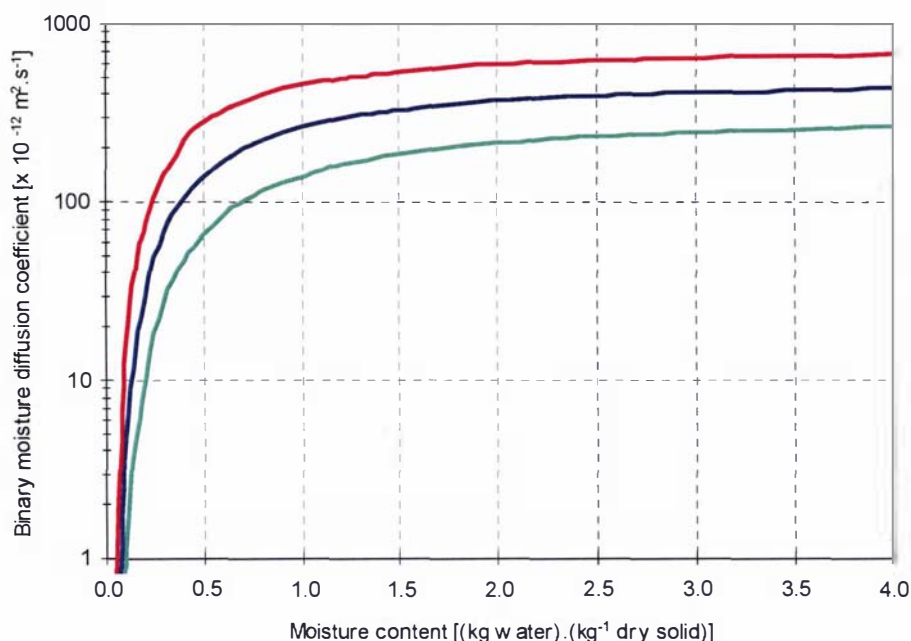


Figure 4.2: Predicted binary moisture diffusion coefficient for maltodextrin DE5 as a function of moisture content and temperature. Isothermal temperatures: — 40 °C; — 60 °C; — 80 °C.

It is clear that the binary moisture diffusion coefficient can span several orders of magnitude over a typical drying concentration range. The temperature effect is also significant. Future work should construct an apparatus to measure the isothermal thin slab drying kinetics of maltodextrin solutions. From such data, the calculation procedures given by Yamamoto (1999) can be used to confirm the predictions made here. This was not possible here in the time available.

4.5 MOISTURE SORPTION ISOTHERMS

Prediction of the moisture content at the surface of a drying droplet during the falling rate drying period requires knowledge of the surface water activity, a_w [–]. To determine the water activity-moisture content relationship, the moisture sorption isotherm is required. Moisture sorption isotherms present the hygroscopicity of a substance, that is, the amount of water holding capacity, in a particular humidity and temperature environment.

Moisture isotherms are typically obtained gravimetrically by exposing the sample to atmospheres of known water activity (or relative humidity/100) at constant temperature and measuring the weight change with time until equilibrium occurs. There are a number of ways for achieving a controlled relative humidity environment [Bell and Labuza (2000)], however, the use of saturated salt solutions is the most commonly used method. To measure a true adsorption isotherm, the powder should be dried to zero moisture content. However, this drastically increases the experimentation time, therefore, it is not uncommon to measure a

working isotherm [Foster (2002)]. The working isotherm does not require the powder to be dried first, but measures the initial moisture content which is then used to correct the moisture gains/losses for the powders exposed to relative humidities greater than zero [Foster (2002)].

2.5000 g of powder was weighed out into preweighed aluminium dishes (50 mm diameter × 18 mm depth) and then placed into plastic desiccators containing various saturated salt solutions [refer to Bell and Labuza (2000)] to give the desired water activity. The desiccators were placed into a temperature controlled oven at 30 °C. The salt solutions were made up above their saturation concentration with analytical grade salts in reverse osmosis (RO) water.

The weight gain/loss of the powders was measured at the end of a four week period. Preliminary trials showed that this time was sufficient to ensure that the error in the moisture measurement (usually ± 0.2% w/w or 2 mg per dry gram, Bell and Labuza (2000)), was larger than the weight change and hence the moisture content was assumed to reach ‘pseudoequilibrium’ [Bell and Labuza (2000)]. The initial moisture content of the powder was obtained by placing it over phosphorus pentoxide which gives a relative humidity close to 0%. The moisture content of the powder, X_p powder [(kg water).(kg⁻¹ dry powder)], at each relative humidity was calculated using Equation (4.2).

$$X_p = \frac{m_i u_i + (m_f - m_i)(1 + u_i)}{m_i} \quad (4.2)$$

where m_i , m_f and u_i are the initial mass of the powder [(kg water + dry powder)], the final mass of powder [(kg water + dry powder)] and the initial moisture content of the powder [(kg water).(kg⁻¹ dry powder)] respectively. The moisture sorption isotherms for the potential coating materials at 30 °C are presented in Figure 4.3.

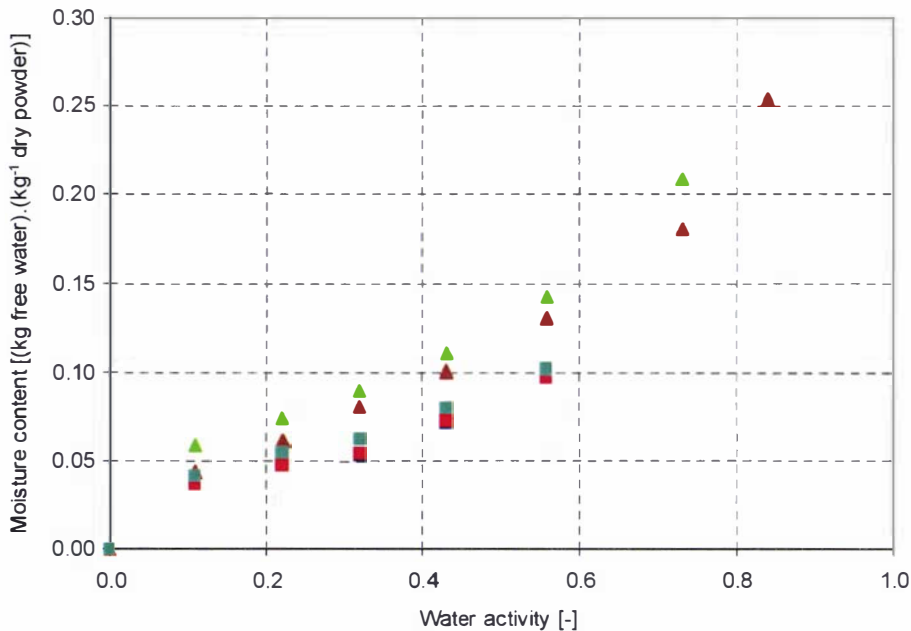


Figure 4.3: Moisture sorption isotherms for potential coating materials at 30 °C: ■ maltodextrin DE5 (hidden behind maltodextrin DE10); ■ maltodextrin DE10; ■ maltodextrin DE18; ▲ whey protein isolate; ▲ gum arabic.

It can be seen that there was only a slight difference in the isotherms for the maltodextrins, with the higher dextrose equivalents absorbing more moisture and each relative humidity value. Gum arabic and whey protein isolate absorb more moisture than the maltodextrins. It was not possible to measure the full isotherm for each material although saturated salt solutions with water activity up to 0.97 were employed. This was due either to the development of mold at high water activity or the dissolution (and subsequent hardening) in the high moisture content conditions.

Figure 4.4 compares the measured moisture sorption isotherms for the maltodextrins with those of Roos and Karel (1991a) and Adhikari (2002).

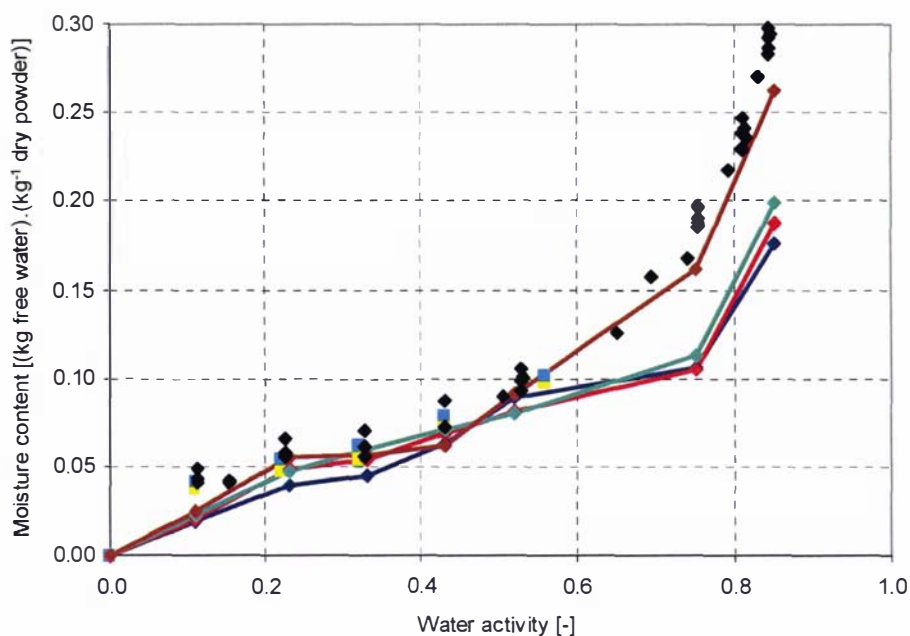


Figure 4.4: Comparison of measured maltodextrin isotherms and literature data. Measured: ■ maltodextrin DE5 (hidden behind maltodextrin DE10); ■ maltodextrin DE10; ■ maltodextrin DE18. Roos and Karel (1991a) data: ◆ maltodextrin DE5; ◆ maltodextrin DE10; ◆ maltodextrin DE15; ◆ maltodextrin DE20. Adhikari (2002) data: ◆ maltodextrin DE6.

Below a water activity of 0.5, the isotherms from Roos and Karel (1991a) showed very little difference in moisture sorption behaviour. Above water activity 0.5, the maltodextrin DE20 showed a significant increase in moisture sorption capacity compared to maltodextrins DE5, DE10 and DE15. The maltodextrins measured in this work show a higher moisture sorption capacity to those of Roos and Karel (1991a). This could be the result of the powder having a broader molecular weight range in their hydrolysis mixtures. The maltodextrins used in this study are from the same source (Grain Processing Corporation, Muscatine, IO, USA) as those used by Roos and Karel (1991a) and have the same average molecular weight. However, the 12 year gap in experiments could have seen a change in manufacture and final product attributes.

The moisture sorption isotherm for maltodextrin DE6 (Glucidex, Roquette, Freres, France) taken from Adhikari (2002) is also plotted. The maltodextrin DE5 data collected in this work agree well with Adhikari's data, hence his data at high water activity was used to generate a polynomial equation (Appendix A2.3.6.5) describing the water activity for maltodextrin DE5 to enable drying kinetics prediction in Chapter 5.

4.6 GLASS TRANSITION TEMPERATURE

The glass transition temperature, T_g [°C], is recognised as a fundamental parameter to explain stickiness [Adhikari (2002)] in amorphous and semi-crystalline low molecular weight sugars and carbohydrates. The glass transition phenomenon is important to the stickiness work conducted in Chapter 6 and is discussed further in Section 6.4.1.

The glass transition temperatures of food ingredients and products are commonly measured by thermal analysis methods such as differential scanning calorimetry (DSC) and dynamic mechanical (thermal) analysis (DMA or DMTA) [Slade *et al.* (1993)]. Other methods including nuclear magnetic resonance (NMR), electron spin resonance (ESR) and thermomechanical analysis (TMA) have been used by a number of researchers [Slade *et al.* (1993)]. The most popular methods to determine the temperature range currently are DSC and DMTA. DSC was chosen in this study due to its availability.

The DSC determines the glass transition as a second-order phase transition with a characteristic change in the specific heat capacity of the sample. Although it occurs over a temperature range, a single temperature is often referred being the glass transition temperature, denoted T_g [Roos (1995); Roos *et al.* (1996)]. Roos (1992) stated that the temperature range of the glass transition region is usually 10 to 20 °C.

The differential scanning calorimeter (DSC-7, Perkin-Elmer Corp., Norwalk, CT, USA) was connected to a low-temperature refrigeration unit. Pyris (version 3.00) software (Perkin-Elmer Corp., Norwalk, CT, USA) was used to make the glass transition temperature measurements. A two-point temperature calibration was performed using the onset melting temperatures of octadecane (28.24 °C) and indium (156.60 °C) standards. Heat flow was calibrated using the latent heat of melting of indium (28.45 J.g⁻¹). 10.0000–15.0000 mg powder samples (dependent on bulk density) were weighed (Mettler Toledo, UMT2, Greifensee, Switzerland) into the bottom of a pre-weighed stainless steel DSC pan (LVC ST. ST. 0319-0218, Perkin-Elmer Corp., Norwalk, CT, USA) and immediately hermetically sealed with a crimping device. The standard aluminium pans were not appropriate because they ruptured due to the greater than 2 bar pressure created as water desorbed from the samples in to the sealed environment. The stainless steel capsules are able to withstand pressures up to 24 atmospheres. Facilities to weigh the pans in a controlled relative humidity environment were not available at the time. The weighing and crimping was done quickly to minimise the moisture gain or loss to the laboratory ambient air. The pans were placed in the DSC thermal chamber for analysis.

An empty stainless steel pan was used as the reference sample. The dry box of the DSC was kept free of moisture using desiccant (silica), and flushed with dry nitrogen. The sample head was purged with dry nitrogen (20 ml.min⁻¹) to avoid condensation of moisture from the air.

The following thermal profile was used (based closely on the method recommended by Höhne *et al.* (1995)): hold at 50 °C below the expected T_g for 5 min, heat to 30 °C above the expected T_g , hold for 5 min at this temperature, then rapidly cool (quenching) to the start temperature. The thermal profile was immediately repeated to remove the thermal history of the sample (annealing). T_g was determined as the onset temperature of the endothermic shift in baseline during the second heating cycle. All heating and cooling cycles were programmed at 5 °C.min⁻¹ as recommended by Foster (2002). Duplicate analysis on each sample was performed with the average and standard deviation of the measurements reported.

Foster (2002) discussed the various definitions of T_g in terms of their location on the heat flow profiles. The onset temperature (defined by the Pyris software as the intersection of the extrapolated tangent at the first limit, and the extrapolated tangent at the inflection point) was used in this work. According to Foster (2002), reported onset T_g in the literature are likely to be the T_g of this definition.

Figure 4.5 presents selected thermograms from the DSC showing the variability in the temperature range over which the glass transition occurs in the maltodextrins at different water activities.

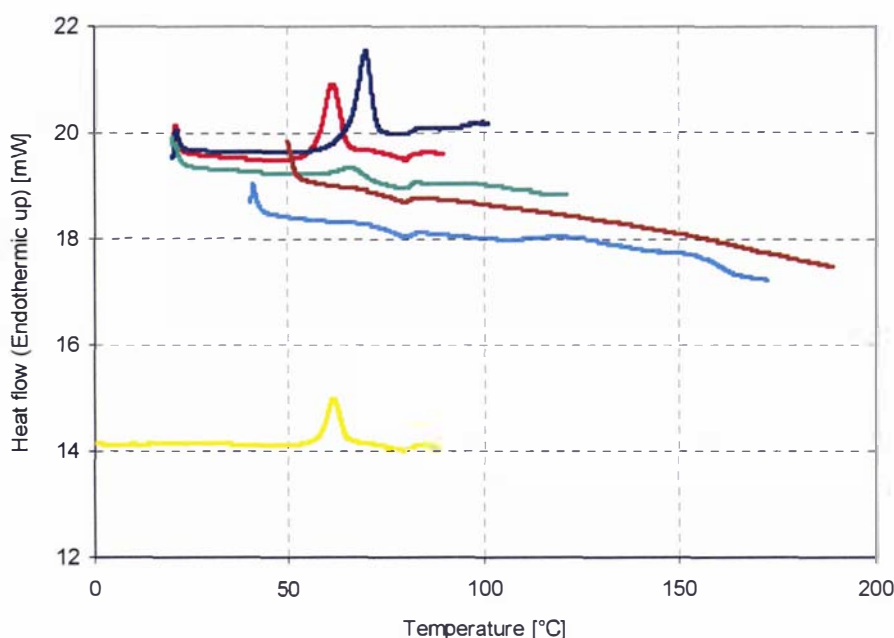


Figure 4.5: Selected thermograms from the DSC showing the variability in the temperature range over which the glass transition occurs in the maltodextrins at different water activities. — maltodextrin DE18 ($a_w = 0.22$); — maltodextrin DE18 ($a_w = 0.43$); — maltodextrin DE5 ($a_w = 0.43$); — maltodextrin DE5 ($a_w = 0$); — maltodextrin DE10 ($a_w = 0.11$); — maltodextrin DE5 ($a_w = 0.73$).

The thermal peaks for maltodextrin DE18 at high water activity were relatively narrow making T_g easy to determine. However, for maltodextrin DE5 and DE10, particularly at low water activities, peaks spanning up to 20 °C were observed making the interpretation of the onset glass transition temperature difficult to determine. The same broadening of the thermogram profile was seen when Roos and Karel (1991b) compared the low molecular weight sucrose to a (4:1) mixture of sucrose and Amioca, the latter being a high amylopectin waxy corn starch. The difficulty in measuring the T_g of other high molecular weight polymers has been noted by Zeleznak and Hosney (1987) and Matveev *et al.* (1997).

Figure 4.6 presents the T_g profiles of maltodextrins from Roos and Karel (1991a) along with data collected for the maltodextrins used in this study.

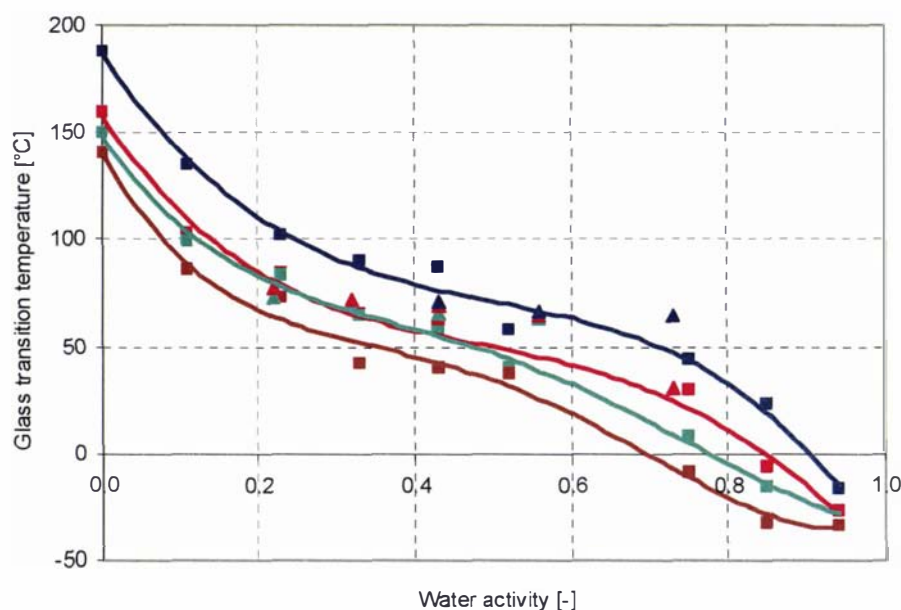


Figure 4.6: Glass transition temperature profiles for maltodextrin DE5, DE10, DE15 and DE20 from Roos and Karel (1991a) and data collected in this study. Roos and Karel (1991a) maltodextrin data: ■ DE5; ■ DE10; ■ DE15; ■ DE20. Experimental data: ▲ DE5; ▲ DE10; ▲ DE18. The solids lines are 4th order polynomial equations fitted to the Roos and Karel (1991a) data. Note: the T_g of DE15 at $a_w = 0$ is extrapolated for curve fitting purposes.

The glass transition temperature is a strong function of water activity (and hence moisture content). The limited data collected in this work fell close to those given by Roos and Karel (1991a). They used a linear relationship to describe the T_g dependence on water activity for the range $a_w = 0.11$ – 0.85 . Outside this range they assumed that the shape of the relationship was sigmoidal because of the very high viscosity of the non-plasticised material and the low glass transition temperature of water, respectively. Due to the similarity in results a polynomial correlation was fitted to the Roos and Karel (1991a) data (Appendix A2.3.6.6) for modelling predictions in this thesis.

4.7 SOLUTION VISCOSITY

The viscosity of a liquid is a measure of the internal resistance offered to the relative motion of different parts of the liquid [Shaw (1985)]. The solution viscosity was measured as it is an important variable in the droplet impact and spreading, and droplet drying and stickiness micro-level processes.

Viscosity measurement techniques include capillary flow methods and rotational methods [refer to Shaw (1985)]. In this work measurements were made on a Paar Physica Rheolab MC1 rheometer (rotational method) using a Z2.1 concentric cylinders geometry.

The maltodextrin solutions (0 to 40% w/w) were made up by weight; maltodextrin DE5 powder was dissolved at 85 °C whilst mechanically stirring in a covered beaker to minimise evaporation. Two total solids measurements were made on the solutions by oven drying at 85 °C (until zero mass change) to determine the final solids content to account for both evaporative losses and the water associated with the powder. Immediately after cooling to room temperature the solutions were subjected to viscosity measurements. The solutions were subjected to a constant shear stress (CSS) with a shear sweep from 1 mN.m to 50 mN.m

or to a shear stress at which solution vortexing was observed. At this time, the run was stopped and repeated but this time only up to a shear stress just before vortexing occurred. Then, the sweep was reversed to look for hysteresis. Measurements were made at 1 s intervals. The average viscosity was taken over 4 runs.

The solutions were slightly non-Newtonian showing a small degree of shear thinning behaviour with increasing shear stress. Whilst the shear thinning nature of the solutions meant a single viscosity is not representative of the solution over a wide range of shear rates, the viscosity of the solutions as a function of concentration were reported at the 1000 s^{-1} shear rate as this was common to all solution concentrations. During droplet impact, the viscosity of the solution will change with time as the droplet undergoes varying degrees of shear during spreading and recoil.

The solutions also exhibited thixotropic behaviour [Shaw (1985)], that is the viscosity of the solution increased with time as it was allowed to stand at room temperature. This was evident in the first shear sweep as the apparent viscosity rapidly fell away as the intermolecular network was broken [Wilkinson (2000)]. Subsequent shear sweeps did not show this behaviour.

The viscosities of the maltodextrin solutions are tabulated in Section 7.5.2.

4.8 SOLUTION SURFACE TENSION

Surface tension was required for the impact and spreading experiments because it controls the recoil behaviour of impacting droplets. The surface tension of a liquid is often defined as the force acting at right angles to any line of unit length on the liquid surface [Shaw (1985)].

The many methods available for the measurement of surface and interfacial tensions can be classified as static, detachment and dynamic [Shaw (1985)]. Methods include capillary rise, droplet volume and droplet weight methods, maximum bubble pressure method, pendant or sessile drop and Wilhelmy plate methods. The dynamic surface tension (DST) and equilibrium surface tension (EST) are both of interest to droplet impact and spreading studies.

EST measurements were made by Wilhelmy plate technique on a Krüss K12 tensiometer (Krüss GmbH, Hamberg, Germany). About 30 ml of solution was measured into a plastic container and placed on the instrument stage. The plate was allowed to travel into the sample at $2\text{ mm}\cdot\text{min}^{-1}$. The surface tension was calculated by the instrument and given via printout. All measurements were carried out at room temperature (approximately $22\text{--}25\text{ }^{\circ}\text{C}$). The platinum plate was rinsed with RO water (and acetone in some cases), then flamed to provide a clean surface between sample measurements.

Single measurements were sufficient for the 20% w/w solids concentration solutions, however, surface tension measurements on the 40% w/w solids concentration solutions were carried out under the 'series of measurements' mode. This was due to the slow time dependency of wetting of the plate and flow back to solution which results in a fall in surface tension readings. One measurement was taken every 10 s for up to a total of 90 readings or until the readings reached a plateau. After this time, skin formation on the surface of the solution resulting from localised evaporation caused an increase in surface tension values. This was also observed by Williams *et al.* (2004) for milk and milk concentrates.

Excessive shaking of the solutions was avoided as this caused foaming which led to erroneous results. In some instances, it was necessary to degas the solutions under vacuum.

The results of the surface tension measurements are tabulated in Section 7.5.2.

4.9 DROPLET–SURFACE CONTACT ANGLE

For a droplet spreading on a surface, the contact angle is the angle made between the intersection of the solid and liquid three-phase contact line. The measurement of contact angles can be used to characterise the surface by providing an indicator of cleanliness or to determine more fundamental information such as the solid–vapour and solid–liquid surface tensions [Spelt and Vargha-Butler (1996)]. Contact angle measurements were required for the droplet impact and spreading experiments in Chapter 7.

Numerous techniques are available including: axisymmetric drop shape analysis (ASDA) of sessile drops, capillary rise at a vertical plate, the use of a goniometer telescope [Spelt and Vargha-Butler (1996)] or the simple photographic and angle measurement technique. The latter was employed here with the aid of camera system I as described in Section 7.4.3.

The contact angle can be dynamically measured as it advances or recedes on a surface, termed advancing and receding contact angles respectively, or it can be measured as a static quantity, usually termed an equilibrium contact angle. It is important that the correct terminology is used when quoting contact angles since, in general, advancing contact angles are greater than the equilibrium contact angles which are in turn greater than receding contact angles as the latter leaves a thin film behind on its retraction. All three warranted investigation for Chapter 7.

The advancing contact angle is of interest to predict the maximum spread diameter of a droplet. To measure this, the syringe was mounted just above the sample surface and the volume of the droplet on the surface was grown continuously to near 100 μl , to advance the droplet across the surface. However, dynamic contact angles are known to increase with increasing contact line velocity [Pasandideh-Fard *et al.* (1996)]. Unfortunately, the rate of volume delivery could not produce the very high spreading velocities expected (around 2 m.s^{-1}) during a droplet impact event. This rendered advancing contact angle measurements of limited use.

The receding contact angle is of interest to predict the final (recoiled) spread diameter of a droplet. This was done by using the needle to continuously withdraw solution from the already advanced droplet. However, the droplet remained pinned on the surface at the maximum spreading diameter achieved during the advancing experiments. In these cases, the receding contact angle was merely an artefact of the droplet size reduction and thus not representative of that actually occurring during droplet recoil. Given these difficulties along with the inherent subjectivity in identifying the three-phase line needed to calculate the contact angle, the receding and advancing contact angles were not further investigated.

Other investigators [Pasandideh-Fard *et al.* (1996); Mourougou-Candoni *et al.* (1999)] were able measure the contact angle during the actual impact and spreading event. Unfortunately, the camera system employed here to follow the dynamics of the 10 μl (2.8 mm diameter) droplets did not have a suitable magnification to allow this.

The equilibrium contact angles of pure water on the pure and surface lecithinated anhydrous milkfat lecithinated plates were able to be measured by adding 5 incremental volumes of approximately 20 μl . After each advancement a photo was taken and the angle measured. The existence of a dependency of contact angle on droplet size noted by Buckton (1990) and McGuire and Yang (1991) was checked and not found to be significant above 10 μl . There was no difference in measurements when the needle remained in the droplet during advancement or when the increments were added drop-wise. As solution was added the droplets were found to pin and then jump to their next spread diameter. There appeared to be a threshold, balancing the surface energy and the weight force of the droplet and possibly an activation energy or barrier to droplet advancement over the surface. According to Shaw (1985), contact angles are rarely single-valued quantities, but a range of meta-stable contact angles exist. When this was exceeded the droplet jumped to its next stable position. The equilibrium contact angle results are reported in Section 7.9.1.

4.10 PARTICLE SIZE ANALYSIS

Particle size analysis (PSA) measurements were made on the coating substrate (glass ballotini®, Potters spec C, minimum roundness 75%, US sieve 40–60, Potters Industries Inc., Valley Forge, PA, USA) and atomiser spray delivered from a Glatt® Würster coater (UniGlatt D7852, Glatt® Process Technology GmbH, Binzen, Germany). These were both important to the coating trials conducted in Chapter 8.

All PSA measurements were performed on a Malvern Mastersizer (model MSS, Malvern Instruments Limited, Malvern, Worcestershire, UK). Substrate PSA data were collected by placing a 10 g sample onto a dry powder feeder which directed the particles past the laser beam in the Mastersizer chamber. The 1000 lens was used with at least 5000 sweeps. The lower and upper obscuration bounds were set at 2 and 40%. On average the obscuration was 5–10%. As mentioned in Section 3.5, a small spray droplet size and narrow size distribution are critical to achieving high coating quality. Spray droplet size distributions were collected by directing the spray into the path of the laser beam. To standardise the measurements, the nozzle was placed 5 cm from the laser beam path and positioned such that the beam passed through the centre of the spray. This gave obscurations within the set bounds and reproducible results. At larger distances, smaller Sauter mean diameter droplet sizes were obtained, which results from the dispersion of the spray to give lower obscuration rates and results from the increased amount of droplet evaporation over the larger distances. Beam alignment and a background measurement were made before each measurement. Spray droplet PSA results for the spray for a variety of formulations were collected by spraying at 2 bar atomisation air pressure and at 3.5 $\text{ml}\cdot\text{min}^{-1}$ coating solution flowrate. Figure 4.7 shows the particle size distribution (PSD) of the an uncoated and 20% w/w maltodextrin DE5 coated glass ballotini® sample and the PSD of a 20% w/w maltodextrin DE5 spray droplet solution.

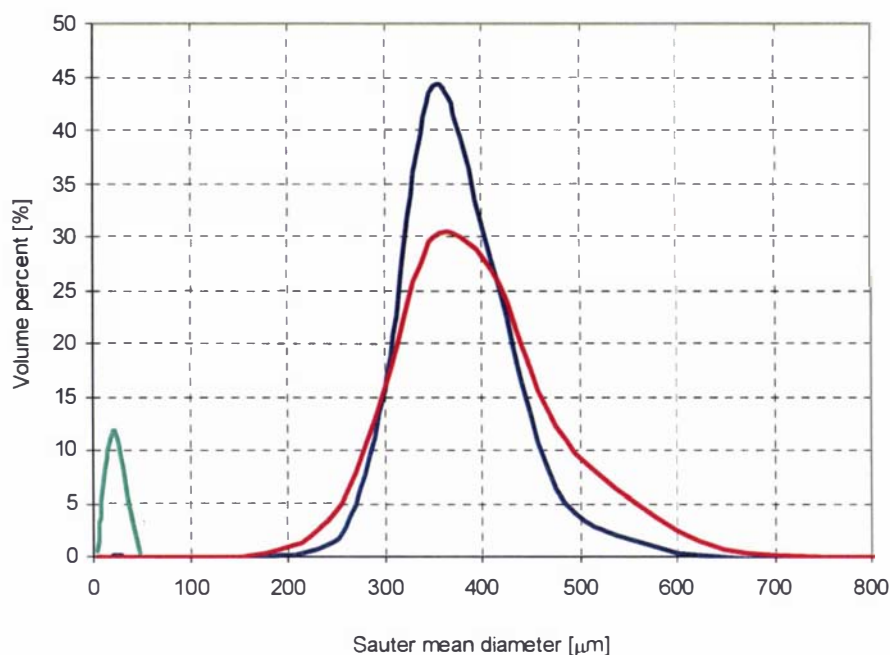


Figure 4.7: Particle size distribution of an uncoated and 20% w/w maltodextrin DE5 coated glass ballotini® sample and a 20% w/w maltodextrin DE5 spray droplet size distribution at 2 bar atomisation air pressure and 3.5 g.min⁻¹ coating solution flowrate. — uncoated ballotini®; — coated ballotini®; — spray.

The PSA shows a normal size distribution for the substrate ballotini® spread about a mean particle diameter (MPD) of 300 μm. The MPD was taken to be the Sauter mean diameter of $D(3,2)$ from the software analysis. There was no sign of spray droplet drying or inter-particle agglomeration in the coated substrate (monomodal, normally distributed) having a MPD of 333 μm. The spray droplet size is also normally distributed with a MPD of 14 μm. This gave a particle/droplet size ratio greater than 10, as suggested by [Guignon *et al.* (2002)] for successful coating without inter-particle agglomeration.

4.11 COATING MASS

The amount of coating mass collected by the substrate particles was used as a measure of the amount of spray droplet drying occurring in the population based pilot-scale coating trials (Chapter 8). A 15.0000 g sample of coated glass ballotini® was placed into 80 °C water to dissolve the coating. The solution was filtered in a Buchner funnel with filter paper (595, 70 mm, Schleicher and Schuell MicroScience GmbH, Dassel, Germany) to remove the ballotini®. The filtrate was then poured into a pre-weighed beaker and evaporated at 80 °C for 24 h (constant weight). The coating mass was reported as the grams of dry coating material per gram of uncoated substrate. Tests were carried out in duplicate with the average results reported. All samples were pre-dried at 80 °C for 24 h (constant weight) to remove sample moisture content variability. In some cases, spray-dried droplets were present, that is, PSA measurements yielding bimodal distributions with a second peak having a MPD less than 10 μm. These samples were sieved prior to coating mass measurement.

4.12 COATING MORPHOLOGY

Samples were mounted onto double-sided tape and fixed to aluminium specimen stubs. Loose beads were removed using an air puffer. The samples were sputter coated with approximately 100 nm of gold. The images were viewed using a Cambridge 250 Mk3 scanning electron microscope at HortResearch, Palmerston North. Photographs were taken at the chosen magnifications on Ilford FP4 black and white film. 3 sub-samples were taken from each sample to ensure a representative image was taken.

4.13 CONCLUSIONS AND RECOMMENDATIONS

Potential coating materials for dairy industry applications include maltodextrins of various dextrose equivalent, whey protein isolate and gum arabic. Some physical properties of the maltodextrins were measured and/or predicted for use throughout the thesis. Future work should measure the binary moisture diffusion coefficient for these materials to enable more accurate mathematical model predictions.

CHAPTER 5

SINGLE DROPLET DRYING KINETICS AND MODELLING

5.1 INTRODUCTION

To achieve successful coating, it is important to optimise the drying conditions, particularly to avoid over-drying of droplets before impact. Genskow (1990) stated that optimisation of the drying process by statistical methods is usually a tedious process involving many pilot trials [as cited in Achanta and Okos (1995)], which is only made more onerous when there are many potential coating materials to trial. The ‘focused literature review’ (Chapter 3) determined that a predictive tool for droplet drying could enable prediction of the surface moisture content, which is important from both a droplet impact and adherence perspective and an inter-particle agglomeration perspective. Such predictions would greatly reduce the number of trials needed for product development and process optimisation.

This chapter identifies and selects an appropriate model to describe the drying kinetics of a single droplet. The model is then validated against experimental results on a single droplet drying rig. The model is used to predict the outcome of process variable changes under industrially relevant conditions in order to draw guidelines on the design and operation of a Würster-style coater for coating dairy powders.

5.2 CONCEPTUAL MODELS OF THE DROPLET DRYING PROCESS

During air drying of droplets, transport of heat occurs from the bulk air to the droplet surface, primarily by convection and, within the droplet by conduction and convection. Mass transfer occurs in the opposite direction, from the droplet centre towards the surface, by a number of mechanisms. External heat and mass transfer from the surface are relatively well described in the chemical engineering literature. However, describing both the internal heat and mass transfer is more difficult. Material dependent morphological changes, moisture sorption equilibria, internal vaporisation and internal circulation complicate the mathematics required to adequately model the internal drying process.

To gain an understanding of the physical process to be modelled, the 5 stage drying concept proposed by Dolinsky and Ivanicki (1984) [as cited in Nesic and Vodnik (1991) and Dolinsky (2001)] is shown in Figure 5.1 and described below.

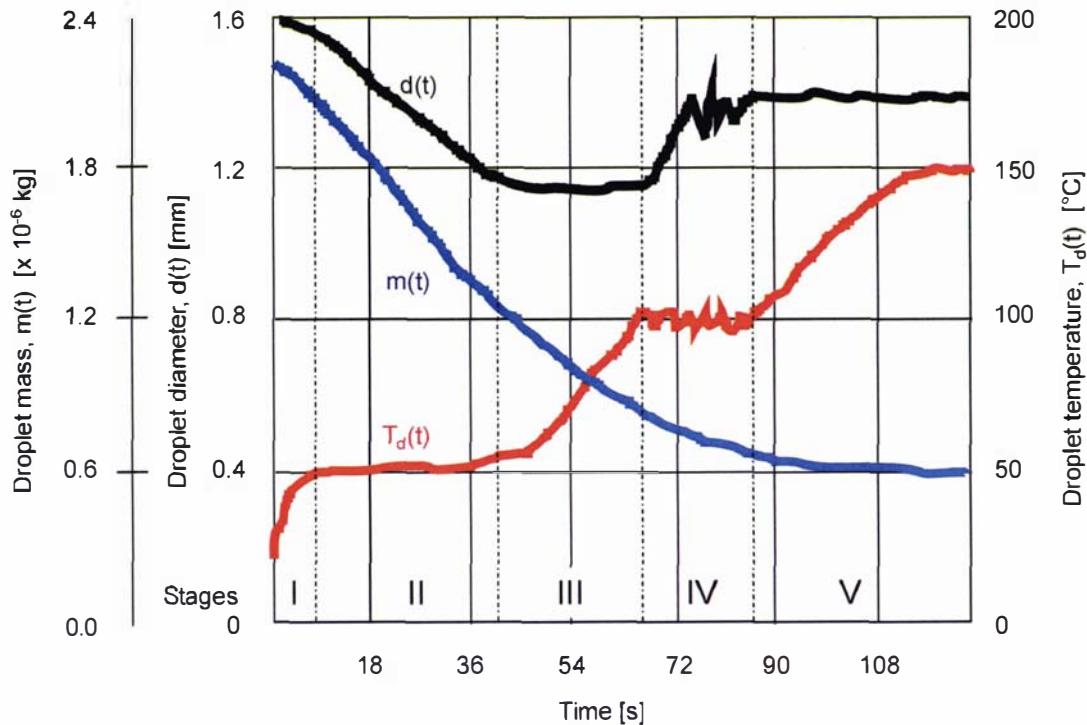


Figure 5.1: 5 stage drying concept proposed by Dolinsky and Ivanicki (1984) [adapted from Dolinsky (2001)].

First stage: *initial heating and evaporation*, the period of droplet heating from its initial temperature up to the equilibrium temperature, which is most often close to the wet bulb temperature for the air temperature and humidity.

Second stage: *quasi-equilibrium evaporation*, the period of equilibrium evaporation during which intensive removal of moisture from the droplet surface occurs. The droplet temperature is slightly higher than the wet bulb temperature and constantly increases due to the rising concentration of solids at the surface.

Third stage: *crust formation and growth*, which begins when the surface solids concentration reaches or exceeds a critical value. Solid separation in the form of crystallisation or agglomeration begins, forming a crust. The crust thickness grows towards the interior of the droplet, while the evaporation front is maintained at the wet core–solid crust interface. The dynamics of this stage primarily depend on the crust permeability for vapour diffusion.

Fourth stage: *dehydration and boiling*, which occurs when the droplet temperature reaches the boiling point. This can only happen when the air temperature is higher than the boiling temperature for a given total pressure. A large amount of vapour is generated, causing the internal pressure in the particle to rise. Depending on the permeability and the mechanical characteristics of the crust, the particle can crack or inflate, allowing the vapour to escape and relieve the pressure difference, or it can explode causing the particle to completely disintegrate.

Fifth stage: *porous particle drying*, when the bound liquid phase is evaporated from the almost dry, porous particle with a decreasing rate, while the temperature asymptotically approaches the surrounding air temperature.

The first two stages of drying are called the constant drying rate period and the remaining three are called the falling drying rate period. Given the low temperature conditions ($< 80\text{ }^{\circ}\text{C}$) because to substrate limitations encountered in an air-suspension particle coating operation, only the first 3 physical stages need to be modelled in this work. Mathematical descriptions of these three physical processes were then sought.

Keech (1997) described four mechanistic drying models based on simple 'pictures' of the moisture movement mechanisms such as, wetted surface models, receding evaporative interface models, effective diffusion models and surface diffusion models. Farid (2003) identified from the literature four different approaches to mathematically describe droplet drying. However, it is difficult to categorise the models into distinct groups as many contain both common and/or distinct assumptions and calculation methods. In addition, the most suitable model will depend on the solution being dried and the stage of drying. For example, the wetted surface model would apply well in the early stages of drying a very low solute concentration droplet or porous material, where transport by convection will be important during and immediately after droplet formation. A surface diffusion model may apply when drying to very much lower moisture contents, i.e. to an equivalent monolayer region. A receding interface model applies when transfer of water-vapour through dry solids occurs, often in the last stages of drying, assuming the droplet temperature is above the solvent vapour-point. This type of transport is common when drying easily crystallised materials. Crystallisation is not usually spontaneous because of the composition of liquid foods and so a rigid matrix will often be formed at a late stage of drying. van der Lijn (1976) states that a molecular diffusion model applies to the drying of coffee extract, where the droplets remain liquid up to a late stage of the drying and cool down to a glass-like structure.

Given that the constant rate drying period is rarely observed in concentrated foodstuffs [Cheong *et al.* (1986); Dolinsky (2001); Räderer (2001)] mass transfer by diffusion is thought to be the most significant water movement process during the drying of many liquid foods. For this reason, the majority of the mathematical models for predicting the kinetics of spray-dried solute containing liquids can be categorised into two broad groups; receding interface models and effective diffusion models.

The receding interface model considers drying to take place in two stages [Adhikari (2002)]. In the first stage, a free liquid interface exists between the air stream and the droplet and drying takes place as if it were a pure solvent droplet. Water movement from the interior of the droplet maintains the wetted surface. After some time (usually when the surface concentration reaches saturation), a crust or skin appears at the surface due to solute accumulation and the associated increase in viscosity which reduces the molecular mobility to effectively separate the air stream and the solution at the droplet core. Water can no longer move easily from the core to the surface. This means that evaporation now takes place at the solution–crust interface and continually recedes towards the core as the crust thickness grows. At this stage, capillary effects in the crust are considered negligible and water is transported through the crust by vapour diffusion. The crust resistance becomes prominent (as the crust grows in thickness) such that the evaporation rate diminishes. However, the structure, and in particular the porosity of the crust have been ignored, largely because of the difficulty in quantifying these parameters [Cheong *et al.* (1986)]. Works of Audu and Jeffreys (1975), Cheong *et al.* (1986), Nesic and Vodnik (1991) and Dolinsky (2001) all employed receding interface models. The different interpretations have resulted in many forms of mathematical expressions to describe the temperature and moisture content history of drying droplets [Adhikari (2002)]. The fundamental assumptions made in this type of model can be found in Cheong *et al.* (1986), Nesic and Vodnik (1991) and Dolinsky (2001). These include:

- Heat is transferred from the drying air to the crust by convection only.
- Heat is transferred through the crust by conduction only.
- Below the solute saturation concentration the droplet evaporates as if it were a pure solvent. The change in volume of the droplet corresponds to the amount of water evaporated ('ideal shrinkage').
- When the surface concentration reaches saturation a crust forms and grows in thickness towards the centre of the droplet.
- At this time, the droplet is spherical with a rigid crust that neither shrinks nor inflates and is free of fractures.
- Evaporation occurs only at the crust–wet core receding interface.
- Moisture is transferred through the crust pores by vapour diffusion and is represented by an effective diffusion coefficient. There is no hold up of water in the crust volume.
- The wet core density remains constant.
- There is no temperature gradient in the droplet.

Skin or crust formation is commonly observed [Achanta and Okos (1995); Räderer (2001)] in the drying of foodstuffs, however, all the receding interface models assume a constant outer droplet radius after crust formation (i.e. after surface saturation is reached) which is not likely to be correct. The dairy industry commonly spray dries liquids and slurries above their saturation concentrations and the final dried particle size is observed to be smaller than that of the atomised droplet, thus indicating droplet shrinkage above their saturation concentration [D. L. Pearce, Fonterra, Palmerston North, personal communication, 1 March, 2004].

Although the receding interface conceptual model more accurately depicts the physics of the drying of single droplets, the effective diffusion model employing solute-fixed coordinates, proposed by Crank (1956), has had similar success, is mathematically rigorous and yet easy to implement, because it automatically accounts for droplet shrinkage. This model type uses a coordinate transformation in which the independent distance (spatial) variable is expressed in terms of the mass of water-free solute rather than the actual distance. The major assumption is that the droplet is solid (non-hollow), remains perfectly spherical and the change in volume of the droplet corresponds to the amount of water evaporated ('ideal shrinkage'). There is also no distribution of temperature in the droplet. The diminishing evaporation rate as drying proceeds is accounted for by an effective binary moisture diffusion coefficient which is usually a least squares fitted correlation that is strongly dependent on moisture content and to a lesser extent temperature. However, such diffusivity is difficult to measure from independent experiments, particularly under isothermal conditions [Farid (2003)]. This increased experimental effort is offset by a decrease in the modelling effort required. This approach has since been employed by several researchers [van der Lijn (1976); Wijnhuizen *et al.* (1979); Sano and Keey (1982); Ferrari *et al.* (1989); Meerdink (1993); Yamamoto and Sano (1995); Hecht and King (2000b); Räderer (2001); Adhikari (2002)]. Sano and Keey's model includes the inflation and rupture of a central bubble in the droplet to leave a central void which is in agreement with observations of industrially spray-dried particles (see Figure 5.3(d)). According to Adhikari (2002), the solute-fixed coordinate system offers several advantages. (1) The solution requires minimal computer resources. (2) Since the grid moves with the solute, it does not require interpolation schemes to locate the new, actual position of the gas–liquid interface. (3) For a spherical geometry the grid contains more shells near the outer edge of the droplet where mass transfer is mainly limited due to skin formation. This helps to gain a better resolution and adapt to the concentration profile, which is very steep close to the surface [Räderer (2001)].

Figure 5.2 depicts the conceptual descriptions of that currently modelled by the two types of models.

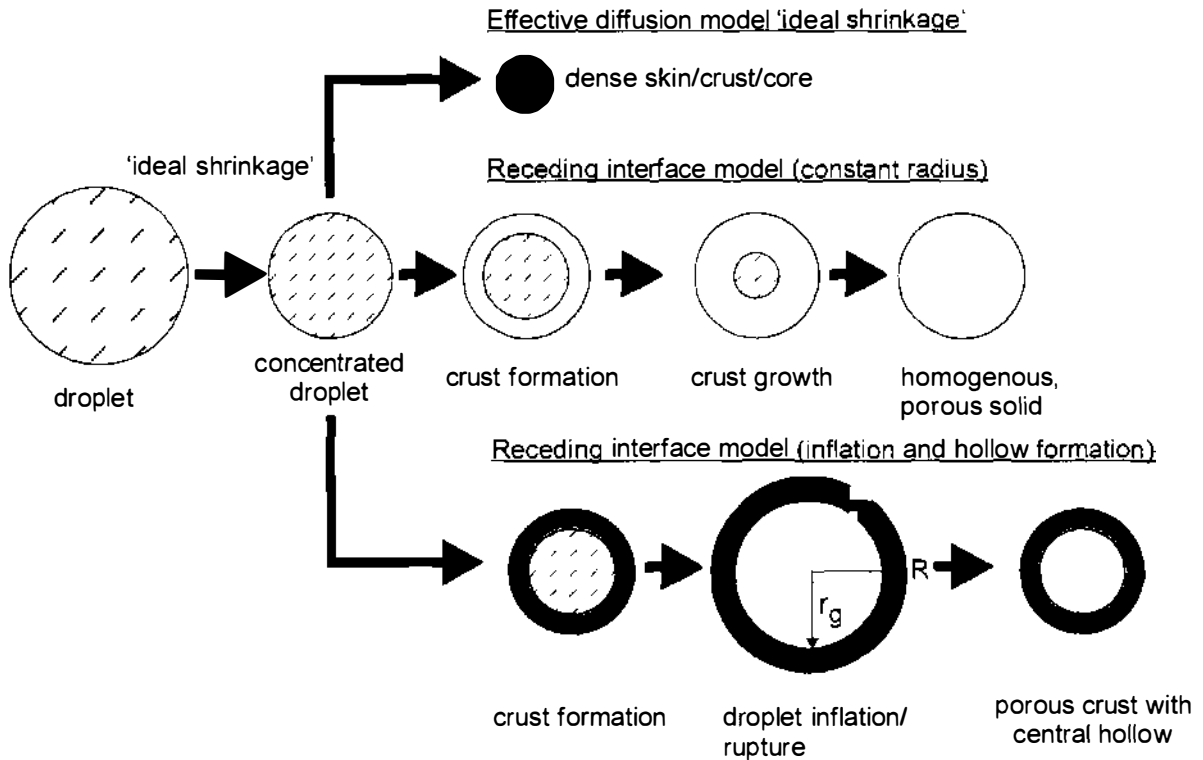


Figure 5.2: Conceptual descriptions for droplet spray drying that the two major mathematical model type categories (receding interface and effective diffusion models) are based upon.

These are ideal spherical cases and by no way represent all the possible drying scenarios. In reality, spray-dried droplets can show indentations, wrinkled surfaces, cracks, fractures, varying degrees of porosity and varying degrees of inflation and deflation. It is possible that the true drying behaviour could best be modelled with a combination of both these major model types. The Nesic and Vodnik (1991) model was a mixture of both the receding interface and effective diffusion models. Before crust formation, termed the 'gel phase', the diffusion coefficient was that used by Wijnhuizen *et al.* (1979), i.e. a strong function of moisture content similar to the effective diffusion models. However, after crust formation, a crust diffusion coefficient ($D_{eff} = 1.5 \times 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$) was employed and the evaporation rate diminished as the crust thickness grew, similar to the receding interface models.

To better understand which type of drying kinetic model to employ, scanning electron micrographs representative of typical spray-dried powders were examined. Figure 5.3(a–d) shows varied and complex morphological features of some spray-dried droplets.

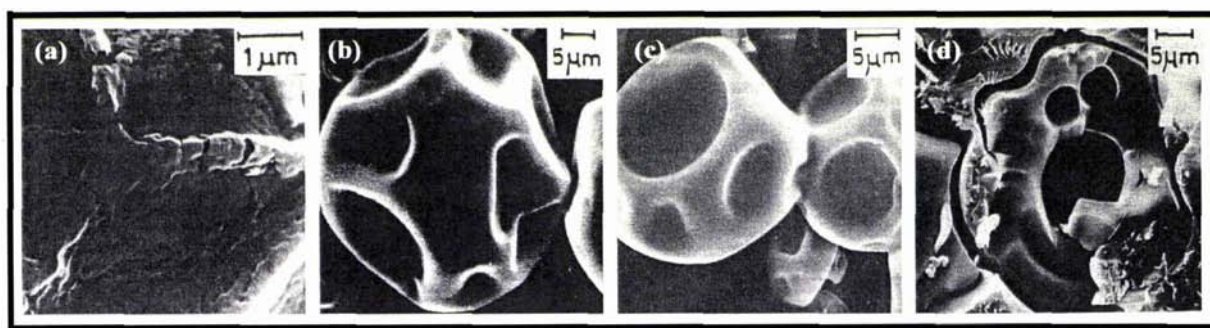


Figure 5.3: Scanning electron micrographs of spray dried droplets depicting complex morphological features [adapted from Rosenberg *et al.* (1985)]. (a) cracking in maltodextrin DE20; (b) indentations in gum arabic; (c) no cracks but indentations in maltodextrin DE10; (d) vacuole development in gum arabic (cross-section of a particle shown with three vacuole (hollows) in the centre).

Figure 5.3(a) shows evidence of cracking in maltodextrin DE20. However, maltodextrin DE10 (Figure 5.3(b)) shows no sign of cracking but, rather a smooth non-porous surface with large indentations. The same is also seen for gum arabic (Figure 5.3(c)). These indentations are caused by the condensation of water vapour creating a vacuum and collapsing part of the droplet surface upon droplet. During the spray drying of milk and other liquids, vacuoles (hollows) are usually formed in the dried particles [van der Stege and Walstra (1987); Hecht and King (2000a)]. Figure 5.3(d) shows three vacuoles forming in the middle of a spray-dried gum arabic particle. Verhey (1972) showed that the vacuoles are initially formed by entrapment of air bubbles; during drying these bubbles expand, since the rapidly developing hard skin of the droplet hinders droplet shrinking, and part of the water-vapour formed thus moves to the existing vacuole. According to Hayashi (1980) [as cited in Sano and Keey (1982)] the voidage of skim milk particles produced by spray drying usually varies between 13–35%. In this case, Sano and Keey's model could be employed. However, as mentioned earlier, the drying air temperatures in an air-suspension powder coating operation in the dairy industry are low because of substrate limitations. Most importantly, since the rheological properties of the crust, in particular, the porosity and elasticity are not accounted for mathematically, let alone measured and known, it remains debatable whether to employ a receding interface model or an effective diffusion model.

It is debatable whether the additional complexity of formulating and implementing a receding interface model can be justified because it does not account for the complex morphological features and shrinkage that occur when dairy droplets are spray-dried above their solids saturation concentrations. For this reason, and the reasonable success obtained by other researchers, the effective diffusion model was selected as the model to be developed in this work.

5.3 CONTROLLING DRYING MECHANISMS

The assumption of a uniform internal temperature is supported by many researchers [Kerkhof and Schoeber (1974); van der Lijn (1976); Ferrari *et al.* (1989); Meerdink (1993); Adhikari (2002)] and makes the mathematical model easier to implement. The assumption is reasonable for the severe temperature and relative velocity conditions in the spray drying environment. However, air-suspension particle coating operations (particularly for dairy applications) are run at much lower temperatures and an internal temperature gradient may exist in the droplet.

As an alternative modelling approach, Farid (2003) calculated the Lewis number ($Le = \alpha_T/D_w$) used for coupled heat and mass transfer problems, which compares the thermal diffusivity, α_T [$\text{m}^2.\text{s}^{-1}$] to the mass diffusivity, D_w [$\text{m}^2.\text{s}^{-1}$] of water-vapour in the crust. He calculated that the Lewis number varied from 0.06–0.1 for the drying of skim milk droplets, which indicated that the drying process was thermal-diffusion controlled rather than mass-diffusion controlled. This is in direct contrast to all investigations to date which, when assuming mass diffusion control, assume uniform internal temperature. According to Liou (1982) [as cited in Ferrari *et al.* (1989)] and Frias *et al.* (2001), in liquid or semi-solid foods, the time constant for internal heat transfer is much smaller than for internal mass transfer.

Farid then developed a receding interface model using a discretised temperature profile and a uniform time dependent moisture content. In general, the model correlated well with literature experimental data and predicted a significantly higher surface temperature compared to the bulk droplet temperature when under industrial spray drying conditions. However, there are differences between skim milk droplet spray drying and that expected in air-suspension particle coating. Farid used a diffusivity of water-vapour in a skim milk powder crust of $2.72 \times 10^{-5} \text{ m}^2.\text{s}^{-1}$ [Chen *et al.* (1999)] in calculating the Lewis number. This value is similar to water diffusivity in air suggesting the crust of a skim milk powder droplet is more a porous crumb rather than a thick glassy skin. Nesic and Vodnik (1991) calculated the skim milk crust diffusivity to be $1.5 \times 10^{-6} \text{ m}^2.\text{s}^{-1}$ with no evidence of particle inflation or rupture above 100 °C which suggests a fragile or porous crust. In contrast, Sano and Kee (1982) and Ferrari *et al.* (1989) report concentration dependent diffusivity values of the order $1 \times 10^{-10} \text{ m}^2.\text{s}^{-1}$ for skim milk droplet drying. When drying a maltodextrin DE11 droplet at 50 °C, Adhikari (2002) found the moisture diffusivity to be of order $10^{-10} \text{ m}^2.\text{s}^{-1}$. The disparity between these values is a direct result of how the two models are used to predict the diminishing evaporation rate as drying proceeds. The receding interface models use crust growth to increase mass transfer resistance while the effective diffusion models use a logarithmically decreasing binary moisture diffusion coefficient correlation to increase mass transfer resistance as the droplet dries. Substitution of this wide ranging value into the Lewis number equation would quite rightly suggest either a mass or thermal diffusion controlled process. However, in light of the less severe drying conditions in an air-suspension particle coater and the model developed by Farid, the assumption of a uniform internal droplet temperature warrants further investigation.

The Biot number can be considered as a yardstick to explore whether the process is thermally internal or external controlled. The Biot number characterises the internal heat transfer resistance in the product to the external heat transfer resistance in the fluid (air) [Incropera and DeWitt (1981a)] and is given by Equation (5.1).

$$Bi_h = \frac{\text{internal thermal resistance (conductive)}}{\text{boundary layer thermal resistance (convective)}} = \frac{h_g L_c}{\lambda_d} \quad (5.1)$$

where h_g , L_c and λ_d are the gas side heat transfer coefficient [$\text{W}.\text{m}^{-2}.\text{°C}^{-1}$], the characteristic length of the body [m] and the body (droplet) thermal conductivity [$\text{W}.\text{m}^{-1}.\text{°C}^{-1}$] respectively. L_c is generally determined from the volume/surface area ratio of the object [Incropera and DeWitt (1981a)]. However, the characteristic length for a sphere has been defined differently by numerous researchers. For a sphere, Holman (1986), Ferrari *et al.* (1989) and Farid (2003) all used the radius. van der Lijn *et al.* (1972) used the diameter and Incropera and DeWitt (1981a) and Adhikari (2002) used the diameter/6.

Many researchers quote a critical Biot number for which the assumption of uniform temperature profile is reasonable. According to Incropera and DeWitt (1981b), if $Bi_h \leq 0.1$ this assumption is valid. This critical Bi_h was stated for $L_c = \text{diameter}/6$. Liou (1982) [as cited in Ferrari *et al.* (1989)], claims that the Biot number is small ($Bi_h \ll 1$) in many practical drying situations. Campo *et al.* (2004) also used the same criteria as Incropera and DeWitt (1981b).

Farid quoted the critical Bi_h from Mills (1992) to be 0.1 and used the droplet radius, R , as the L_c in the Bi_h calculation, which he calculated to be 0.15. If the critical Bi_h (based on the lumped capacitance model) from both Mills (1992) and Incropera and DeWitt (1981b) is used then the critical Bi_h calculated by Farid and used here should in fact be 3×0.1 (since the L_c used by Farid and in this work is $3 \times L_c$ specified by Incropera and DeWitt (1981b)).

Similarly, the mass transfer Biot number can be defined to determine whether the process is mass transfer internal or external controlled. It is defined as the ratio of the internal mass transfer (diffusive) resistance to boundary layer mass transfer (convective) resistance [Incropera and DeWitt (1981a)].

$$Bi_m = \frac{\text{internal mass transfer resistance}}{\text{boundary layer mass transfer resistance}} = \frac{k_g L_c}{D_w} \quad (5.2)$$

where k_g is the gas side mass transfer coefficient [m.s^{-1}] and D_w is the binary moisture diffusion coefficient [$\text{m}^2.\text{s}^{-1}$] inside the body. L_c is the characteristic length of the body [m]. As Bi_m tends towards infinity, the assumption that resistance to mass transfer is situated entirely in the dispersed droplet phase is valid. According to Chen *et al.* (1999), for a 10 mm diameter droplet of skim milk in a study by Ferrari *et al.* (1989), the corresponding Bi_m was found to be less than 0.1, suggesting thermal diffusion control. However, Kerkhof and Schoeber (1974) noted that the Biot number for heat transfer is much lower than that for mass transfer, again suggesting mass diffusion control.

To determine the controlling mechanism, Equations (5.1) and (5.2) representing the Biot numbers for heat and mass transfer respectively, as well as the Lewis number, were calculated at the beginning and towards the end (assuming a 50% reduction in droplet radius) of drying scenarios for the experimental work conducted in this thesis (single droplet drying tests) and anticipated industrial-scale conditions. The results are presented in Table 5.1. The droplet radius was taken to be the characteristic length in the Biot calculations. Representative values for the droplet radius, droplet temperature and droplet concentration at the beginning and end of a drying scenario were used. The thermal properties were calculated as a function of both moisture content and temperature. The relative droplet–air velocity was taken to be the actual air velocity used in the experiments and the terminal droplet velocities for the predicted industrial-scale conditions. A range of mass transfer Biot and Lewis numbers were calculated based on the average moisture diffusivity in the particle $2.72 \times 10^{-5} \text{ m}^2.\text{s}^{-1}$ [Chen *et al.* (1999)] for the heat transfer limiting case to $1 \times 10^{-10} \text{ m}^2.\text{s}^{-1}$ [Adhikari (2002)] for the mass transfer limiting case. The Biot numbers for heat and mass transfer were calculated with the following respective equations:

$$Bi_h = \frac{h_g R}{\lambda_d} = \frac{Nu}{2} \left(\frac{\lambda_a}{\lambda_d} \right) \quad (5.3)$$

$$Bi_m = \frac{k_g R}{D_w} = \frac{Sh}{2} \left(\frac{D_v}{D_w} \right) \quad (5.4)$$

where R is the droplet radius [m], and Nu and Sh are the Nusselt and Sherwood numbers [–] calculated by well accepted correlations for heat and mass transfer containing h_g and k_g respectively (refer to Equations (A2.47) and (A2.53)).

Table 5.1: Heat transfer and mass transfer Biot numbers and Lewis number under various drying conditions

Droplet radius [μm]	Drying air temperature [°C]	Droplet temperature [°C]	Solids concentration [% w/w]	Bi_h [–]	Bi_m [–]	Le [–]
<i>Single droplet drying tests</i>						
1000	80	25	20	0.14	3–740,000	0.005–1400
500	80	70	80	0.23	2–670,000	0.004–1100
<i>Industrial coating conditions</i>						
10	80	25	20	0.05	1–300,000	0.005–1400
5	80	70	80	0.11	1–340,000	0.004–1100

The calculations in Table 5.1 show that, for the industrial conditions, the heat transfer Biot numbers are below the critical value, $Bi_h < 0.3$. This means that no significant temperature gradient will exist within the droplet during drying and discretisation of the droplet temperature is not required. However, for the single droplet drying tests investigated here, a uniform temperature distribution may not be a valid assumption towards the end of the drying process (when droplet thermal conductivity decreases by one half). As drying progresses in the single droplet experiments, there will be conditions and occasions when drying will exhibit both internal thermal diffusion and internal mass diffusion control. To best represent this and to broaden the models applicability both temperature and moisture content were modelled.

In summary, the effective diffusion model employing the solute-fixed coordinate system was selected as the conceptual model for development in this study. This allows the simple discretisation of the moisture content so that the surface moisture content can be predicted. The temperature distribution in the droplet was also discretised so that the surface temperature can be accurately predicted. This will give more accurate predictions of droplet surface properties than obtainable by existing literature models. It will also be more widely applicable to different solutes and droplet sizes.

5.4 MATHEMATICAL MODEL SUMMARY

The mathematical model used here to predict single droplet drying kinetics is summarised below. The nomenclature used in the equations is given in Appendix A1. The full mathematical formulation and implementation is given in Appendix A2. A copy of the program source code written in Matlab® 7 (The Mathworks, Inc., Natick, MA, USA) is contained on the CD inside the back cover of this thesis and discussed in the Appendix A3.

5.4.1 Assumptions

The following assumptions were used in the model development:

1. A single droplet is representative of the entire population in a dilute spray system.
2. Non-turbulent air flow conditions exist, i.e. constant relative velocity between air and the droplet after deceleration to terminal velocity.
3. The droplets are solid (non-hollow), and remain, perfectly spherical [Ferrari *et al.* (1989)], and the change in volume of the droplet corresponds to the amount of water evaporated ('ideal shrinkage') [Ferrari *et al.* (1989); Räderer (2001)].
4. The product is compact, non-porous and homogenous without cracks or air bubbles [Räderer (2001)] allowing the mode of internal moisture transfer to be represented by an effective diffusion coefficient.
5. No internal convection, component segregation or droplet oscillations.
6. The gas phase is an infinite medium.
7. Ranz and Marshall (1952a) correlations for gas side heat and mass transfer coefficients hold true.
8. No chemical reactions and negligible heat of crystallisation [Ranz and Marshall (1952a)].
9. The droplet surface moisture content is in equilibrium with the water-vapour pressure at the surface. Thus, the moisture partial pressure driving force can be determined from the moisture sorption isotherm.

The validity of the assumptions is discussed in Appendix A2. A summary of the key equations is given below. The nomenclature describing the variables is given in Appendix A1 and Appendix A2.

5.4.2 Summary of key equations

The change in internal droplet moisture content as a function of time and position is described by Fick's second law but given in solute-fixed coordinates by Equation (5.5) for spherical coordinates:

$$\frac{\partial u}{\partial t} = \frac{\partial}{\partial z} \left(C_s^2(r, t) r^4 D_w(u, T_z) \frac{\partial u}{\partial z} \right) \quad \text{for } 0 < z < Z \text{ and } t > 0 \quad (5.5)$$

Internal convection is assumed to be negligible, hence the change in internal droplet temperature as a function of time and position for a sphere is given by Fourier's second law [taken from Farid (2003)]:

$$\frac{\partial T_r}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \alpha_r(C_w, T_r) \frac{\partial T_r}{\partial r} \right) \quad \text{for } 0 < r < R \text{ and } t > 0 \quad (5.6)$$

The radius and solids content relationship described by Equation (5.7) was used to convert between the two coordinate systems for the internal nodes.

$$\frac{dz}{dr} = C_s r^2 \quad (5.7)$$

The droplet velocity was calculated by considering a momentum balance over a falling droplet, subject to the constraints that the droplet moves in the vertical direction only and behaves like a rigid sphere as given by Equation (5.8) [taken from Meerdink (1993)].

$$\frac{dv_d}{dt} = \left(\frac{\rho_d - \rho_a}{\rho_d} \right) g - \frac{3 C_D \rho_a (v_d - v_a)^2}{8 \rho_d R} \quad \text{for } t > 0 \quad (5.8)$$

At time zero the droplet is assumed to have a uniform initial moisture content and temperature distribution and a known initial droplet velocity (i.e., exiting the atomiser).

$$u = u_i \quad \text{for } 0 < z < Z \text{ at } t = 0 \quad (5.9)$$

$$T_d = T_{d,i} \quad \text{for } 0 < r < R \text{ at } t = 0 \quad (5.10)$$

$$v_d = v_{d,i} \quad \text{at } t = 0 \quad (5.11)$$

A Neumann boundary condition (2nd type) was used to reflect the symmetry at the droplet centre, i.e., no flow across the boundary to give a one dimensional modelling scenario for both mass and heat transfer.

$$\frac{\partial u}{\partial z} = 0 \quad \text{for } t > 0 \text{ at } z = 0 \quad (5.12)$$

$$\frac{\partial T}{\partial r} = 0 \quad \text{for } t > 0 \text{ at } r = 0 \quad (5.13)$$

A Robbins (3rd type) boundary condition was used to describe both mass and enthalpy conservation at droplet surface given by Equations (5.14) and (5.15) respectively.

$$D_{u,s}(u_s, T_s) C_{ss}^2 R^2 \frac{\partial u}{\partial z} = -F_{wvR} \quad \text{for } t > 0 \text{ at } z = Z \quad (5.14)$$

$$\lambda_{d,s} \frac{dT_s}{dr} + \Delta H_v F_{wvR} = -h_g^* (T_a - T_s) \quad \text{for } t > 0 \text{ at } r = R \quad (5.15)$$

These equations were used to formulate the numerical solution scheme described below.

5.4.3 Numerical solution

The partial differential equations for droplet moisture content and droplet temperature were approximated using the expanded Taylor series to yield finite difference equations. The spatial central differences technique was selected over the forward and backward differences technique because of its higher degree of accuracy (i.e. truncation error $\approx \Delta x^2$). The droplet was divided into J nodes, each containing the same amount of solute, $4\pi \Delta z$ [kg]. The computer software package Matlab® 7 (The Mathworks, Inc., Natick, MA, USA) was used to numerically solve the formulated problem, because of its availability and its library of useful ODE functions to make the implementation easier. The discretisation of time was handled by Matlab® 7 using the ODE15s solver. This solver routine is used for 'stiff' problems, in which diffusion is often considered to fall [Frias *et al.* (2001)].

5.5 EXPERIMENTAL METHOD SELECTION

Adhikari (2002) stated that the techniques for studying single droplet drying kinetics fall into two categories: levitation and free-flight. The levitation method can be further categorised into two subcategories: non-intrusive and intrusive. Intrusive levitation involves the suspension of a droplet either at the tip of a glass filament or thermocouple while the non-intrusive levitation employs various physical forces to freely levitate it [Adhikari (2002)]. Räderer (2001) and Adhikari (2002) reviewed these techniques, discussing their advantages, disadvantages and the parameter levels investigated by the various researchers employing the techniques.

The intrusive mode of levitation was selected as it was directly available to this study. Numerous experimental studies [Ranz and Marshall (1952a, b); Audu and Jeffreys (1975); Cheong *et al.* (1986); Yamamoto and Sano (1995); Hecht and King (2000a); Adhikari (2002); Lin and Chen (2002)] have been made on the drying of single droplets containing dissolved solids (salts, sugars or foodstuffs) whilst suspended from the tip of a fine filament, a wire or a nozzle. Although it is probably not the best technique, it is the most commonly employed and its shortcomings are well documented. The most widely recognised limitations of this technique are the additional heat transfer from the supporting filament and most importantly the non-uniform evaporation and shrinkage due to its fixed position relative to the direction of air flow. The first limitation is minimised by first employing a fine filament and heat flow from this source is incorporated into the model to factor out the effect. The second limitation could not be modified given the current experimental set-up. This limitation was noted and accepted. Despite these limitations, Adhikari (2002) achieved reasonable modelling success with data obtained from the same rig as used in this study.

5.6 EXPERIMENTAL SET-UP

The experimental set-up used to collect the droplet drying kinetic data described below was designed, built and resides at the School of Engineering at The University of Queensland, St. Lucia, Australia. Below is a brief description of the apparatus. A detailed description of its construction can be found in Adhikari (2002).

5.6.1 Set-up overview

A schematic diagram of the single droplet drying rig is shown in Figure 5.4.

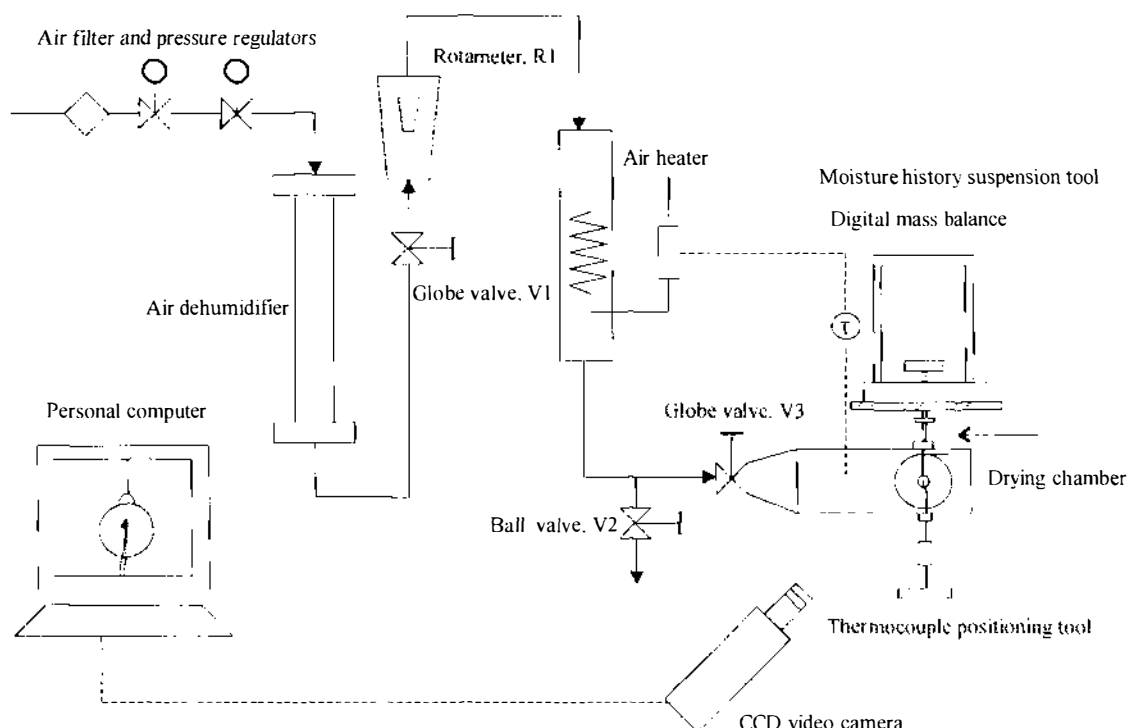


Figure 5.4: Schematic diagram of the single droplet drying rig.

The apparatus had five key functional parts: an air delivery and heating system; the main drying chamber; a moisture content history monitoring system; a temperature history monitoring system; a data acquisition system and an image acquisition system. These are discussed separately below.

5.6.2 Air delivery and heating system

There were two pathways available to deliver air to the drying chamber. Pathway one (shown above) was used in this study and is described as follows. Air was brought to the air dehumidifier (silica gel column) by reducing its pressure from 1600 kPa to 200 kPa through a series of pressure regulators and filters to dampen pressure fluctuations and filter out oil and water droplets in the compressed air line. The air from the dehumidifier (cylindrical column containing silica) passed through a rotameter (R1) which was used to manually set the air flowrate to the drying chamber. The air then passed through a cylindrical chamber where it was heated using an electric element air heater (1.5 kW) to the desired working temperature. The temperature in the drying chamber was monitored by a 0.5 mm junction thermocouple (K-type, Omega Engineering Inc., Stamford, CT, USA) inserted in the hot air stream just in front and above the drying droplet. The air temperature was controlled by a solid-state relay micro-level processor based auto-tuning (proportional-integral-differential) controller (BTC-9090, ECEFast™, Electro Chemical Engineering Pty Ltd, Rydalmere, NSW, Australia) by direct feedback. Finally, the air passed through the main drying chamber where it came in contact with the droplet which was suspended at the tip of a glass filament.

5.6.3 Main drying chamber

The drying chamber was made up of a 150 mm long and 50.8 mm internal diameter insulated glass tube. A photograph of the chamber along with the various components is presented in Figure 6.4. It had two sections. The upstream section was 100 mm long and the downstream section was 50 mm long. A photographic window of 50 mm in diameter was also located at

this junction point in addition to a top and bottom port for the introduction of thermocouples and components for the stickiness work conducted in Chapter 6. After the air passed over the suspended droplet it exited to atmosphere.

5.6.4 Data and image acquisition system

The filament, along with the droplet, was hooked to the micro-balance (HM 202, A&D Company Ltd, Tokyo, Japan) which was set to a precision mode of ± 0.01 mg to log the mass loss from the droplet. A data acquisition card (PLCD-8115, Advantech Co., Ltd, Taiwan) along with a customised program written with the supplied software (VisiDAQ, version 3.11) allowed the continuous logging of the air temperature, droplet temperature and mass balance readings (via RS-232 serial port) to a personal computer (Compaq, Presario).

Morphological changes in the drying droplet were monitored with a CCD camera (Sony®, SSC-M370CE, Sony Company, Tokyo, Japan) magnified by a stereomicroscope (Stemi 2000-C, Carl Zeiss Jena GmbH, Oberkochen, Germany). The analogue image was recorded constantly and digitised by a video capture card (WinFast TV2000 XP, Leadtek Research Inc., Taiwan) and bundled software (Ulead VideoStudio 6 SE DVD, Taiwan) at a rate of 30 frames per second.

It was not possible to simultaneously collect the temperature data and the moisture data with the current experimental set-up because coupling of the wire thermocouple to the mass balance resulted in unstable mass balance readings. Because of the fine nature of the wire thermocouple, it was not possible to suspend the droplet from it without the aid of the glass filament used for the collection of the moisture content history data. As a result, the collection of the moisture content and temperature history data had to be made separately as detailed below.

5.6.5 Moisture content history monitoring system

Figure 6.4(item B) in Chapter 6 shows the droplet suspension system. It was comprised of an upper and lower section joined with a rubber disc. The lower section was a tapered glass filament of 0.2 to 0.4 mm in diameter. The thin end of the filament was heated to form a spherical knob (0.5 mm in diameter) to increase the wettable area in order to suspend droplets of around 2 mm in diameter. The other end of the glass filament is 1.5 mm in diameter and 12.7 mm long which was inserted into the rubber disc. The upper section was a stainless steel hook on which 3 brass cylinders were fixed. The total weight of the suspension system was 27 g to act as a dead load and dampen any perturbations to the system that could affect mass measurements. The balance gives mass versus time data which were converted to moisture loss.

5.6.6 Temperature history monitoring system

The temperature history of a drying droplet was monitored through a wire thermocouple (70 μm in diameter, K-type, Omega Engineering, Inc., Stamford, CT, USA). It was not possible to suspend the drops on the thermocouple junction (electrically arced 300 μm bulb) alone. The droplet was again suspended from the glass filament and the thermocouple junction introduced into the droplet from below.

The centring of the thermocouple in the evaporating droplet is critical to the correct droplet temperature measurement. Many researchers [Downing (1966); Lin and Chen (2002)] have

reported erroneous droplet temperatures as the droplet climbs the thermocouple wire due to capillary forces. This is typically seen as a rise in the expected droplet temperature as the immersion depth of the thermocouple bulb is reduced and is exposed to the air temperature. In this work, the thermocouple was kept in the centre of the droplet using the thermocouple positioning tool (item C in Figure 6.4). During the collection of the temperature histories a fine screw allowed real time adjustment of the thermocouple position inside the droplet as it continuously shrunk. This way the droplet temperature was always taken from the centre of the droplet.

5.7 EXPERIMENTAL PROTOCOL

5.7.1 Key variable and level selection

The key variables considered as most important arising from the ‘focused literature review’ in Chapter 3, and in the model, are polymer type (largely via the binary moisture diffusion coefficient), initial polymer concentration and drying air temperature. Minor variables were determined to be relative humidity and air velocity.

Experimental work should aim to mimic conditions likely to be encountered on the industrial-scale. However, given the limitations imposed by the experimental set-up it was not possible to achieve these conditions. These limitations are discussed in the Section 5.9. Unless stated otherwise the base conditions for the trials used 6 μl droplets dried at a standard air velocity of 0.30 m.s^{-1} . Two temperature ($40 \pm 0.5 \text{ }^{\circ}\text{C}$ and $78 \pm 1 \text{ }^{\circ}\text{C}$) and two initial solids concentration levels ($20 \pm 0.5\% \text{ w/w}$ and $40 \pm 1\% \text{ w/w}$) were investigated. It should be noted that the moisture content history plots are given in units of $(\text{kg water}).(\text{kg}^{-1} \text{ dry solid})$. Initial solids concentrations of 20 and 40% w/w (total basis) correspond to moisture contents, u , of 4 and 1.5 $(\text{kg water}).(\text{kg}^{-1} \text{ dry solid})$ respectively.

5.7.2 Solution preparation

All solution concentrations were prepared by mass rather than volume to eliminate the uncertainty from temperature fluctuations. The solution preparation procedure was as follows. Each powder was dissolved at $85 \text{ }^{\circ}\text{C}$ (lid on to prevent evaporative losses) while stirring with the exception of whey protein isolate which was dissolved at $45 \text{ }^{\circ}\text{C}$ to ensure the protein did not denature. The solutions were allowed to cool to room temperature. The maltodextrin DE5 solutions then became cloudy within a matter of hours suggesting a nucleation event and subsequent reduction in supersaturation. As a result, all solutions were allowed to stand for 24 h to provide a consistent starting point between trials. Solutions were used for up to 2 days of testing.

Two total solids measurements were made on each solution by oven drying at $85 \text{ }^{\circ}\text{C}$ until zero mass change. This was to account for both evaporative losses and the water associated with the dissolved powder.

5.7.3 Moisture content and temperature history data collection

The working section along with suspension systems were heated up until the steady-state drying air temperature was reached. The drying air was quickly swung out to atmosphere to bypass the chamber using valves V2 and V3 in Figure 5.4 and a $6 \pm 0.2 \text{ }\mu\text{l}$ droplet produced at the tip of a $10 \text{ }\mu\text{l}$ gas-tight micro-syringe (Hamilton Company, Reno, NV, USA) was transferred to the knob of the glass filament. The bypass was necessary to prevent premature

droplet evaporation during transfer which took approximately 20 s. The drying air was immediately swung back into the drying chamber. For pure water droplets this volume gave an average mass of 5.79 ± 0.18 mg (95% confidence interval, $n = 4$) and were considered to be of the 'same size' in the experimental trials. Below this size the background noise in the digital mass readings (from air flow perturbations) became significant. This was also the largest droplet size that could be physically suspended from the glass filament with ease.

Moisture content histories were carried out in duplicate followed by duplicate temperature histories. Occasionally, a third replicate was required in cases of insufficient reproducibility. It was found that both the higher temperature and higher initial solids concentration trials showed less reproducibility than their lower level counterparts.

The logged raw data was collated and appropriate moisture content and temperature histories were first averaged and then matched for presentation.

5.8 PRELIMINARY RIG TESTING

Before any experiments were performed the consistency of conditions was investigated. This would allow experimental limitations to be identified and eliminated or at least quantified if they could not be significantly reduced to acceptable levels.

5.8.1 Air velocity

The air velocity profile across the working section was measured with a hot wire anemometer (VelociCalc®, model 8347A-M-G, TSI Incorporated, Shoreview, MN, USA) which showed that the air velocity in the vicinity of the suspended droplet was nominally flat for all velocities and temperatures investigated. As long as the filament remained at the same position for all experiments the error introduced by non-constant velocity uniformity could be assumed to be negligible. The accuracy for the velocity measurement is specified to be $\pm 0.015 \text{ m.s}^{-1}$ according to the manufacturer.

5.8.2 Relative humidity

The relative humidity (RH) of the air coming out of the pressure regulating system was always 10–11% and it did not change significantly with changes in weather conditions. Hence, the silica gel was not introduced as it added unnecessary pressure drop to the system. A relative humidity sensor (thermistor type, HIH-3602-A, Honeywell International Inc., Morgantown, NJ, USA) was used to measure the relative humidity at the beginning and end of each trial at ambient air temperature with air flow. A psychrometric chart was used to determine the RH at the working temperature. The probe was found to give a linear response when calibrated over saturated salt solutions at 11, 43 and 75% RH. The accuracy of the probe is specified to be $\pm 2\%$ RH according to the manufacturer.

5.8.3 Temperature

Given the sensitivity of the model to drying air temperature, a thorough investigation of the temperature profile in the drying chamber was warranted. Although the drying chamber was well insulated there existed a slight temperature drop towards the periphery of the cylindrical drying chamber and along its length. As a result, the droplet was always centred and remained fixed throughout the trials to ensure comparability. The drying air temperature position was fixed in the centre of the viewing port as indicated in Figure 5.4. According to

Ranz and Marshall (1952a), exploring the air temperature around a 1.0 mm diameter evaporating water droplet requires the thermocouple to be at least 2 mm away to avoid the effect of water-vapour in the air lowering the dry bulb air temperature around the droplet.

Thermocouples were calibrated in ice/water and boiling water. In both instances MilliQ water was used. A regression equation was fitted to correct the measured values to the calibrated values for each individual thermocouple. According to the manufacturer, K-type thermocouples are specified to have an accuracy of $\pm 0.75\%$. The effect of heat conduction through the wire thermocouple to the droplet has been accounted for in the mathematical model.

5.8.4 Droplet suspension system

Collection of accurate mass data from the evaporating droplets is pertinent to the collection of accurate and reliable drying kinetic data. Adhikari (2002) and Brodie (2003) identified two significant sources of error that needed to be accounted for, an offset and a lift (or buoyancy) force on the droplet suspension system. Both studies quantified these differently and applied different forms of corrections to account for them during data analysis (polynomial versus linear corrections respectively) with neither adequately identifying the root cause of error nor eliminating it. Brodie (2003) suspected the lift force on the rubber disc (item B in Figure 6.4) was the significant contribution to the observed anomalies.

After a preliminary testing of the droplet suspension system sensitivity the following modifications were made:

- The rubber disc initially used by Adhikari (2002) on the suspension system to prevent hot air reaching the balance was removed to eliminate the possible lift force.
- Two rubber shields were made and placed over the top port on the drying chamber and bottom entry port to the mass balance. This significantly narrowed the hot air path, reducing the likelihood of hot air reaching the balance.
- An additional 10 g mass was added to the droplet suspension top portion to dampen the effect of perturbations and drag.
- New glass filaments having diameters ranging from 0.2 to 0.4 mm were made to make droplet transfer easier compared to the thinner filament (0.2 mm) used by Adhikari (2002).
- A new flattened hook was fabricated to connect the hook on the droplet suspension system to the mass balance to reduce the hook rotation in the air stream and hence changes in the centre of gravity of the system.
- Polystyrene insulation was added around chamber to minimise environmental perturbations to the suspension system.

Having made these modifications a comprehensive study of the mass balance sensitivity was conducted. There is no evidence to suggest the existence of a drag or buoyancy force or an offset from bypassing the air to load the droplets with the new modifications. This is not surprising given that the air flow is acting on 27 g of suspension mass making any drag or lift force negligible and constant in terms of the data collected. In addition, Adhikari (2002) worked at higher air velocities (1 m.s^{-1}) which would cause a higher buoyancy force on the droplet suspension system. It was found that with the current modifications no adjustment (for buoyancy or offset) to the raw mass data were necessary before calculation of the drying kinetics.

5.8.5 Prediction of the drying of a pure water droplet

To verify that the external heat and mass transfer kinetics had been formulated correctly, the model was used to predict the drying of a pure water droplet. As a water droplet always has a surface of free water, a study of the drying of a water droplet essentially factors out the internal heat and mass transfer sides of the model.

The way in which the numerical model is constructed requires an initial quantity of solute to initialise the discretised grid point positions. Hence, the pure water droplet was simulated using an initial solids concentration of 0.0000001% w/w (maltodextrin DE5).

Figure 5.5 shows the mass and temperature histories of a 6 μl pure water droplet drying at an air temperature of 40 $^{\circ}\text{C}$ and an air velocity of 0.30 m.s^{-1} .

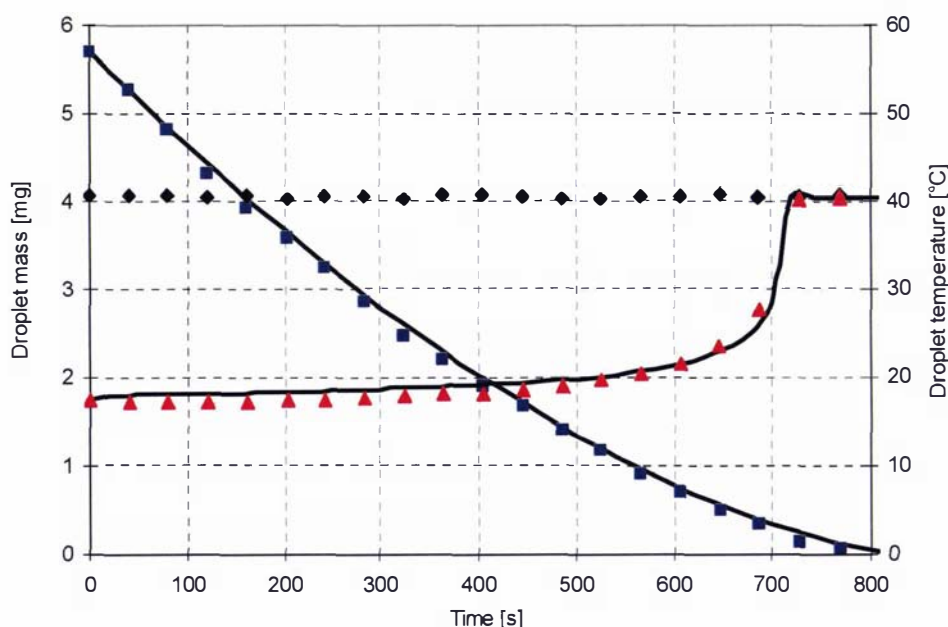


Figure 5.5: Experimental mass and temperature histories along with model predictions for a 6 μl pure water droplet drying at 40 $^{\circ}\text{C}$ and 0.30 m.s^{-1} : ■ experimental mass history; ▲ experimental temperature history; ♦ drying air temperature; — mass and temperature predictions (black).

An almost constant loss of mass occurred over the entire drying period until little or no mass remained, which is consistent with the constant rate period noted in drying theory. The initial droplet temperature was 17.4 $^{\circ}\text{C}$. From this point, as expected, the droplet temperature remained constant at around 17.4 $^{\circ}\text{C}$, i.e. slightly above the wet bulb temperature (16.1 $^{\circ}\text{C}$), for the first 400 s. The temperature of the droplet began to increase after 500 s. At 690 s, the droplet diameter was 0.92 mm. Considering that the thermocouple bulb diameter was approximately 300 μm , it is possible that the bulb was no longer in the centre of the droplet, and could, in part, have been exposed to the drying air temperature, resulting in the higher than expected measured temperature. In most instances, near the end of the drying process, wicking between the glass filament and the thermocouple bulb occurred. Inevitably, the droplet detached from the thermocouple, resulting in the final rapid increase in temperature to the air temperature.

The model predictions (solid black lines in Figure 5.5) were made using the following model system input data: $m_{di} = 5.71$ mg, $v_a = 0.3$ m.s⁻¹, $T_a = 40.54$ °C, $RH = 3.75\%$, $T_{di} = 17.45$ °C. The number of nodes, J , was set to 30. The predictions show that the model was able to predict the trends in both the mass and temperature histories well. This suggests that the mathematical formulation of the gas side heat and mass transfer, including the Nu and Sh correlations of Ranz and Marshall (1952a), was adequate.

It is important to note that, in all the pure water droplet evaporation trials, the experimental droplet temperature was generally 1–2 °C higher than the calculated wet bulb temperature of 16.1 °C. However, when the mass history data were used, the predicted constant rate period droplet temperature was 16.3 °C, which was within the experimental error of the wet bulb temperature ($\pm 0.75\%$ and $\pm 2\%$ for the thermocouple temperature and the relative humidity respectively). This shows that the thermocouple added a significant amount of heat during the collection of the temperature history data confirming that heat conduction along the wire thermocouple requires inclusion in the model. Despite this inclusion, the temperature history was still slightly over-predicted, which was probably because of the inaccuracy in the mathematical terms describing the heat conduction in the glass filament and wire thermocouple (approximated as one-dimensional fins). In reality, the glass filament had a tapered cross-sectional diameter (as described in Section 5.6.5). As mentioned in Section A2.4.5.4 the filament diameter was taken to be the volume weighted diameter (0.31 mm). Predictions were also made with a filament diameter of 0.2 mm since this was the narrowest path length for heat transfer and directly precedes the bulb from which the droplet hangs. However, the rate of evaporation was slightly longer taking an extra 40 s to achieve dryness. This suggested that the volume weighted diameter provides the best approximation at this stage.

It is interesting to note, under these conditions, the relative contributions of the various heat transfer sources. The respective percentages of the total heat transfer rate supplied to the droplet by air convection, filament conduction, thermocouple conduction and radiation ranged from 75.6 to 60.1%, 6.8 to 13.9%, 10.9 to 22.4% and 6.7 to 3.6% between time zero and time 500 s. Radiative heat transfer was relatively low; however, as the droplet size diminished, the contribution of conductive heat transfer, particularly from the thermocouple wire, became significant, which produced the increase in the temperature of the droplet after 600 s. Given the percentage of total heat flow to the droplet contributed by both filament and thermocouple conduction (when added 17.7–36.3%) future work should determine a better mathematical description of these two heat sources to achieve a more accurate temperature history prediction. It should be reiterated that the model was run twice, because the thermocouple was not present during the collection of the moisture content history data and the heat supplied for this source must not be taken into account during the prediction of the moisture content history.

In conclusion, the mathematical model describing external heat and mass transfer worked well for predicting the drying kinetics of a water droplet. It could now be used with inclusion of internal heat and mass transfer to validate experimental data for the drying of polymer solutions.

5.8.6 Validation of Ranz and Marshall's (1952) correlations for Nusselt and Sherwood numbers

Ranz and Marshall (1952a) correlations for gas side heat and mass transfer coefficients are commonly used for spray droplet drying modelling and were selected for use in this work. A

discussion on their applicability to this work is given in Section A2.3.8. Although the model predicted the pure water droplet drying kinetics well, it was necessary to further validate the external heat and mass transfer equations to determine whether the Ranz and Marshall (1952a) correlations (developed under a narrow range of experimental conditions) provided reasonable estimates over the entire range of experimental conditions and whether the droplet drying rig acquired accurate and reliable results. This was done by collecting mass and temperature history data for pure water droplets and comparing the experimentally calculated Nusselt number, Nu [–], and Sherwood number, Sh [–], with those predicted by the Ranz and Marshall (1952a) correlations. Using the approach of Ranz and Marshall (1952a), the equations for Nu and Sh were substituted into the heat transfer and mass transfer equations describing an evaporating pure water droplet, giving the following experimental equations to determine the Nu and Sh numbers.

$$Nu = -\frac{1}{4} \frac{\Delta H_v}{\lambda_a} \rho_d \frac{1}{(T_a - T_s)} \frac{d(d_d^2)}{dt} \quad (5.16)$$

where ΔH_v , λ_a , ρ_d , T_a , T_s , d_d and t are the latent heat of water vaporisation [J.kg^{-1}], the thermal conductivity of air [$\text{W.m}^{-1}.\text{°C}^{-1}$], the droplet density [kg.m^{-3}], the bulk air temperature [°C], the droplet surface temperature [°C], the droplet diameter [m] and time [s] respectively.

$$Sh = -\frac{1}{4} \frac{\rho_d}{D_v} \frac{R_g}{M_w} \frac{(T_f + 273.15)}{P_T} \frac{1}{\ln\left(\frac{1 - P_v/P_T}{1 - P_{vs}/P_T}\right)} \frac{d(d_d^2)}{dt} \quad (5.17)$$

where D_v , R_g , M_w , T_f , P_T , P_v and P_{vs} are the water-vapour diffusivity in air [$\text{m}^2.\text{s}^{-1}$], the universal gas constant [$8.314 \text{ J.mole}^{-1}.\text{K}^{-1}$], the molecular mass of water [18 g.mole^{-1}], the film temperature (arithmetic average of T_s and T_a) [°C], the air pressure of the total system [$101\ 325 \text{ Pa}$], the water-vapour partial pressure at the dry bulb air temperature [Pa] and the saturated water-vapour pressure at the droplet surface temperature [Pa] respectively. ρ_d was calculated at the temperature of the droplet, which remained at the wet bulb temperature and D_v was calculated at T_f . The quantity $d(d_d^2)/dt$ represented the evaporation rate and was obtained from the slope of the d_d^2 versus time plot.

Figure 5.6 shows the experimentally determined Nu and Sh numbers, along with the predicted values calculated from the Ranz and Marshall (1952a) correlations.

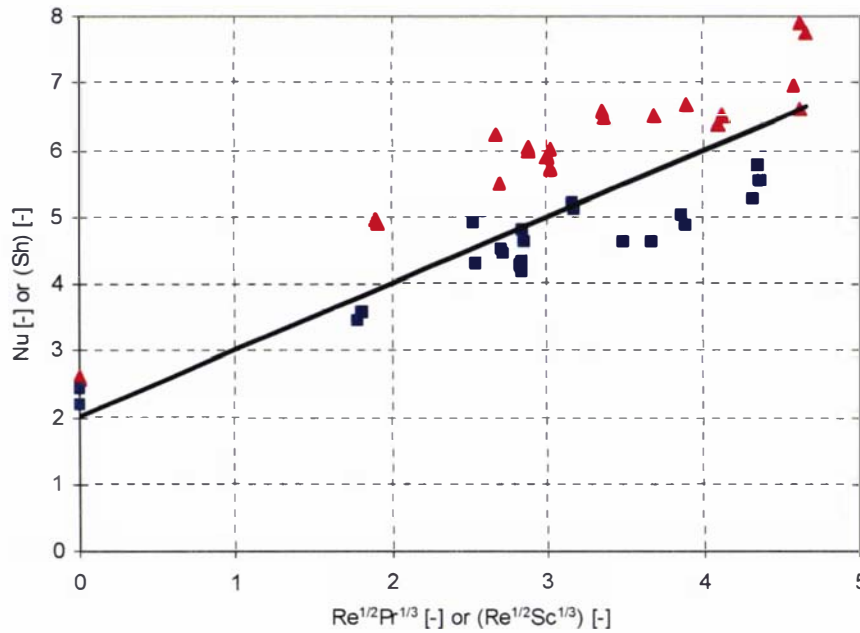


Figure 5.6: Comparison of experimental Nu and Sh numbers with those obtained from the Ranz and Marshall (1952a) correlations: ■ Sherwood number; ▲ Nusselt number; — Ranz and Marshall (1952a) Nu and Sh correlation.

The experiments encompassed a range of conditions (24–90 °C, 0–0.60 m.s⁻¹, 0–6 mg droplets, 0.3–54% relative humidity). The experimental values for Nu and Sh were scattered about those calculated using the Ranz and Marshall (1952a) correlations (black line). The deviation about this line could be further reduced if corrections to the calculated values were made to account for radiative heat transfer from the environment and conductive heat transfer from the glass filament and thermocouple wire and if corrections to the gas side heat and mass transfer coefficients [Bird *et al.* (1960)] for high mass flux conditions were made. Corrections to these data were not made at this time because the calculation of the theoretical Nu and Sh numbers under these conditions required that a constant droplet size be used in the determination of the Reynolds number for the x -axis data values. Ranz and Marshall (1952a) maintained a constant droplet diameter by controlling the fluid feed rate to the tip of the microburette from which the droplet was suspended. In the experiments described here, the evaporation rate was averaged over a continuously shrinking droplet diameter. Lin and Chen (2002) and Adhikari (2002) constructed similar plots, also with data on a continuously shrinking droplet. Adhikari (2002) used the average droplet diameter to calculate the Reynolds number. It is not clear what droplet diameter was used by Lin and Chen (2002). Although the arithmetic average droplet diameter was used to obtain Figure 5.6, the correct diameter to use is debatable. Despite these arguments, the purpose of these experiments was achieved, because the experimental set-up gave results expected by the Ranz and Marshall (1952a) correlations and further justified their use to mathematically describe the external heat and mass transfer in the numerical model.

At an air velocity of zero, the Nu and Sh numbers were found to be higher than those calculated by Ranz and Marshall (1952a). This has been observed by numerous researchers and is attributed to natural convection causing convective air currents in the vicinity of the droplet [van der Lijn (1976)].

5.9 DRYING KINETICS AND MODELLING OF MALTODEXTRIN DE5

A series of experiments to validate the mathematical model over a wide range of conditions was conducted. A discussion on the selection and importance of the key variables and levels is given with respect to an industrial-scale particle coating operation for the dairy industry. Maltodextrin DE5 was the polymer selected for these trials because it represents a potential coating material and is also of interest to the dairy industry due to its common use as a bulking agent and stickiness reducing agent in spray-dried dairy powders.

5.9.1 Initial solids concentration and air temperature

Process economics are important in the food industry. For this reason, high initial solids concentrations are required to reduce evaporative energy costs and minimise the coating time to achieve the desired coating thickness. However, solution solubility and viscosity will be limiting factors in determining the in-feed solids content and the atomisation performance. Current industry pressure nozzles are able to atomise solutions and slurries of up to 150 mPa.s at greater than $10\,000\text{ s}^{-1}$ [D. L. Pearce, Fonterra Palmerston North, personal communication, 17 March, 2003]. As a result, two initial solids concentrations were selected for use in the majority of this work, 20 and 40% w/w maltodextrin DE5.

Process economics is also affected by the drying air temperature. A higher air temperature produces more rapid drying (at lower cost), but dairy powder coating is temperature constrained because the substrate powder is likely to contain a surface layer of milkfat [Chen (2001); Kim *et al.* (2002)]. Therefore, increasing the temperature of the powder surface above 35 °C (when milkfat is almost 100% liquid [Foster (2002)]) can result in unwanted inter-particle agglomeration and subsequent fluid bed collapse. As a result, a low temperature limit of 40 °C was used but, as this requires long processing times, an upper temperature limit of 78 °C was selected for comparison.

Figure 5.7 and Figure 5.8 show the effects of the initial solids concentration (20 and 40% w/w) and the drying air temperature (40 and 78 °C) on the moisture content and temperature histories of maltodextrin DE5 droplets. Model predictions are also shown.

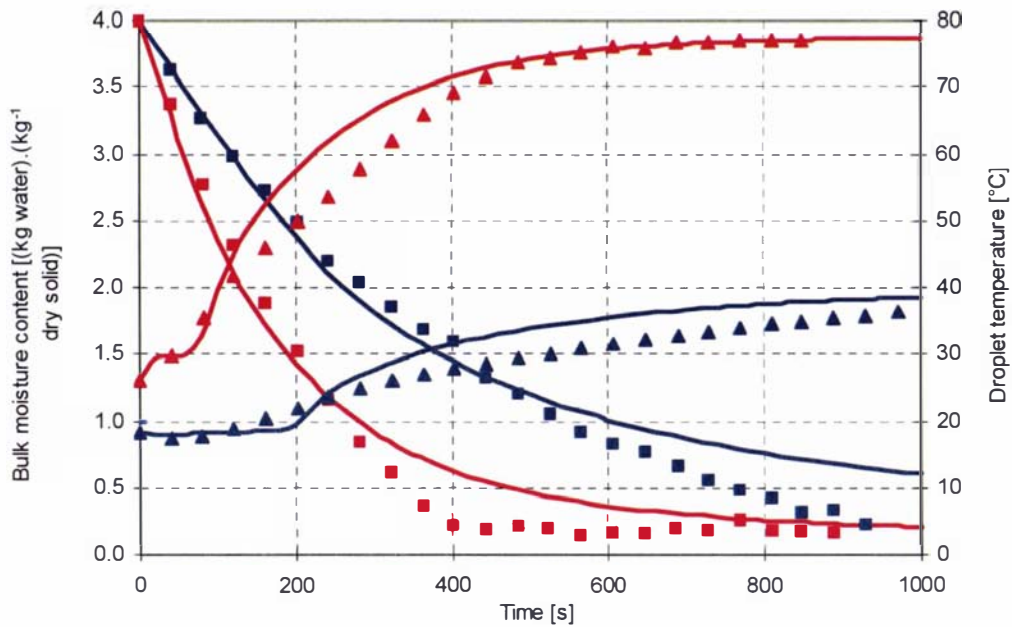


Figure 5.7: Effect of drying air temperature on the moisture content and temperature histories of 20% w/w maltodextrin DE5 droplets along with model predictions: ■ moisture content history at 40 °C air temperature; ■ moisture content history at 78 °C air temperature; ▲ temperature history at 40 °C air temperature; ▲ temperature history at 78 °C air temperature; — moisture content and temperature predictions (blue and red respectively).

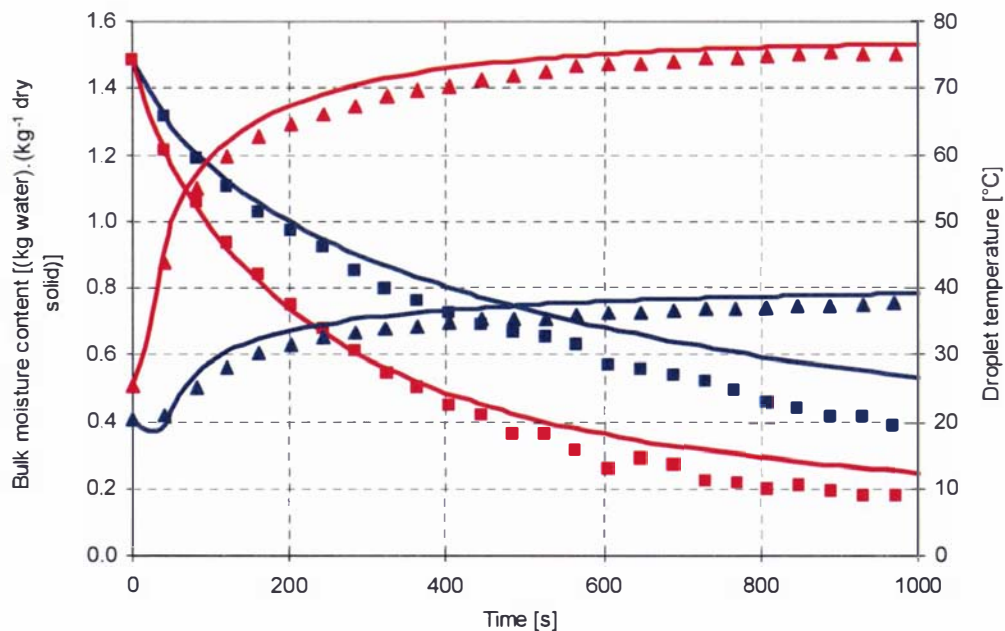


Figure 5.8: Effect of drying air temperature on the moisture content and temperature histories of 40% w/w maltodextrin DE5 droplets along with model predictions: ■ moisture content history at 40 °C air temperature; ■ moisture content history at 78 °C air temperature; ▲ temperature history at 40 °C air temperature; ▲ temperature history at 78 °C air temperature; — moisture content and temperature predictions (blue and red respectively).

The higher initial solids concentration in Figure 5.8 resulted in a substantially lower drying rate over the initial period, because of skin formation, which was clearly evident in all trials but occurred at different times and to various extents depending on the conditions. Menting and Hoogstad (1967) found that skin formation occurred earlier at higher initial solids

concentrations, which was probably the reason for the slower drying kinetics of the more concentrated droplets, i.e. a result of the diffusion resistance. The trends here also followed those of Adhikari (2002) and Hecht and King (2000a) found that the drying rate decreased with increasing initial solids concentration.

The effect of skin formation on the diffusion rate was accounted for in the model by primarily the dependence of the binary moisture diffusion coefficient on the polymer concentration. Both the model predictions and the experiments at 40 °C showed constant rate drying period before skin formation limited water migration to the droplet surface. For example, for the 20% w/w maltodextrin DE5 and 40 °C trial, the experiments showed a constant rate period of 100 s, whereas the model predicted 150 s. For the 40% w/w maltodextrin DE5 and 40 °C trial, both the experiment and the model prediction had a shorter (50 s) constant rate period, as a result of the earlier onset of inhibited moisture movement. Because of this, less moisture was available at the surface to allow evaporative cooling of the droplet; hence this trial had a more rapid increase in temperature than the 20% w/w maltodextrin DE5 and 40 °C trial.

A constant rate drying period was neither observed nor predicted in the 78 °C trials because of the greater influence of the polymer concentration on the higher evaporation rates experienced. Similarly, the 40% w/w maltodextrin DE5 trial had a lower evaporation rate and a higher rate of temperature increase than the 20% w/w maltodextrin DE5 trial.

The model under-predicted the latter stages of drying in all trials, i.e. the predicted moisture contents are higher than experimentally observed. Visual observation of the droplets in the 20% w/w initial solids concentration maltodextrin DE5 trials at 40 and 78 °C revealed small cavities within the droplets. These indicated crack formation near the end of the trial that allowed preferential moisture transport to the surface. The model does not predict morphological behaviour. This under-prediction of the rate of decrease in the droplet moisture content was particularly significant for the 20% w/w maltodextrin DE5 droplets because the rapid rate of evaporation early in the drying process caused the skin to form close to the initial droplet diameter. As drying progressed, these droplets lost more water than the higher concentration droplets and hence experienced more severe shrinkage stresses. The higher stresses, combined with the formation of a thinner skin because of the lower amount of solute available, made the 20% w/w initial solids concentration maltodextrin DE5 droplets more susceptible to stress fractures and subsequent preferential and increased mass transfer.

The temperature histories in all cases were over-predicted by the model, particularly for the 20% w/w initial solids concentration maltodextrin DE5 droplets. This was partly due to the previously mentioned geometry and position inaccuracy in the mathematical terms used to describe the heat contribution from the glass filament and the wire thermocouple. Given that the thermal properties (polymer specific heat capacity, conductivity and density) were all in line with those in the literature (Section A2.3.6) and the fact that the numerical implementation of the internal heat transfer was validated (Section A2.5.2), the majority of the over-prediction will be because of the lower predicted flux which results in a lower rate of latent heat loss. If the morphological changes could be accounted for then better predictions in both the moisture content and temperature histories would result.

Drying time is important from an economic standpoint. Although the 20% w/w initial solids concentration maltodextrin DE5 droplets initially showed a faster rate of evaporation than the 40% w/w initial solids concentration maltodextrin DE5 droplets, they took approximately the same amount of time to dry to completion (i.e. 3–4% w/w total basis required for powdered dairy products), because skin formation caused an internal mass transfer limitation. The

drying time can be reduced by increasing the drying air temperature because it affects the binary moisture diffusion coefficient positively, but the coating of dairy powders has an upper temperature constraint, as explained.

The drying time must be balanced with the overall reduced coating time, when higher initial solids concentration droplets will promote faster accumulation of coating solids. This is a good example of the droplet impact and spreading micro-level process being coupled to the drying micro-level process in an air-suspension particle coating operation.

5.9.2 Air velocity

In many drying applications, higher air velocities are used to increase the drying rate of a product. Given that the constant rate drying period is rarely observed in concentrated foodstuffs [Cheong *et al.* (1986); Zogzas and Maroulis (1996); Dolinsky (2001); Räderer (2001)], controlling external mass transfer with the air velocity would appear to be of limited use. However, it was not clear whether the coating materials of interest in this study showed the same behaviour and there was a need to test the model predictions under various drying air velocities.

A distribution of air and particle/droplet velocities (as well as particle/droplet acceleration and deceleration) will exist in a coater and each particle/droplet will experience a range of these velocities over its lifetime. Regardless of this distribution of velocities and despite high insert gas velocities ranging between 3 and 10 m.s^{-1} used in laboratory-scale coaters [e.g. Christensen and Bertelsen (1997); Maa and Hsu (1997); Dewettinck and Huyghebaert (1998)], it is the air velocity relative to the particle velocity that will determine the external mass and heat transfer rates. Numerous modelling studies for spray drying applications use droplet velocities of around 1 m.s^{-1} [e.g. Adhikari (2002); Farid (2003)], assuming that the droplet velocity takes on the air velocity. The use of such high velocities could be justified only under turbulent conditions, when acceleration between various regions in the process equipment can occur. Such modelling exercises and experimental studies would under-predict the actual drying time. If turbulence does not exist, the particle/droplet will experience, for the most part, a relative velocity equal to its terminal velocity (less a small degree of slip). This is important to note, because attempts to increase the air velocity in the Würster insert with a view to decreasing the drying time will not significantly alter the relative velocity that the droplet/particle will experience. Therefore, the only means that the operator has to affect the drying rate by velocity control is at atomisation. Higher initial droplet velocities will lead to higher initial drying rates. As small droplets decelerate very quickly, the amount of control is likely to be minimal. Once the droplet has impacted the substrate or decelerated, there is little the operator can do via velocity control to increase the drying rates in a Würster coater. However, in a top-spray application, a little more control is afforded, as the operator can use the counter-current air velocity and the initial droplet velocity from the atomiser to control the drying rates of the droplets. Once again, when the droplet/particle is in the pneumatically conveyed air stream, there is little that can be done.

With these operating limitations in mind, the drying rates at two air velocities of 0.30 and 0.72 m.s^{-1} were examined experimentally to validate the mathematical model. These air velocities are much higher than those expected in a Würster coater for a small 10 μm diameter (ideally sized; Guignon *et al.* (2002)) droplet set to impinge a 100 μm diameter powder particle, which has a terminal velocity of around 0.003 m.s^{-1} . The current experimental set-up cannot achieve this low velocity. Instead, a typical dairy industry atomiser delivers 100 μm diameter droplets to give a terminal velocity of 0.30 m.s^{-1} , which is within the range studied

in this work. Figure 5.9 and Figure 5.10 show the results of drying maltodextrin DE5 droplets at 0.30 and 0.72 m.s⁻¹ and air temperatures of 40 and 78 °C.

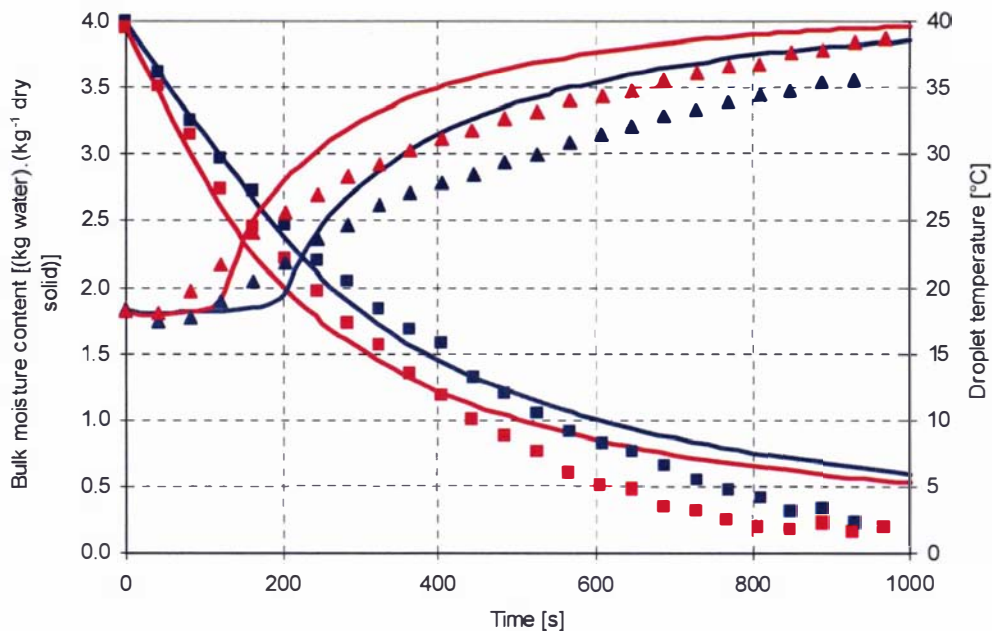


Figure 5.9: Effect of the drying air velocity on the moisture content and temperature histories of 20% w/w maltodextrin DE5 droplets drying at 40 °C along with model predictions: ■ moisture content history at 0.30 m.s⁻¹ air velocity; ■ moisture content history at 0.72 m.s⁻¹ air velocity; ▲ temperature history at 0.30 m.s⁻¹ air velocity; ▲ temperature history at 0.72 m.s⁻¹ air velocity; — moisture content and temperature predictions (blue and red respectively).

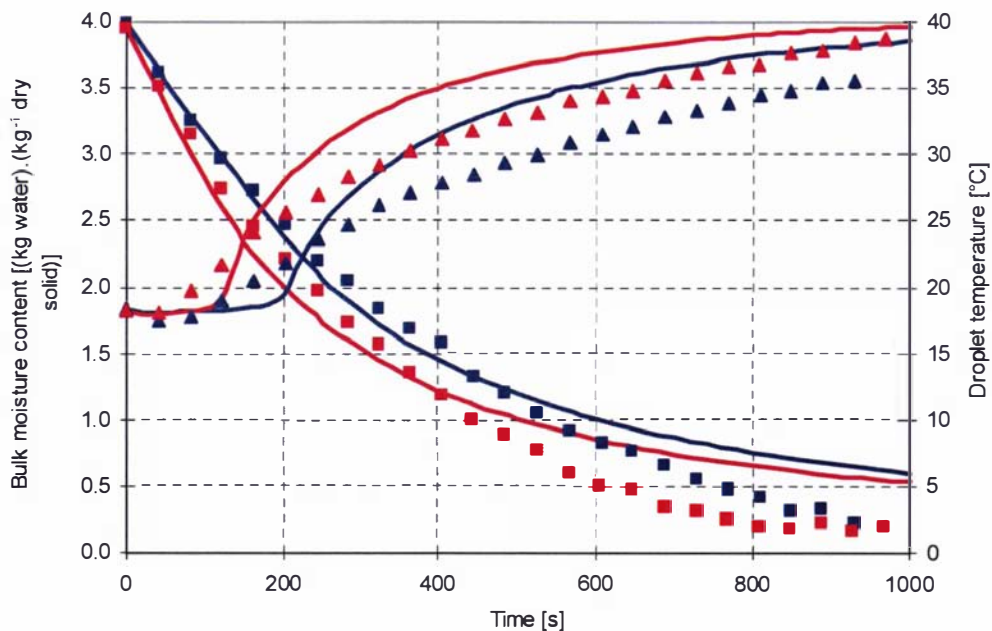


Figure 5.10: Effect of the drying air velocity on the moisture content and temperature histories of 40% w/w maltodextrin DE5 droplets drying at 78 °C along with model predictions: ■ moisture content history at 0.30 m.s⁻¹ air velocity; ■ moisture content history at 0.72 m.s⁻¹ air velocity; ▲ temperature history at 0.30 m.s⁻¹ air velocity; ▲ temperature history at 0.72 m.s⁻¹ air velocity; — moisture content and temperature predictions (blue and red respectively).

The effect of the air velocity was more significant for the dilute droplet (refer to Figure 5.9) than for the concentrated droplet (refer to Figure 5.10), which is in agreement with the findings of Dolinsky *et al.* (1988) [as cited in Dolinsky (2001)]. For the 20% w/w initial solids concentration maltodextrin DE5 droplets, the difference originated from increased mass transfer during the constant rate period, which was seen as an initial constant temperature in the temperature profile, before the surface of the droplet became concentrated and a skin formed. The rate of evaporation was initially higher for the 20% w/w maltodextrin DE5, 0.72 m.s⁻¹ trial (up to 250 s) and then the profiles had similar evaporation rates (similar slopes) up until 700 s, when the moisture content profile for the 20% w/w maltodextrin DE5, 0.72 m.s⁻¹ case began to taper off and both profiles converged at 1000 s.

The model predicted well the experimental data for the 40% w/w initial solids concentration maltodextrin DE5 droplets. However, for the 20% w/w initial solids concentration maltodextrin DE5 droplets, the temperature history was over-predicted by 5 °C and the moisture content history was under-predicted. There was also a significant discrepancy between the predicted and experimental data late in the drying process for the 20% w/w initial solids concentration maltodextrin DE5 droplets. Again this could be partially explained by the appearance of cracks in the skin structure towards the end of the drying process. Another possible explanation for the lack of fit is that the kinetic data from which the binary moisture diffusion coefficient equation was derived [refer to Adhikari (2002)] were for 40% w/w initial solids concentrations. Hence, the equation extrapolated the binary moisture diffusion coefficient at the 20% w/w initial solids concentration, which may explain the extended constant rate period predicted by the model.

After a skin forms at the droplet surface, the drying process becomes internal mass transfer limited and increasing the air velocity will serve only to increase the droplet temperature (via increased air/droplet heat transfer). This is shown in Figure 5.10 for the 40% w/w maltodextrin DE5, 78 °C, 0.72 m.s⁻¹ case; the droplet heated slightly faster than at 0.30 m.s⁻¹ even though there was little difference in the evaporation rates. Although not evident under these conditions, in some circumstances, a slight increase in mass transfer may be expected because of the dependence of the binary moisture diffusion coefficient on temperature (refer to Figure 4.2).

In conclusion, air velocity has little influence on mass transfer in the falling rate period [Vaccarezza *et al.* (1974); Chiang and Petersen (1985); Yusheng (1988); Khraisheh *et al.* (1997)]. Attempts to increase the external mass transfer kinetics by increasing the air–droplet relative velocity will not significantly shorten the drying time for coating with high initial solids concentrations. When applied to an industrial-scale process, higher air velocities will serve only to increase operating costs for little or no return in terms of processing time. The impact of air velocity on design also needs to be considered. Higher air velocity will reduce the residence time during flight up the Würster insert, which may result in wet particles circulating through to the fluid bed region, causing unwanted inter-particle agglomeration.

5.9.3 Initial droplet size

The initial droplet size is a controllable variable and is a key determinant in the quality of the coated product, particularly the spreading and coalescence of droplets to form a coherent film. In these experiments, the droplets were 2.2 mm in diameter; but as explained industrial spray droplets are as small as 10 µm in diameter. Drying droplets this small was not possible, so two larger sizes, 4 µl and 6 µl, were studied. Figure 5.11 presents the moisture content and temperature histories of 6 µl and 4 µl droplets drying at 78 °C and 0.30 m.s⁻¹.

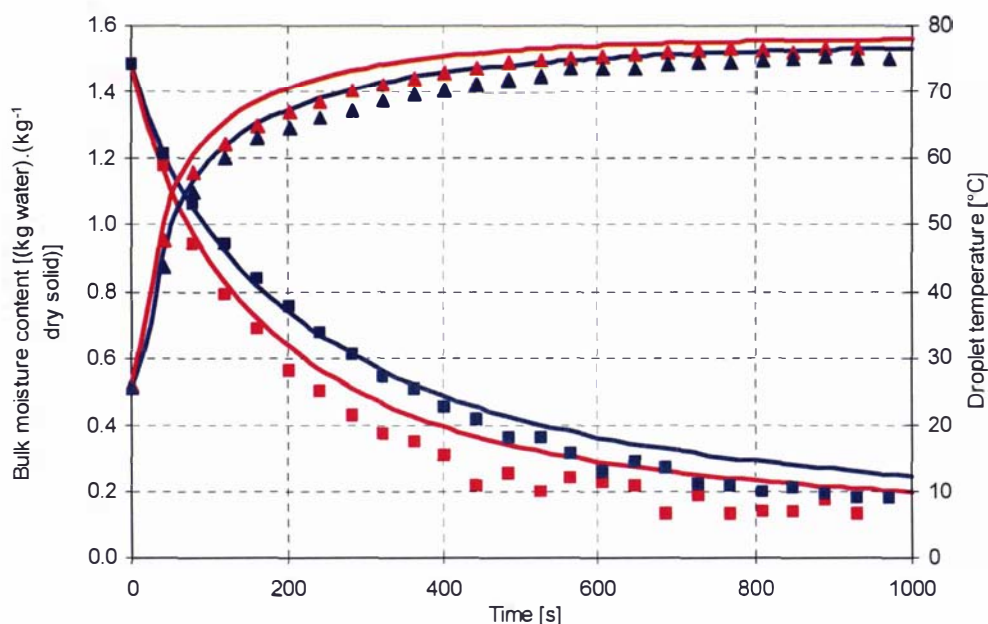


Figure 5.11: Effect of initial droplet size on the moisture content and temperature histories of 40% w/w maltodextrin DE5 droplets drying at 78 °C and 0.30 m.s⁻¹ along with model predictions: ■ moisture content history 6 μl droplet; ▲ moisture content history 4 μl droplet; ▲ temperature history 6 μl droplet; ▲ temperature history 4 μl droplet; — moisture content and temperature predictions (blue and red respectively).

Although there appeared to be a difference in the experimental initial drying rates, the two profiles had almost identical evaporation rates when plotted by mass loss (not shown here), meaning that the evaporation rate per unit area was slightly higher for the smaller droplet. This occurred because the heat and mass transfer coefficients were predicted to be on average 9% and 7% higher respectively for the smaller droplets because of the lower thermal mass and slightly different effect of velocity on the small droplet. Although the trend predictions of the model were correct, the actual model over-predicted the absolute moisture content for the small droplet and consequently over-predicted the temperature history.

Audu and Jeffreys (1975) found that smaller droplets develop a thicker crust during drying. With reference to 2 mm diameter pure liquid droplets, Downing (1966) stated that, if suitable corrections for internal droplet circulation and droplet distortion are applied, the results should apply directly to droplets of a few hundred microns in diameter simply by dynamic similarity using the Reynolds number.

5.9.4 Effect of wetting agent

Wetting agents can be used in coating formulations to promote the spreading of droplets on hydrophobic dairy powder surfaces. However, they are well known to reduce the evaporation rate from water surfaces [van der Lijn (1976)], because they lower the equilibrium surface vapour pressure. Even a minute quantity can lead to significantly lower evaporation rates [Downing (1966)]. The model presented here assumed no segregation of components during drying (as occurs when a surfactant is present at the surface). Instead, experiments to observe the effect of surfactant were carried out to determine if it is significant enough to warrant incorporation into the model at a later date.

A 40% w/w initial solids concentration maltodextrin DE5 droplet containing 2% w/w Ultralec P (ADM, Decatur, IL, USA) was selected for trial. Incorporation of 2% w/w Ultralec P into the 40% w/w initial solids concentration maltodextrin DE5 droplet reduced the surface tension of the droplet from 68.7 to 42.4 mN.m⁻¹. At 40 °C, the largest droplet size that could be suspended from the glass filament was 4 µl, as the weight force of larger droplets overcame the surface tension attaching them to the glass filament. The degree of reproducibility was low because of small differences in the initial mass suspended from the filament, making comparisons difficult. As a result, no conclusions could be drawn.

Instead, water droplets were used, either as pure water or containing 2% w/w Performix E (ADM, Decatur, IL, USA) or Ultralec P. In these experiments, it was possible to suspend 5 µl droplets. The surfactants did not fully dissolve but rather existed as a dispersion. The evaporation rates were 6.5, 5.9 and 5.3×10^{-9} m².s⁻¹ respectively for drying air conditions of 40 °C and 0.30 m.s⁻¹. The lower evaporation rates of the droplets containing surface-active compounds were in agreement with van der Lijn (1976). The Ultralec P droplets also showed a small morphological change, suggesting that there was a sufficient concentration at the surface to enable a small crust to form and to alter the shape of the droplets towards the end of drying, resulting in the lower observed evaporation rate. This was not observed for the Performix E droplets.

The mechanisms by which the evaporation rate is diminished for surfactant-containing droplets were not further explored in this work. Meerdink (1993) found that segregation occurred in slab drying of solutions containing sucrose and sodium caseinate, the latter concentrating at the surface. The segregation was not adequately described by the binary moisture diffusion coefficient equation but was well described by the Maxwell-Stefan multicomponent diffusion equation. In contrast, Adhikari (2002) found that simple mass-weighted averaging of the binary moisture diffusion coefficients provided reasonable predictions for multicomponent mixtures. This segregation of components should be borne in mind when optimising drying rates. The effect of segregation on the evaporation rate is likely to be determined by the relative rates at which the surfactant concentrates at the surface and of the competing process of the formation of the solute skin at the surface. This is an area for further work.

5.9.5 Relative humidity

Film formation has been noted to be enhanced under higher humidity conditions [Fukumori (1994); Kage *et al.* (1996)] but at the expense of increased inter-particle agglomeration. In a coater, the partial pressure of the water-vapour in the surrounding air will vary significantly depending on operating conditions and location. In the spray zone, higher relative humidities, which will increase as the air (along with evaporated water) gradually cools towards the top of the Würster insert, are expected. As the fluid bed region is flushed with incoming air, it has a lower relative humidity.

In the experiments presented in this work, the relative humidity was constrained by the experimental set-up. Although a relative humidity generator existed with the rig, it could not provide a consistent humidified air supply. As a result, the relative humidity from the compressed air line was used (9–11% at 20–25 °C), which gave a relative humidity of around 4% at 40 °C and around 0.5% at 78 °C.

Thus the effect of relative humidity was not investigated in this work. However, its effect on drying kinetics is significant only when the process is externally mass transfer limited, i.e.

during the constant rate period [Räderer (2001)], when it lowers the external humidity driving force. As most concentrated foodstuffs enter into the internal-moisture-diffusion-controlled regime almost immediately, the effect of humidity on the evaporation rate is likely to be minimal in the spray zone. Hence, relative humidity does not lend itself as a control variable for the evaporation rate.

High relative humidity has an important side effect: the sorption of surface moisture as defined by the moisture sorption isotherm of the solute. At high relative humidities, high surface moisture contents exist (refer to moisture sorption isotherms in Figure 4.3), which can lead to surface stickiness through depression of the surface glass transition temperature. This therefore makes relative humidity an important issue in the spray zone for the success of droplet-particle adherence and in limiting inter-particle agglomeration.

5.9.6 Deficiencies in the model

The accuracy of the drying model predictions was determined by the simplifying assumptions and the accuracy of the (measured and estimated) physical parameters. The latter were investigated in Appendix A2. This section discusses the inaccuracy in the model predictions stemming from the simplifying assumptions listed earlier.

5.9.6.1 Morphological changes

The one-dimensional moisture diffusion equation assumes ‘ideal shrinkage’, which was not observed in the droplet drying experiments. Figure 5.32 shows that warping of the surface skin and subsequent morphological changes occurred during the drying of the maltodextrin DE5 droplets.

From the morphological observations and inspection of the samples with drying time, it was clear that the droplets (especially at high initial solids concentrations and high temperatures) formed a skin almost immediately, and that the thickness grew inwards towards the liquid core of the evaporating droplet.

Cracking can greatly affect the mass transfer rate. Although the formation of a glass crust greatly reduces moisture diffusivity [Räderer (2001)], the rigidity of the crust causes severe stresses, which can lead to warping and, more importantly, fractures [Sano and Keey (1982)]. Evaporation from these fissures can greatly increase the drying rate late in the drying process.

It is possible that the morphological changes and subsequent cracking, leading to preferential moisture transfer, were responsible for the under-prediction in the moisture content history towards the end of the drying process. The binary moisture diffusion coefficient correlation used in this mathematical model was taken from Adhikari (2002) and was developed from slab drying (50 mm diameter, 1 mm deep circular discs) experiments. It can be argued that the measurement of the binary moisture diffusion coefficients via slab or droplet drying kinetics intrinsically takes into account the morphological behaviour. However, it is possible that the fixed nature of the films in the circular discs may have led to different morphological features from those developed during droplet drying.

Alternatively, part of the inaccuracy in the model predictions towards the end of the drying process could be due to the droplet surface area actually being larger than predicted by the model. This occurred because a rigid skin formed, which subsequently did not shrink but instead warped. This was particularly severe for the 20% w/w initial solids concentration

maltodextrin DE droplets, which did not shrink as much as expected (Figure 5.32(a–e)); given that the droplets were almost completely dry, they should have been close to only 20% of the initial volume because the density change was not significant. Clearly, this was not the case. The 40% w/w initial solids concentration maltodextrin DE5 droplets (Figure 5.32(k–t)) did not appear to shrink significantly at all.

Surface morphological changes are difficult to account for in a mathematical model, because the mathematics behind these surface modifications such as folding, wrinkling and fissures are extremely complex and to date have not been modelled. Achanta and Okos (1995) concluded that more research is required to develop a crust thickness predictor and to understand stress development and breakage during drying. Morphological development during the drying of a range of polymer solutions are investigated in Sections 5.12–5.14.

5.9.6.2 Internal circulation effect

Internal circulation effectively reduces the thickness of the boundary layers and increases the values of the overall Nusselt and Sherwood numbers [Downing (1966)], which can result in models under-predicting the moisture content history, particularly in the early stages of drying. Using the image acquisitions system, internal circulation was evident in the 20% w/w initial solids concentration maltodextrin DE5 droplets. Similar observations were reported by several researchers [Menting and Hoogstad (1967); Yamamoto and Sano (1995)]. This usually ceased at the time at which the droplet temperature started to increase from the wet bulb temperature to the air temperature [Yamamoto and Sano (1995)]. The model accurately predicted the moisture content in the initial stages of drying, suggesting that skin formation in all cases was rapid, which effectively limited the influence of internal circulation on heat and mass transfer.

5.9.6.3 Other error sources

The temperature history was still slightly over-predicted in all cases. The majority of this over-prediction is due to the under-predicted mass flux which results in a lower rate of latent heat loss. Secondly, some inaccuracy is present in the mathematical terms describing the heat conduction in the glass filament and wire thermocouple (approximated as one-dimensional fins). Given the percentage of total heat flow to the droplet contributed by these heat sources, future work should determine a better mathematical description to achieve a more accurate temperature history prediction. An additional error source is the fact that the moisture and temperature histories could not be determined simultaneously. This introduced small errors arising from different droplet load times and droplet sizes.

The accuracy of the calculations of the gas side heat and mass transfer coefficients is limited by many unknowns. However, many corrections can be included in the calculations. van der Lijn (1976) described the potential deviations from the Nusselt and Sherwood numbers and quantified their effects. These included the effects of net mass flow, the Soret effect, deviations from continuum theory, unsteady-state, local variation in transfer coefficients, free convection, non-infinite medium, radiation, mass flux on heat flux, internal circulation and oscillations, and turbulence. Most of these effects can be dismissed with simple calculations given by van der Lijn (1976). For engineering purposes, such minor corrections are often not warranted if the general trends provide sufficient understanding of the process involved [van der Lijn (1976)], and these are not included in the model presented here.

5.9.7 Conclusions

The drying kinetic data for maltodextrin DE5 droplets gave valuable insight into controlling droplet drying. The effects of initial solids concentration, drying air temperature, air velocity and droplet size on the drying kinetics of maltodextrin DE5 were all accurately predicted by the model under the experimental conditions investigated. However, late in the drying process when skin morphological development becomes significant the model under-predicted the evaporation rate. This deviation is probably a result of both higher observed (than predicted) droplet surface areas and the possibility of preferential moisture transport from crack development.

5.10 'HYBRID DROPLET DRYING MODEL'

To better predict the drying kinetics at the end of the drying process, the morphological changes need to be accounted for in the mathematical model. Ignoring for the meantime, the occurrence of, and subsequent mathematical difficulty in describing surface wrinkling and cracking, the discrepancy between the model predictions and experimental data could be partially reduced by predicting a higher evaporation rate at the end of the drying process. One method is to predict a larger droplet radius and hence surface area than that currently predicted via the 'ideal shrinkage' assumption. This is justified considering the fixed radius observations in Figure 5.32, particularly images (f–j) and (k–o).

As a first approximation, the mathematical model was modified to include a critical fixed-radius (more correctly, fixed-surface area) criterion, similar to that employed by the receding interface models [e.g. Audu and Jeffreys (1975); Cheong *et al.* (1986); Dolinsky (2001)]. An explanation of how this works follows. Initially, droplet drying is predicted on the solute-fixed coordinate system and droplet shrinkage is considered ideal, i.e. a perfect sphere in which the degree of radial shrinkage corresponds to the amount of water lost. This ensures that the current accurate predictions over the first 500 s of drying remain unchanged. At a particular point in time (set by a predetermined surface condition) the model holds the droplet radius constant as drying progresses. This gives a larger surface area for evaporation to occur from, thus increasing the evaporation rate later in the drying process. Hence, the model can essentially switch from an 'ideal shrinkage' model to a 'modified-receding interface' model giving increased predictive flexibility being able to predict droplets that do not form rigid skins and droplets that do, regardless of the surface moisture content. The word 'modified' is incorporated in this work because the new model contains two essential differences compared with the existing receding interface models; the critical condition at which the skin forms, and the internal structure of the droplet. The new model is called the 'hybrid droplet drying model'. The two key differences between the new model and the receding interface models are discussed below.

The critical condition at which the droplet radius is set to become a constant in receding interface models is usually specified by a surface moisture content. This criterion has been used to successfully model the droplet drying kinetics of skim milk, sodium sulphate and colloidal silica [Nesic and Vodnik (1991)]. Nesic and Vodnik (1991) used the condition that the surface concentration must be $\geq$ the saturation concentration because it was found that some materials slightly exceeded their saturation concentration before solid crystals were observed (e.g. sodium sulphate). Audu and Jeffreys (1975) assumed in their model and observed from experiments, that a crust forms immediately for drying suspensions that were well above their saturated solids concentrations. However, it is debatable as to whether this

criterion would model dilute solutions such as those used in spray coating applications. In addition, the saturated surface criterion could not be used in this study because the saturation concentration of maltodextrin DE5 is approximately 17% w/w (Grain Processing Corporation, Maltrin® brochure, 1999). Even at 40% w/w, the solutions were viscous but able to flow and would not be able to form a rigid skin, suggesting that a concentration and viscosity much higher was required as the point at which the radius should become fixed in this new model.

In the new model, it is proposed that the surface becomes rigid based on the proximity of the droplet's surface to the surface glass transition temperature, T_g . T_g was first introduced in Section 3.11 with reference to film formation and stickiness. The reader is referred immediately to Sections 6.4.1 and 6.4.2 for a background on glass transition and stickiness respectively. From this discussion, and in contrast to the humidification studies employed by researchers investigating powder stickiness, this study is interested in the point at which the droplet surface approaches and then passes through its glass transition temperature from the reverse direction (drying), first exhibiting a 'rubbery' (10^6 – 10^8 Pa.s) and hence 'sticky' and malleable character, to then exhibit a 'glassy' rigid structure, above 10^8 Pa.s. At some point defined by a critical $X = (T - T_g)$ value, it is assumed that a rigid surface develops such that the surface skin is mechanically strong enough to resist the volume change and fix the droplet radius for the remainder of the drying time. Given the discussion in Sections 6.4.1 and 6.4.2 critical X values from 0–40 °C are considered to represent a reasonable temperature range over which a rigid skin may form.

Instead of using the surface condition only, the critical X value was set to hold for the second node in from the surface (i.e. the $J-1$ radial position) meaning that for the skin to form the condition must hold for the first one and a half shell volumes thus giving a slightly greater initial skin thickness to impart some form of mechanical integrity. 60 nodes were used in these simulations to more accurately predict the conditions just beneath the surface node. Figure 5.12 shows the effect of critical X value and the variable density calculation schemes on the model predictions for the 40% w/w maltodextrin DE5 droplet drying at 78 °C. The calculation scheme for this comparison is termed the 'collapsed shell' for reasons that will be discussed later.

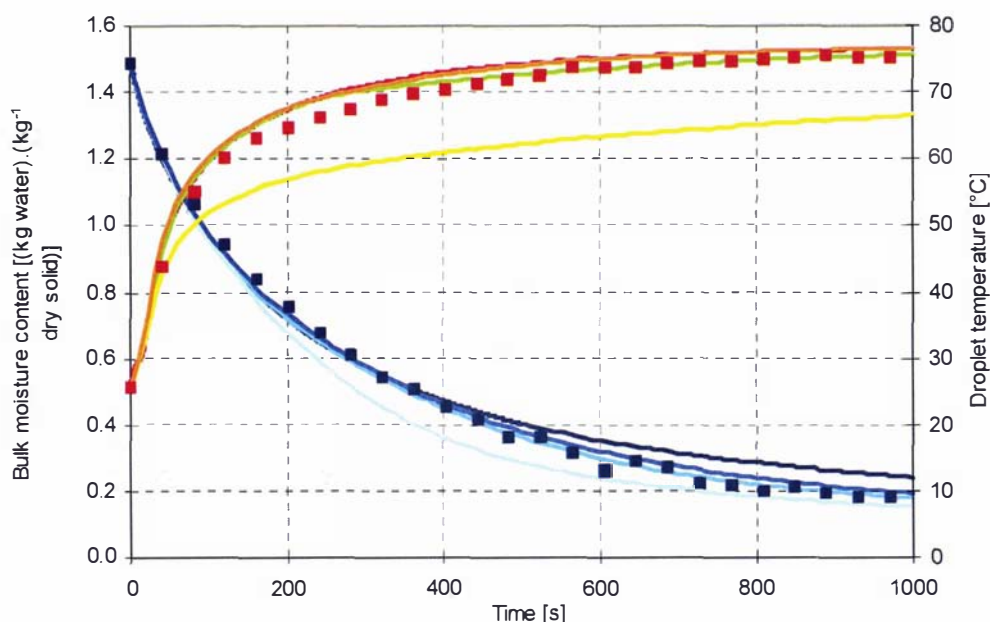


Figure 5.12: Effect of critical X value and the variable density calculation schemes on the droplet temperature on the moisture content predictions for 40% w/w maltodextrin DE5 droplets at 78 °C: ■ experimental moisture content; ■ experimental temperature. 'Ideal shrinkage' model predictions: — moisture content; — temperature. 'Collapsed shell', critical $X = 20$ °C predictions: — moisture content; — temperature. 'Collapsed shell', critical $X = 40$ °C predictions: — moisture content; — temperature. 'Dense skin-porous crumb', critical $X = 20$ °C predictions: — moisture content; — temperature.

At a critical X value of 20 °C, which was the best estimate given the literature on powder stickiness, an excellent fit is obtained. At a critical X value of 40 °C, an over-prediction in the bulk moisture content results because the droplet radius at which this condition is met is too early (< 20 s) in the drying process and results in a too larger surface area. Reducing the critical X to zero (lies beneath the 'ideal shrinkage' prediction) results in an under-prediction of the drying rate similar to the 'ideal shrinkage' model as the radius is fixed too late in the drying process (> 1000 s). This was expected because a critical X value of zero is the minimum theoretical value that an amorphous material could exhibit 'rubbery' character. Referring to Figure 5.32(k-o), there is little change in the droplet radius after 120 s of drying time. This corresponds closely to the time (235 s) at which the critical $X = 20$ °C condition is met.

It must be noted that surface conditions were not measured so there is no physical evidence to suggest that the droplet radius is arrested at any particular surface critical X value. The time at which the radius becomes fixed is not sensitive to the critical X value at the surface due to the steep inflection of the surface T_g profile (refer to Figure 5.23). It is however, sensitive to the position of the first nominated node and to the number of adjacent nodes at which the condition is set to occur. The model predictions here are solely to illustrate a proposed surface (or rather a surface shell volume) condition at which the droplet radius can become fixed for high molecular weight skin-forming materials that do not form a crust at their saturation concentration as used by the receding interface models. The actual point at which the radius will become fixed will depend on the moisture content, temperature, material type, thickness and structural character (elasticity, porosity) of the skin in addition to the difference between the droplet internal and external system pressure. Thus the model is a convenient method to account for the increased surface area that is not currently predicted by the 'ideal shrinkage' model. Further research is required to determine the time and the droplet

morphology, particularly the surface skin thickness and structural properties at which drying droplets maintain a constant radius and therefore define constitutive relationships for use in the model.

The increased area that results from fixing the droplet radius at the critical X condition gives a greater evaporation rate late in the drying process. The receding interface models assume that the capillary effects in the crust are negligible (i.e. no liquid transport to the surface) and evaporation occurs at the crust–wet core interface with moisture transport via water-vapour diffusion through the pores to the droplet surface (i.e. of the order of 10^{-5} – 10^{-6} $\text{m}^2 \cdot \text{s}^{-1}$). Cheong *et al.* (1986) stated that, the structure, and in particular the porosity of the crust have been ignored, largely because of the difficulty in quantifying the parameters. Hence, it remains debatable as to where the water evaporates, making the increased surface area assumption and evaporation at the droplet surface plausible. The benefit of this assumption is that the mode of moisture transport is not prescribed in the crust and the effective diffusivity accounts for all modes of moisture transport. This is particularly relevant in this study because the temperatures are lower than the boiling point of water.

Once the radius is fixed, further drying can proceed via two pathways to yield a ‘collapsed shell’ structure or ‘dense skin–porous crumb’ structure. These better represent the internal droplet structure observed in spray drying studies. The following paragraphs briefly discuss the morphological features of these droplet structures followed by a description of the calculation procedure and its physical interpretation.

The skin/crust thickness in the receding interface models grows at a rate that is dependent on the drying conditions, such that the amount of water evaporating is replaced by an equivalent amount of solid as crust, between the surface and the wet core [Audu and Jeffreys (1975); Cheong *et al.* (1986)]. Since the internal wet core concentration of the droplet is assumed to remain constant once saturation is reached [e.g. Nesic and Vodnik (1991)] or at the initial density [e.g. Audu and Jeffreys (1975)], the final droplet structure is that of a homogeneously porous droplet of the same density as the initial droplet solute. However, according to Achanta and Okos (1995), the thickness of the skin/crust that forms is a function of the drying process conditions and a material (single solute/solvent system) which is initially homogeneous and dried rapidly, is transformed to a composite material with two layers, a dense skin and a porous crumb. A glassy skin and porous crumb structure was noted for the drying whey protein isolate droplets (Section 5.14). On the other hand, gum arabic produced thick dense skins all the way to the centre of the droplet once dried (Section 5.14). This suggests that both extremes, a low density, porous crumb structure as well as a thick, dense solid structure or some intermediate structure can be observed during drying below the boiling point temperature of the solvent and is material and drying conditions dependent. Hassan and Mumford (1993a,b,c) and Hassan and Mumford (1996) comprehensively studied skin and crust forming materials during drying and classified them into three categories (Section 6.2.1) also noting a dense skin with porous crumb beneath. Some of the possible internal structures observed during the drying of droplets from both Hassan and Mumford (1996) and in Section 5.12 are depicted schematically in Figure 5.13.

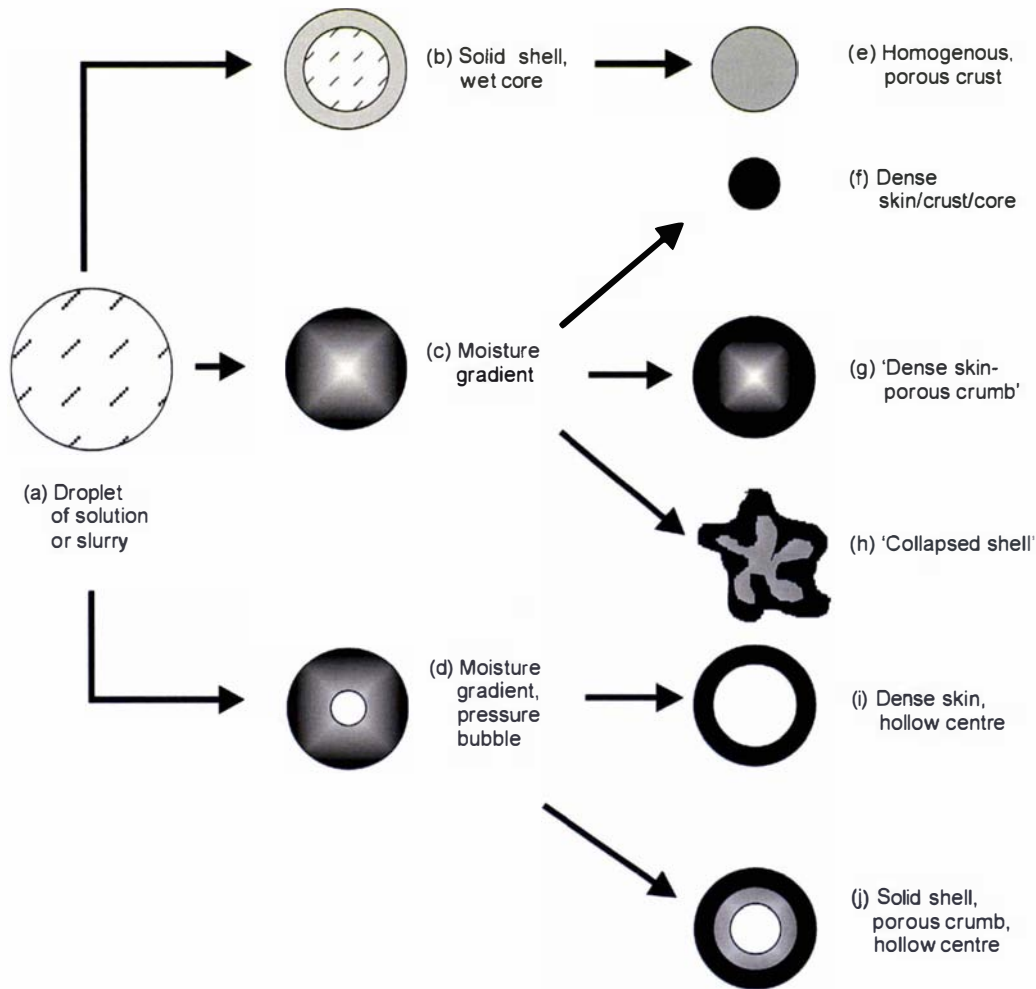


Figure 5.13: Possible internal structures during droplet drying.

Starting from an initially homogeneous solution of water and solute (dissolved or slurried), a flexible mathematical model should be able to account for the variations in internal droplet structure shown in Figure 5.13. To further extend the model, two calculation pathways are included to predict the ‘collapsed shell’ and ‘dense skin–porous crumb’ droplet structures depicted by Figure 5.13(g) and (h) respectively. The essential differences between these two calculation pathways and the ‘ideal shrinkage’ calculation pathway are discussed below with reference to the droplet radii and binary moisture diffusion coefficient predictions represented by Figure 5.14–Figure 5.16.

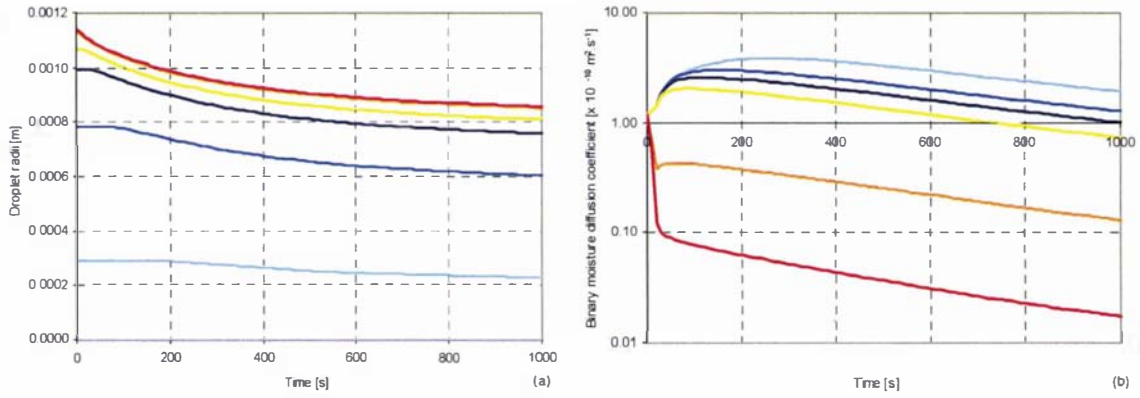


Figure 5.14: ‘Ideal shrinkage’ structure model: (a) internal node radii and (b) binary moisture diffusion coefficient as a function of these radii for a 40% w/w maltodextrin DE5 droplet drying at 78 °C. — $j = 0.5$; — $j = 1.5$; — $j = 19.5$; — $j = 29.5$; — $j = 39.5$; — $j = 58.5$; — $j = 59.5$. Note: the binary moisture diffusion coefficients are calculated at the nodal interfaces (backward interfaces are shown, hence for $j = 0.5$, $D_w = 0$).

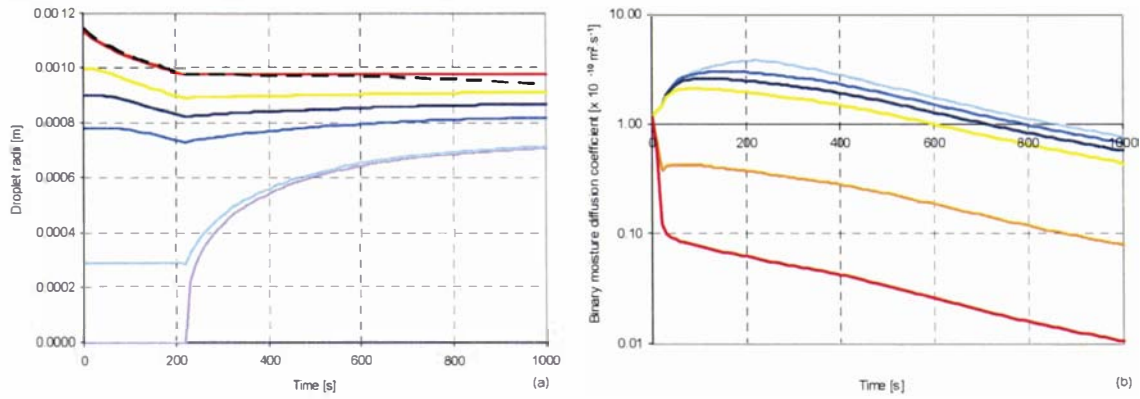


Figure 5.15: ‘Collapsed shell’ structure model: (a) internal node radii and (b) binary moisture diffusion coefficient as a function of these radii for a 40% w/w maltodextrin DE5 droplet drying at 78 °C for a critical $X = (T - T_g) = 20$ °C. — $j = 0.5$; — $j = 1.5$; — $j = 19.5$; — $j = 29.5$; — $j = 39.5$; — $j = 58.5$; — $j = 59.5$. — — receding skin interface. Note: the binary moisture diffusion coefficients are calculated at the nodal interfaces (backward interfaces are shown, hence for $j = 0.5$, $D_w = 0$).

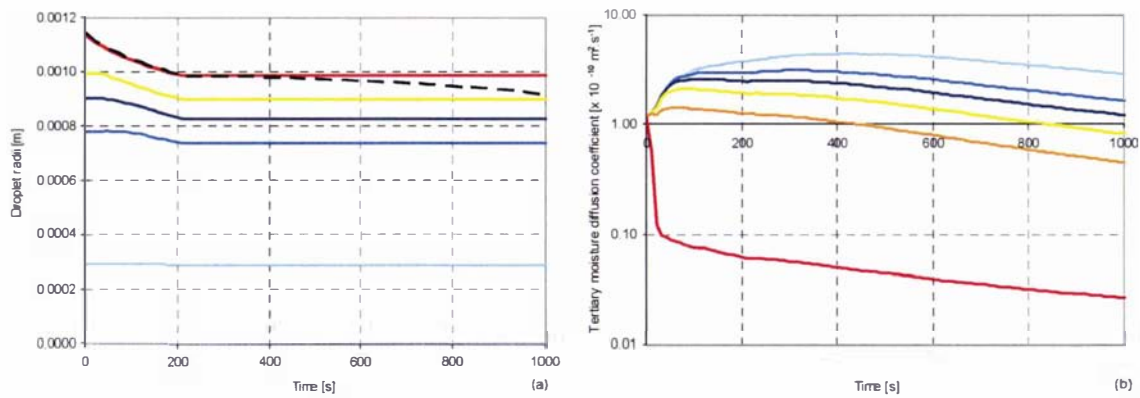


Figure 5.16: ‘Dense skin-porous crumb’ structure model: (a) internal node radii and (b) binary moisture diffusion coefficient as a function of these radii for a 40% w/w maltodextrin DE5 droplet drying at 78 °C for a critical $X = (T - T_g) = 20$ °C. — $j = 0.5$; — $j = 1.5$; — $j = 19.5$; — $j = 29.5$; — $j = 39.5$; — $j = 58.5$; — $j = 59.5$. — — receding skin interface. Note: the tertiary moisture diffusion coefficients are calculated at the nodal interfaces (backward interfaces are shown, hence for $j = 0.5$, $D_w = 0$).

Under the ‘ideal shrinkage’ calculation scheme, the droplet radius continuously shrinks as shown in Figure 5.14(a) and the change in volume of the droplet corresponds to the amount of water evaporated. This results in the profiles for the binary moisture diffusion coefficient as a function of position in Figure 5.14(b). The binary moisture diffusion coefficient profile for $j < 40$ increases over the first 200 s because of its dependence on temperature. After 200 s, the profiles diminish as the droplet dries due to the strong dependence on moisture content. In contrast, the surface node decreases from the outset of drying because it rapidly loses water.

When the fixed-radius criterion is applied, the droplet radius shrinks ‘ideally’ for the first 235 s and then remains constant to give the ‘collapsed shell’ structure (Figure 5.15(a)). After this time, ‘ideal shrinkage’ is still assumed but the order of the radii calculations are reversed from the current ‘ideal shrinkage’ model and proceed from the surface to the centre resulting in the central node moving towards the surface node. It must be noted that the movement of the central node towards the droplet surface does not leave a hollow cavity but instead is used to represent the collapsing in of the other side of the droplet. This represents the ‘collapsed shell’ structure shown in Figure 5.13(h). This is one of many shapes which convolution could represent, for example, a deflated soccer ball, or in an extreme case, a three-dimensional object such as a flat or folded disc. Intermediate cases could be those shown in Figure 5.3(b) and (c) for industrial spray-dried droplets in which collapse is common. Nevertheless, the complex structure that forms can be modelled as a pseudosphere of shrinking volume and fixed surface area. For model calculations proceeding via this pathway, it should be made clear that, it is in fact, the droplet surface area that remains constant not the droplet radius. No evidence could be found for the same morphologies as those shown in Figure 5.3 under low temperature coating or spray drying conditions, which is a direct result of the fact that, there has been no commercially driven interest in this, until now. However, the single droplet drying tests (Figure 5.32(a–e) and (k–o)) under low temperature conditions do show the same indentations and beginnings (or to a lesser extreme) of what could be described as a ‘collapsed shell’ structure.

The skin thickness is the distance between the droplet radius and the innermost node that exceeds the critical X value (black dashed line in Figure 5.15(b)). The skin thickness immediately begins to grow when the droplet radius becomes constant. After 1000 s, the skin interface has receded into the droplet to give a predicted thickness of 41 μm . At this time, the droplet has not fully dried, having a bulk moisture content of 0.2 (kg water).(kg⁻¹ dry solid) (refer to Figure 5.12). At 1730 s (not shown) the skin interface and the central node converge to give a skin thickness of 224 μm and a bulk droplet moisture content of 0.1 (kg water).(kg⁻¹ dry solid). After this time the droplet shrinks very slowly as no viscous bulk remains and water now diffuses through the dense skin only. The binary moisture diffusion coefficient profile is not significantly different to that predicted by the ‘ideal shrinkage structure’, however, slightly lower values are predicted. This slowed moisture movement is offset by the much smaller diffusional distance resulting in the increased mass transfer and hence increased rate of evaporation shown in Figure 5.12 (critical $X = 20$ °C) for the ‘collapsed shell’ structure. Given that the diameter of the glass filament at the top of the images in Figure 5.32(a–e) is 0.2 mm, the droplet diameter at 900 s is approximately 1 mm. This suggests that the dense skin accounts for approximately 83% of the droplet volume which is in agreement with the observation that a viscous solution at the centre remained after the 1000 s of drying time (discussed in Section 5.14).

For the ‘dense skin–porous crumb’ structure case (Figure 5.16(a)), the droplet shrinks ‘ideally’ up until 235 s at which time the droplet radius becomes fixed. However, in contrast to the ‘ideal shrinkage’ structure and ‘collapsed shell’ structure models, the ‘dense skin–

porous crumb' structure model holds all internal radii constant at this point, hence 'ideal shrinkage' is no longer assumed. In this case, as water evaporates from the droplet surface, an equal volume of air replaces the lost water from the internal nodes giving rise to an internal porosity. The appearance of air is only to account for the diffusion of water-vapour through the porous structure. No assumption is made on how the air got there. By assuming air occupies the pores the issue of collapse is avoided when the water-vapour condenses. This is reasonable given the low temperatures, low pore volume and rigid skin structure.

Again the skin thickness immediately begins to grow when the droplet radius becomes constant. After 1000 s, the skin interface has receded into the droplet to give a predicted thickness of 93 μm . At 1730 s (not shown) the skin interface has grown to give a skin thickness of 388 μm and a bulk droplet moisture content of 0.1 (kg water).(kg⁻¹ dry solid).

The constant droplet surface area and volume along with porosity development, should in theory significantly affect the rate of moisture movement. Firstly, porosity development will enhance the rate of mass transfer since water-vapour diffusion through the air-space of a pore can be as high as $10^{-5} \text{ m}^2.\text{s}^{-1}$ (dependent on pore structure) as opposed to $10^{-10} \text{ m}^2.\text{s}^{-1}$ in a dry solid. However, at the same time the increased diffusional distance for water-movement in the 'dense skin-porous crumb' structure will act to slow the evaporation rate. To account for these effects, the mathematical description for the binary moisture diffusion coefficient had to be modified to describe the now tertiary component system (water-solid-air). Given that the internal structure was not measured, and the common acceptance of an effective diffusion coefficient used in the drying literature, a simple estimated value using heat transfer analogies for thermal conductivity was justified. Analogous to heat transfer (as already discussed in Section A2.3.7), the actual mass transfer system will most likely be best described by a model that predicts between the two extremes of the series and parallel models. The 'dense skin-porous crumb' model was run using various constitutive mathematical models to describe heat conduction but modified to describe the moisture diffusion coefficient (note binary is dropped). The models used were, the series model, the parallel model, the effective medium theory model, the Krischer model and parallel model with a constrictivity/tortuosity factor. The series, parallel, effective medium theory and Krischer models are described in Rahman (1995) and the equations are given in Section A2.3.7. The parallel model with constrictivity/tortuosity factor developed in the soil science literature (taken from Bronlund (1997)) was found to provide the best fit to the experimental data from the diffusivity descriptions used under this calculation scheme and is given by $D_{w,\text{porous}}$ [$\text{m}^2.\text{s}^{-1}$] below.

$$D_{w,\text{porous}} = \frac{\delta}{\tau_2} \varepsilon_a D_v + (1 - \varepsilon_a) D_w(u, T) \quad (5.18)$$

where D_v is the diffusivity of water-vapour in air [$\text{m}^2.\text{s}^{-1}$] (i.e. assuming an open, non-constricted pore system) and $D_w(u, T_d)$ is the effective binary moisture diffusion coefficient through the solid phase [$\text{m}^2.\text{s}^{-1}$] calculated with Equation (A2.34). δ/τ_2 is the constrictivity/tortuosity factor which accounts for the structural influence of the pore system on reducing the water-vapour diffusivity in the air. A value of $\delta/\tau_2 = 3 \times 10^{-5}$ gave the best fit to the experimental data as shown in Figure 5.12. The fit to the experimental data is better than that of the 'ideal shrinkage' structural model but not quite as good as that of the 'collapsed shell' structural model. The very low δ/τ_2 value suggests that the series model dominates and indicates the system has a very complex and narrow pore structure many of which could be closed. Future work should measure the moisture diffusion coefficient and porosity character for materials that show the two extreme structural differences so a less

empirical and more accurate description of the moisture diffusion coefficient can be determined.

In this ‘dense skin–porous crumb’ structure model, the tertiary moisture diffusion coefficients close to the surface are similar to those predicted by the other models. This is because the region near the surface is sufficiently dry before the radius becomes fixed and hence subsequent porosity development is minimal. However, the predicted moisture diffusion coefficients at the internal nodes remain greater for the drying period shown as porosity development occurs and allows increased mass transfer.

Figure 5.17 shows the predicted porosity development in selected nodes for the ‘dense skin–porous crumb’ structure model.

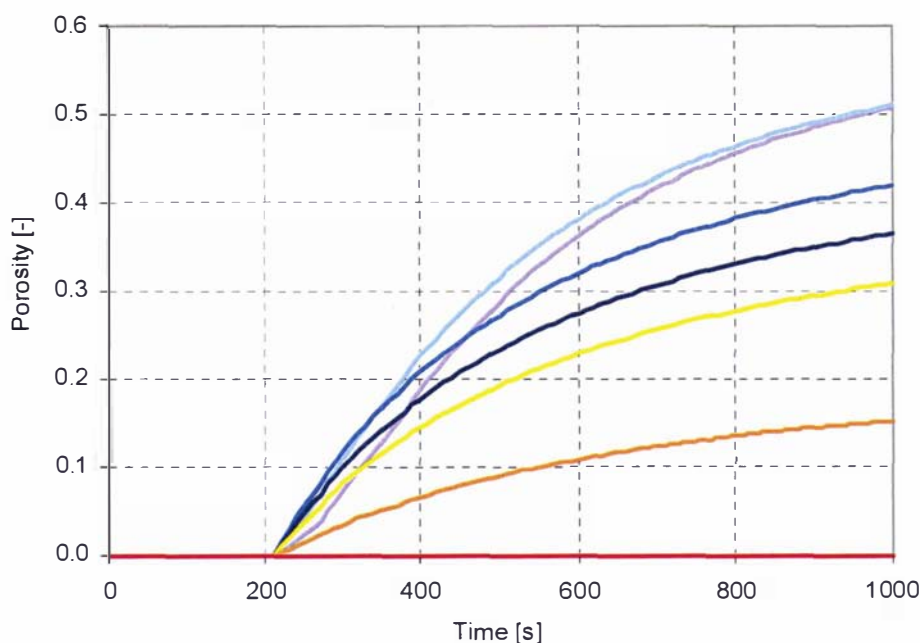


Figure 5.17: Porosity development in a 40% w/w maltodextrin DE5 droplet drying at 78 °C predicted by the fixed-radius, $X = (T - T_g) = 20$ °C model (‘dense skin–porous crumb’ structure). — $j = 1$; — $j = 2$; — $j = 20$; — $j = 30$; — $j = 40$; — $j = 59$; — $j = 60$.

The nodes closest to the surface lose a significant amount of their initial moisture up until 235 s and hence have less available volume to be taken up by air-space after 235 s. This results in a diminishing porosity gradient towards the surface which gives rise to the ‘dense skin–porous crumb’ structure that is modelled in line with what has been experimentally observed.

In order to calculate the rate of internal moisture diffusion, the ODE for droplet moisture must account for the amount of air-space in each node. To do this, the solute-fixed coordinate based ODE for internal moisture diffusion was converted from Equation (A2.86) to Equation (5.19) which incorporates both the shell volume and shell mass to account for the significantly lower nodal density with air inclusion.

$$\frac{du_j}{dt} = \left[\begin{array}{c} D_{w,j-1/2} 4\pi r_{j-1/2}^2 \frac{1}{2} \left[\frac{m_{s,j-1}}{V_{t,j-1}} + \frac{m_{s,j}}{V_{t,j}} \right] \frac{(u_{j-1} - u_j)}{(r_j - r_{j-1})} - \\ D_{w,j+1/2} 4\pi r_{j+1/2}^2 \frac{1}{2} \left[\frac{m_{s,j}}{V_{t,j}} + \frac{m_{s,j+1}}{V_{t,j+1}} \right] \frac{(u_j - u_{j+1})}{(r_{j+1} - r_j)} \end{array} \right] \frac{1}{m_{s,j}} \quad (5.19)$$

The nomenclature for Equation (5.19) are given throughout Appendix A2.

In summary, the new ‘hybrid droplet drying model’ establishes a new critical surface condition so that the droplet radius can become fixed based on the critical X concept. The model also proposes a more flexible calculation scheme to better represent the range of observed droplet internal structures; dense, non-porous skin and core (‘ideal shrinkage’), ‘collapsed shell’ and the ‘dense skin–porous crumb’ structures. Further work is required to measure both the crust radius, thickness and internal density development as a function of the material and the drying conditions to determine which model more accurately depicts the actual drying process. At this stage, the discrepancy between the current ‘ideal shrinkage’ model predictions and the experimental data is considered acceptable for the engineering applications for which the model was developed.

5.11 INDUSTRIAL-SCALE PREDICTIONS

Although the model was able to predict the effect of droplet size it remains questionable whether it is able to give accurate predictions at the sizes of industrial-scale interest (10 to 100 μm in diameter) without the experimental means to test such predictions. However, the mathematical model was used to predict the outcome of process variable changes under industrially relevant conditions in order to draw guidelines on the design and operation of a Würster-style coater for coating particles. Since the surface moisture content and temperature cannot be measured in an industrial-scale coating process, their prediction is valuable. Of particular importance is to use these predictions to draw conclusions on product quality and process control. This section demonstrates that the model can be used to define a window between which droplets are sticky enough to adhere during impingement but dry enough to prevent agglomeration. Figure 5.18 highlights the challenge under investigation and the variables under operator control.

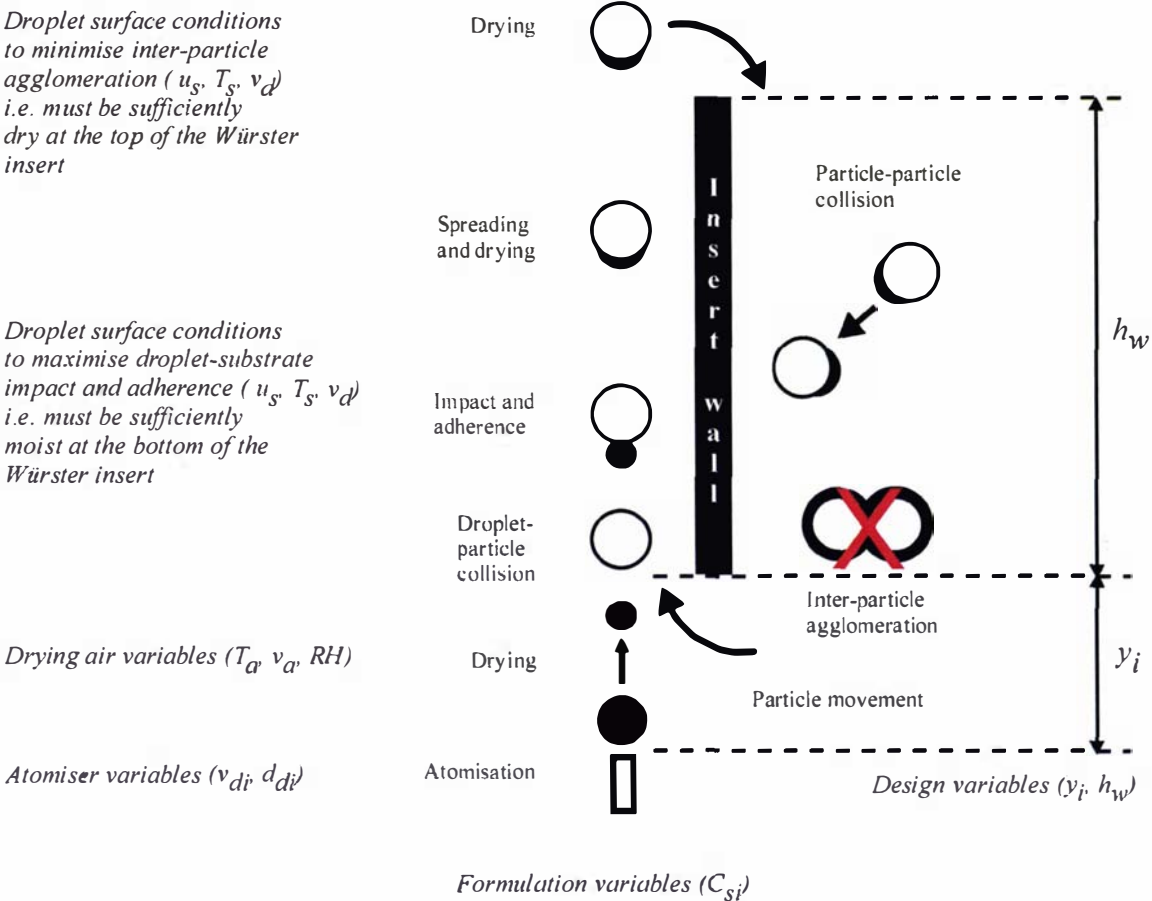


Figure 5.18: Micro-level examination of the key control variables in a Wurster coater:
○ = substrate particle; ● = atomised droplet.

There are eight key variables for control by the operator. Six of these variables, at high and low levels, are shown in Table 5.2. The remaining two variables, y_i and h_w , are the distance between the nozzle and the droplet–particle impingement point, and the Wurster height respectively. These are determined for two drying scenarios. The first scenario is to operate under slow drying conditions to ensure the successful impact and adherence of atomised droplets on to the substrate particles. The second scenario is to operate under fast drying conditions to ensure inter-particle agglomeration is minimised.

Table 5.2: Parameters used in the industrial-scale drying kinetics predictions

Initial solids concentration [% w/w]	Initial droplet diameter [μm]	Initial droplet velocity [m.s ⁻¹]	Air temperature [°C]	Relative humidity [%]	Air velocity [m.s ⁻¹]
20(s)	10(f)	100(s)	40(s)	5(f)	1(f)
40(f)	20(s)	200(f)	80(f)	50(s)	10(s)

s = used for slow drying predictions; f = used for fast drying predictions.

In all cases the droplet was set to enter the coater at 20 °C. In reality, this may be higher to reduce the viscosity for successful droplet atomisation. In this example, the ‘ideal shrinkage’ model type was used since no assumption was made on when the skin forms. The model can also be run to simulate industrial-scale conditions for the ‘collapsed shell’ and ‘dense skin–porous crumb’ internal droplet structures.

Figure 5.19 and Figure 5.20 show the predicted moisture content and temperature distribution across the industrial-scale droplets for the slow and fast drying scenarios respectively.

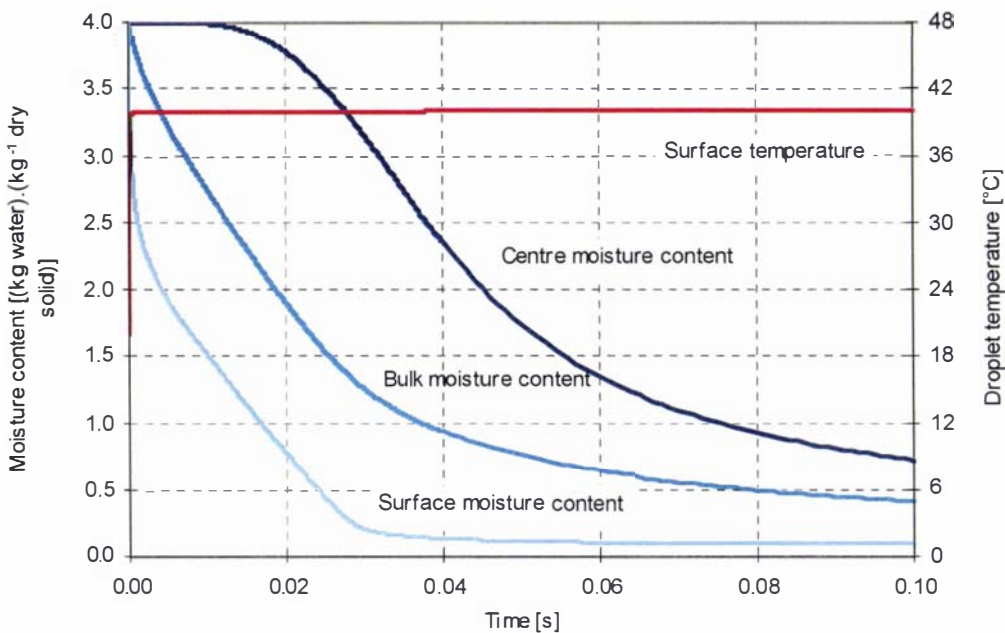


Figure 5.19: Predicted moisture content and temperature distribution in an industrial-scale spray droplet under slow drying conditions: — centre moisture content; — bulk moisture content; — surface moisture content; — surface temperature. Note: the centre and bulk droplet temperatures lie beneath the surface temperature, i.e. there is no discernable temperature difference across the droplet.

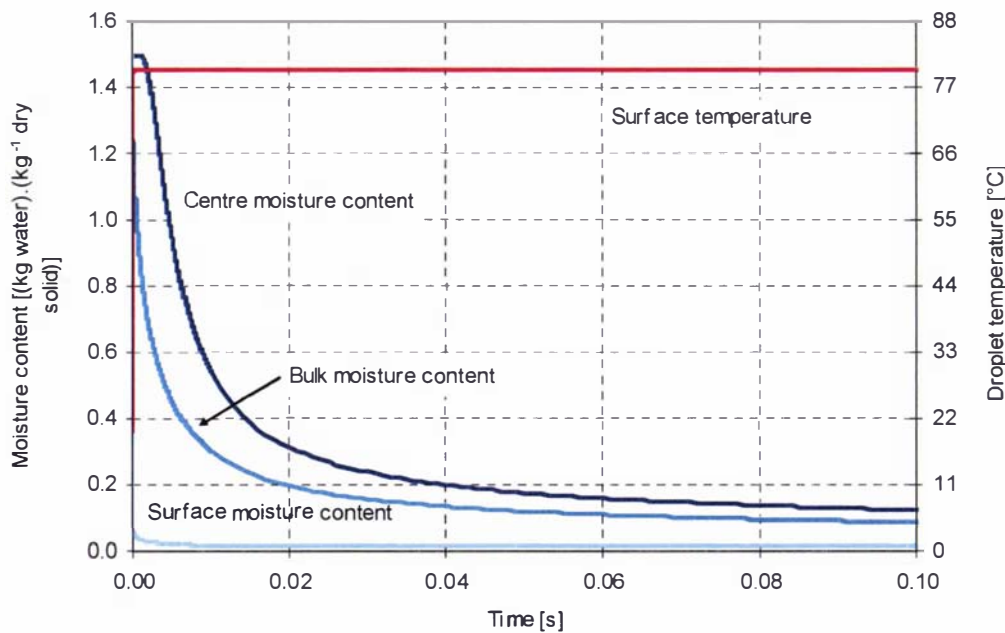


Figure 5.20: Predicted moisture content and temperature distribution in an industrial-scale spray droplet under fast drying conditions: — centre moisture content; — bulk moisture content; — surface moisture content; — surface temperature. Note: the centre and bulk droplet temperatures lie beneath the surface temperature, i.e. there is no discernable temperature difference across the droplet.

In both cases, a significant moisture content gradient exists across the droplet. The slow drying case takes approximately 40 ms for the surface moisture content to dry to its equilibrium moisture content at the 50% relative humidity inside the coater. The fast drying droplet takes a meagre 1 ms to reach its equilibrium surface moisture content at 5% relative humidity in the coater. The bulk moisture content after 100 ms of drying time for the slow drying case is approximately four times that of the fast drying case. The vast difference in surface drying times affords the operator a significant degree of control over the drying time. From a final product point of view, the bulk moisture content required for industrial dairy powders must be around 4% w/w (total weight basis) or $u = (0.042 \text{ kg water}) \cdot (\text{kg}^{-1} \text{ dry solid})$. It took 29 and 0.8 s respectively to reach final moisture contents of 8.6 and 4% w/w total basis for the slow and high drying cases. It is clear that the slow drying case needs a post-drying operation under much lower relative humidity conditions to bring its final moisture content down to 4% w/w.

In both cases the droplet surface temperature almost instantaneously (0.34 and 0.08 ms for the slow and fast drying cases respectively) rises to the drying air temperature. The droplet temperature gradient is not significant which is consistent with the calculated maximum heat transfer Biot number of 0.13 which is one-third of the critical Biot number at which a significant temperature gradient will exist.

In the study of inkjet droplets (around 50 μm in diameter with a surface tension and viscosity close to that of 20% w/w maltodextrin DE5) the impact and spreading process ranged between 20 μs [Asai *et al.* (1993)] to 2500 μs [Holman *et al.* (2002)]. Hence, because they are of the same magnitude, it is still difficult to determine the extent of the effect of simultaneous drying on the impact and spreading process as suggested by Turton *et al.* (1999).

Figure 5.21 and Figure 5.22 show the droplet velocity and flight distance profiles respectively for the slow and fast drying scenarios.

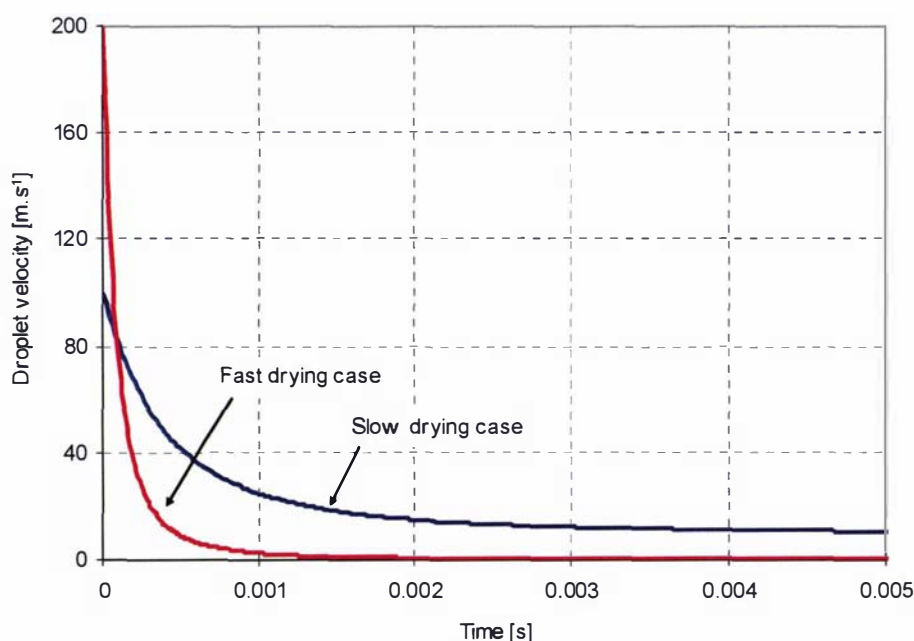


Figure 5.21: Droplet velocity profile for the slow and fast drying scenario cases: — slow drying case; — fast drying case.

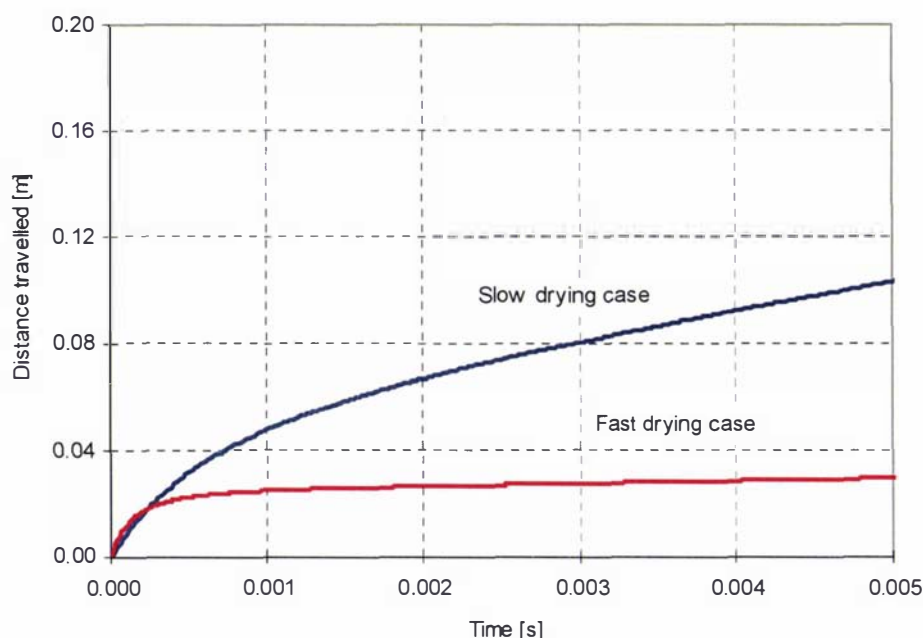


Figure 5.22: Droplet distance profile for the slow and fast drying scenario cases: — slow drying case; — fast drying case.

For the fast drying case, the droplet rapidly decelerates to the drying air velocity (1 m.s^{-1}) and dries at its terminal velocity of 0.002 m.s^{-1} . For the slow drying case, the droplet more slowly attains its terminal velocity (0.005 m.s^{-1}) because the drag is not as significant on this droplet during deceleration to the drying air velocity (10 m.s^{-1}). Despite leaving the atomiser at twice the initial droplet velocity of the slow drying case, the fast drying droplet only travels 30 mm compared to the 100 mm for the slow drying droplet (after 5 ms).

Both Adhikari (2002) and Farid (2003) predicted the drying kinetics of industrial sized ($120 \mu\text{m}$ diameter) spray droplets but without incorporating the droplet velocity prediction. These studies incorrectly used an assumed air velocity instead of a relative droplet–air velocity. It is clear that from the above findings, that droplet velocity is important with the slow and fast drying cases having accomplished 35% and 62% drying of their respective total bulk moisture content by the time the droplet velocity has slowed to its terminal velocity. This high level of evaporation during deceleration is consistent with that stated by Masters (1991).

Using the same critical X value approach, the predicted time the droplet surface remains deformable and sticky can be used to draw design and operating guidelines for coating in a Würster coater. Adhikari (2002) used a critical $X = (T - T_g) = 20 \text{ }^\circ\text{C}$ to draw conclusions on the ‘safe’ spray drying of sugar rich solutions. Above this critical X value, droplets were considered sticky. Aronson and Tsaur (1993) used the same concept to map successful coating in a Würster coater using latexes. Below a critical X value of $-10 \text{ }^\circ\text{C}$ the coatings were porous and cracked. Above a critical X value of $20 \text{ }^\circ\text{C}$ inter-particle agglomeration was prevalent. However, when the process temperature closely matched the T_g of the latex (i.e. critical $X \approx 0$) uniform coating with superior barrier properties resulted.

Figure 5.23 and Figure 5.24 show the droplet surface conditions, including the surface glass transition temperature, as a function of vertical distance in the coater Würster insert after atomisation for the slow and fast drying scenarios respectively.

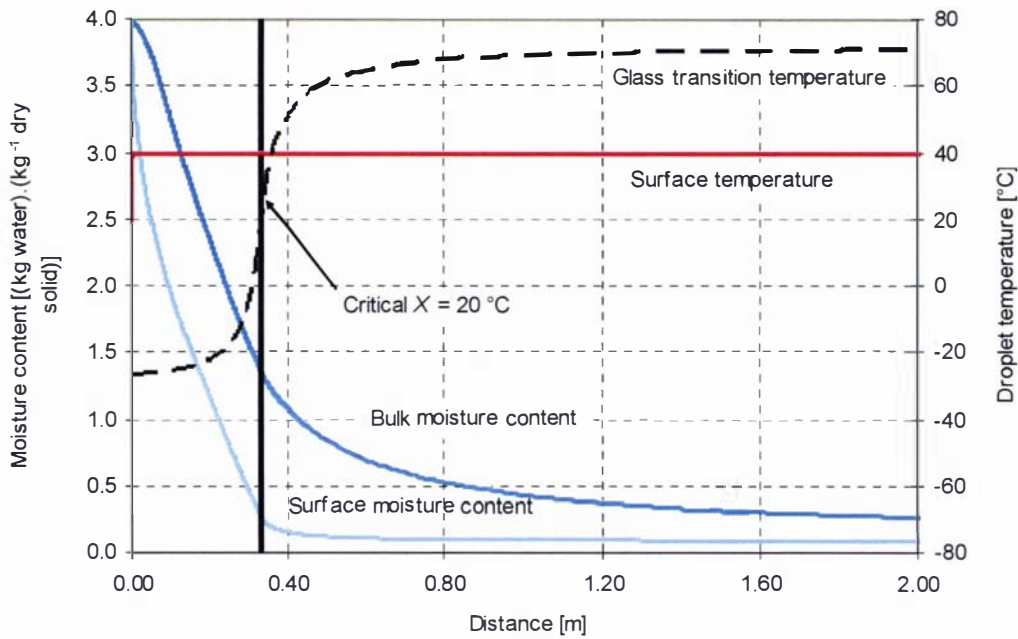


Figure 5.23: ‘Slow drying’ (Table 5.2) prediction of moisture content and temperature distribution in an industrial-scale spray droplet: — bulk moisture content; — surface moisture content; — surface temperature; — — predicted surface glass transition temperature; — distance at which the critical $X = (T - T_g) = 20\text{ °C}$.

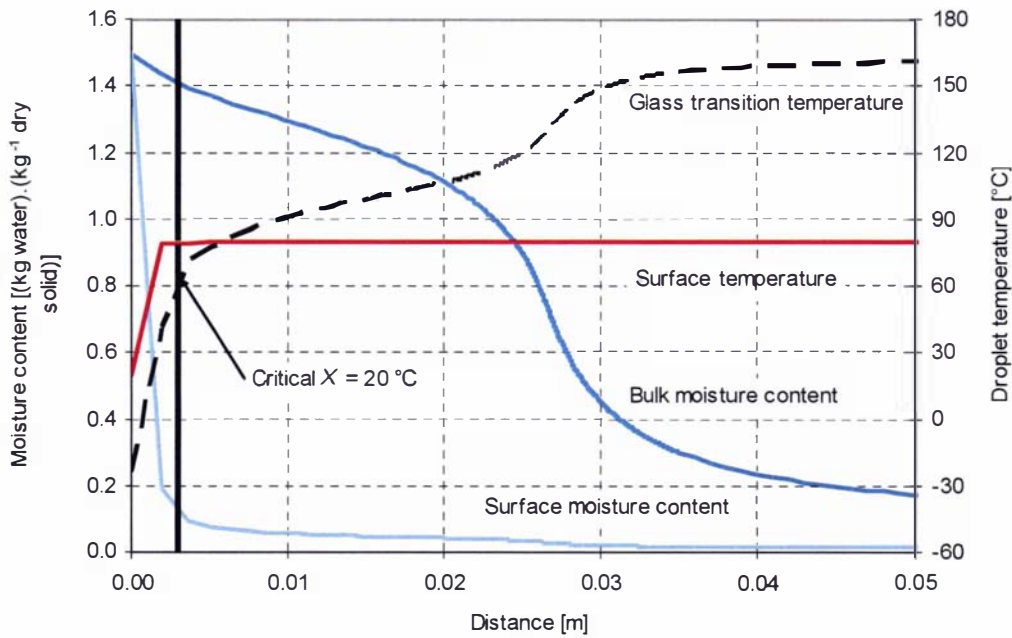


Figure 5.24: ‘Fast drying’ (Table 5.2) prediction of moisture content and temperature distribution in an industrial-scale spray droplet: — bulk moisture content; — surface moisture content; — surface temperature; — — predicted surface glass transition temperature; — distance at which the critical $X = (T - T_g) = 20\text{ °C}$.

The vertical black line in Figure 5.23 and Figure 5.24 represents the position of the droplet when its surface temperature reaches 20 °C above the surface glass transition temperature, i.e. critical $X = (T - T_g) = 20\text{ °C}$. Before this distance, the droplet is still assumed sticky and after this, the droplet is assumed dry and does not pose a risk of inter-particle agglomeration. Hence, the nozzle distance from the powder impact point, y_i , should be set to no further than

330 and 3 mm for the slow and fast drying cases respectively. Even with an additional safety factor by setting critical $X = 0$ °C (i.e. when the droplet surface temperature intersects the surface glass transition temperature), the Würster insert height, h_w , should be at least 367 and 7 mm for the slow and fast drying cases respectively, any higher and the capital costs rise. It is obvious that the coater would not be designed based on the fast drying condition. However, the span in design parameters showed that there is significant opportunity for design optimisation based on the critical X concept.

In summary, the critical X concept is useful for aiding the design and operation of a Würster coater. However, the point at which the droplet surface is no longer sticky is not known. Droplet stickiness during drying needs to be quantified and ideally related to the surface glass transition temperature to make better predictions for the optimisation of spray droplet stickiness during drying.

5.12 DRYING KINETICS OF MALTODEXTRINS DE5, DE10 AND DE18, WHEY PROTEIN ISOLATE AND GUM ARABIC

The trials employing maltodextrin DE5 showed both experimentally and by mathematical model predictions that the critical variables governing the drying process are initial solids concentration and drying air temperature once the drying process is internal diffusion controlled. A third variable not yet investigated is polymer type. It was expected that polymer type will also have a significant effect on the drying kinetics through its physico-chemical properties, particularly the binary moisture diffusion coefficient. The drying kinetics of the remaining potential coating materials being maltodextrin DE10, maltodextrin DE18, whey protein isolate and gum arabic were collected for the base case experimental conditions. Observations on their morphological development were also made.

The drying kinetics for maltodextrins DE5, DE10 and DE18, whey protein isolate and gum arabic at initial solids concentrations of 20 and 40% w/w and air temperatures of 40 and 78 °C are shown in Figure 5.25–Figure 5.28.

5.12.1 Drying kinetics at 20% w/w solids and 40 °C

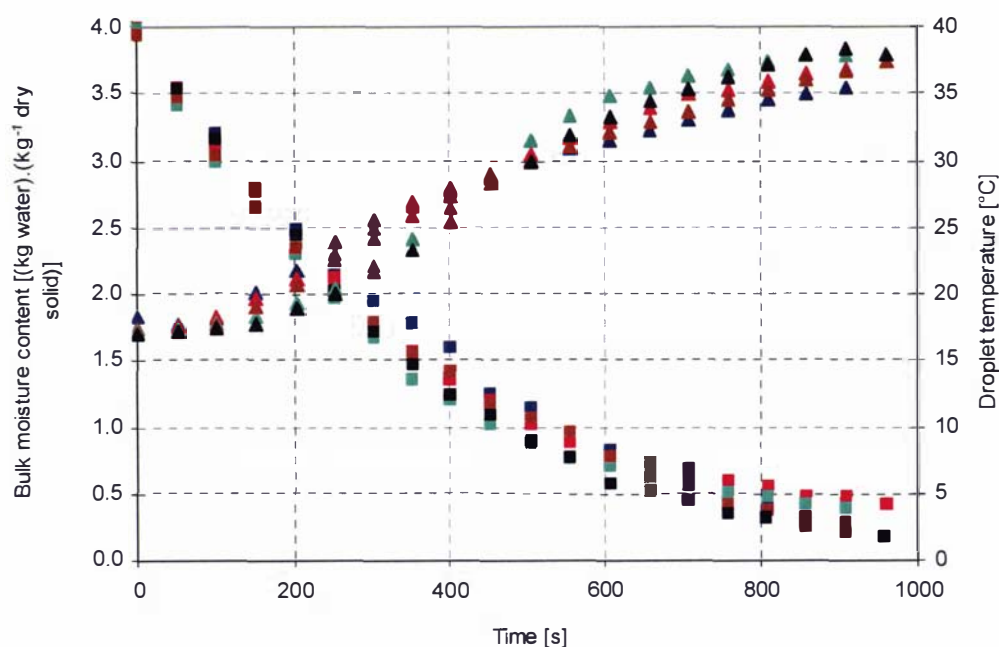


Figure 5.25: Effect of polymer type on the drying kinetics for 20% w/w initial solids concentration droplets drying at 40 °C. Moisture content histories: ■ maltodextrin DE5; ■ maltodextrin DE10; ■ maltodextrin DE18; ■ gum arabic; ■ whey protein isolate. Temperature histories: ▲ maltodextrin DE5; ▲ maltodextrin DE10; ▲ maltodextrin DE18; ▲ gum arabic; ▲ whey protein isolate.

A constant rate period was observed for all polymers up to about 100 s but otherwise the differences between the profiles were not large (Figure 5.25). It is difficult to draw conclusions on the effect of polymer type on the rate of drying because the moisture content profiles overlapped at different times, showing that they were more rapid over different periods during drying. This could have been due to the time-dependent morphological changes in the skin development, which are discussed later.

5.12.2 Drying kinetics at 20% w/w solids and 78 °C

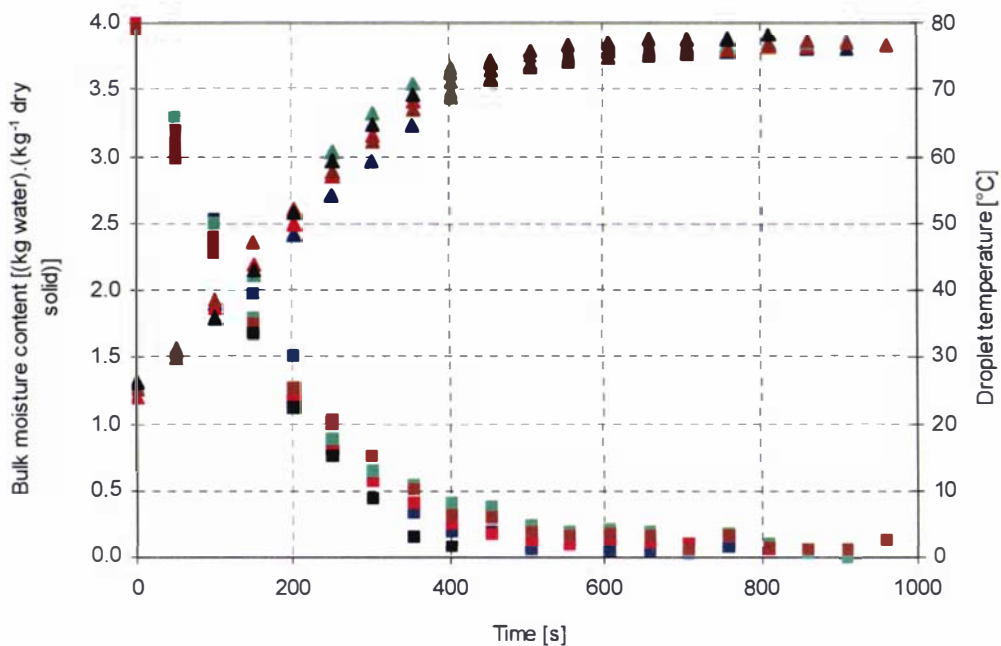


Figure 5.26: Effect of polymer type on the drying kinetics for 20% w/w initial solids concentration droplets drying at 78 °C. Moisture content histories: ■ maltodextrin DE5; ■ maltodextrin DE10; ■ maltodextrin DE18; ■ gum arabic; ■ whey protein isolate. Temperature histories: ▲ maltodextrin DE5; ▲ maltodextrin DE10; ▲ maltodextrin DE18; ▲ gum arabic; ▲ whey protein isolate.

The constant rate period had almost disappeared entirely when the air temperature was increased to 78 °C (Figure 5.26). The whey protein isolate droplet reached a bulk moisture content of zero at 400 s; however, at this point, the droplet underwent a fatal fracture and fell off the filament. In all cases, the final moisture content for the 20% w/w initial solids concentration droplets was lower at the drying air temperature of 78 °C than at the drying air temperature of 40 °C. Again, it is difficult to draw comparisons between the polymers given that the solute represented only 20% of the initial droplet weight.

5.12.3 Drying kinetics at 40% w/w solids and 40 °C

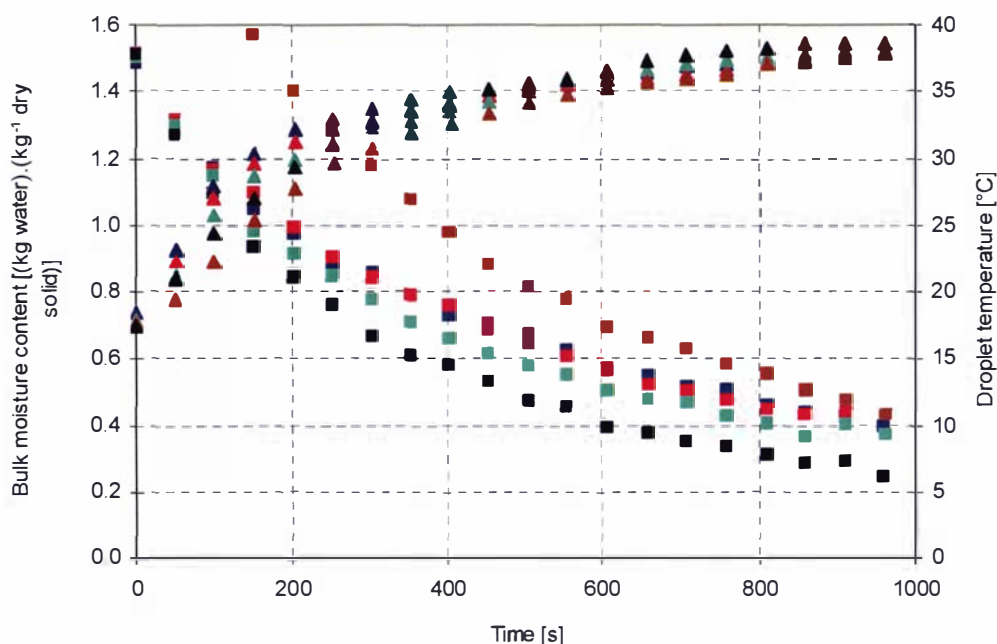


Figure 5.27: Effect of polymer type on the drying kinetics for 40% w/w initial solids concentration (30% w/w for gum arabic) droplets drying at 40 °C. Moisture content histories: ■ maltodextrin DE5; ■ maltodextrin DE10; ■ maltodextrin DE18; ■ gum arabic; ■ whey protein isolate. Temperature histories: ▲ maltodextrin DE5; ▲ maltodextrin DE10; ▲ maltodextrin DE18; ▲ gum arabic; ▲ whey protein isolate.

The drying rate was approximately 3 times slower when the initial solids concentration was 40% w/w (Figure 5.27) compared with 20% w/w (Figure 5.25). There was little difference between the drying kinetics of the maltodextrins DE5 and DE10, but maltodextrin DE18 dried more rapidly. Whey protein isolate dried the most rapidly of all the polymers, but again was brittle in nature. Although still appearing to be soluble at 40% w/w (even 50% w/w) initial solids concentration, the gum arabic solution was too viscous to be syringed and transferred to the glass filament for drying. As a result, the solution was diluted to 30% w/w solids for investigation. Because of the high viscosity, the incorporation of a small amount of air bubbles could not be avoided.

Although not shown here, a 40% w/w initial solids concentration droplet containing both maltodextrin DE5 and whey protein isolate at a 1:1 ratio was also trialled. The drying kinetics were found to lie between those for the pure components.

5.12.4 Drying kinetics at 40% w/w solids and 78 °C

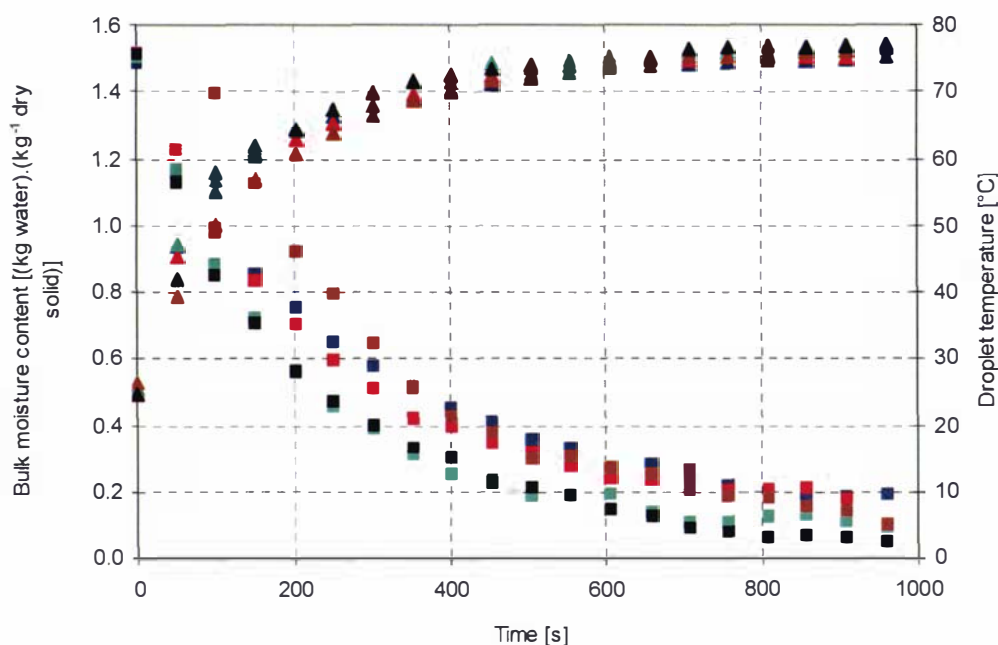


Figure 5.28: Effect of polymer type on the drying kinetics for 40% w/w initial solids concentration (30% w/w for gum arabic) droplets drying at 78 °C. Moisture content histories: ■ maltodextrin DE5; ■ maltodextrin DE10; ■ maltodextrin DE18; ■ gum arabic; ■ whey protein isolate. Temperature histories: ▲ maltodextrin DE5; ▲ maltodextrin DE10; ▲ maltodextrin DE18; ▲ gum arabic; ▲ whey protein isolate.

Drying was faster at 78 °C (Figure 5.28) than at 40 °C (Figure 5.27), but was slower for the 40% w/w droplets than for the 20% w/w droplets (Figure 5.26). The gum arabic moisture content history merged much earlier with the maltodextrin DE5 moisture content history at this higher temperature (350 s compared with 950 s at 40 °C). Also, under these conditions, maltodextrin DE18 dried as rapidly as whey protein isolate.

5.12.5 Conclusions

Because the polymers selected for this study were chosen for their skin-forming ability (therefore they had relatively high molecular weights), the differences in drying kinetics were not as marked as for the polymers compared by Adhikari (2002) (fructose, glucose, sucrose, citric acid and maltodextrin DE6), which showed decreasing moisture diffusivity with increasing molecular weight of the material.

Under all the conditions investigated, there was little difference in the drying kinetics of the maltodextrins DE5 and DE10. This was expected, given that both polymers are likely to have similar diffusion coefficients (for dilute solutions at 30 °C) based on the findings of Adhikari (2002) that maltodextrins DE6 and DE11 were similar being 2.2 and $2.6 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ respectively. Their moisture sorption isotherms and glass transition temperature profiles are also not significantly different (refer to Figure 4.3 and Figure 4.6 respectively). Maltodextrin DE18 dried more rapidly than the other two maltodextrins, which is consistent with its higher solubility and lower average molecular weight, leading to skin formation at a later stage in the drying process.

Although the binary moisture diffusion coefficient data for whey protein isolate were not measured, it is likely that the very dry, brittle crusts, which showed signs of large fractures, allowed increased moisture transfer (refer to Figure 5.33(p–t)). In contrast, the gum arabic skins, although wrinkled, were strong and showed no signs of fracture (refer to Figure 5.33(z–dd)). This is consistent with the SEM studies by Rosenberg *et al.* (1985) and Rosenberg *et al.* (1990) (Section 4.2.4), and the fact that gum arabic is used as a spray drying microencapsulating wall material and is considered to be the standard of excellence in retaining volatile flavour compounds.

5.13 PLASTICISATION OF MALTODEXTRIN DE5 AND WHEY PROTEIN ISOLATE

For good product storage stability (primarily caking), maltodextrin DE5 and whey protein isolate are the preferred coating materials because of their low moisture sorption isotherms and relatively high glass transition temperatures. However, in most cases, once dried, these two materials produced droplets that were brittle in agreement with observations made by Rosenberg *et al.* (1985) and Gennadios *et al.* (1994). Incorporation of a plasticiser should reduce the rigidity of the amorphous skin as it forms, and can therefore be used to reduce brittleness. The incorporation of a plasticiser is also of interest as it can be used to help tailor the performance of a coating material in a final application, e.g. its active release profile. Plasticisers are usually low molecular weight solids, and hence can be used to increase the solids content without sacrificing a significant viscosity increase or alternatively, as pointed out in Section 3.8, lower viscosities can lead to increased spreading rates. The effects of plasticiser addition on the drying kinetics are therefore of interest.

To determine if there was a significant plasticisation effect, two plasticisers were selected (glycerol and maltodextrin DE18) and used at a single concentration ratio of 3:1 (polymer:plasticiser). Glycerol is a commonly used plasticiser in the food industry and data exist on its effect on the drying of various materials [Yamamoto (1999); Shaw *et al.* (2002)]. Maltodextrin DE18 was selected because of its low glass transition temperature and the fact that it has a DE below 20, which means that it is still considered to be a maltodextrin (and not a corn syrup solid). This is desirable when combined with maltodextrin DE5, because one less ingredient needs to be declared on the packaging label.

5.13.1 Maltodextrin DE5 plasticisation

Figure 5.29 shows the droplet drying kinetics of the maltodextrin DE5 plasticisation trials for droplets at a 20% w/w initial solids concentration and drying air temperatures of 40 and 78 °C.

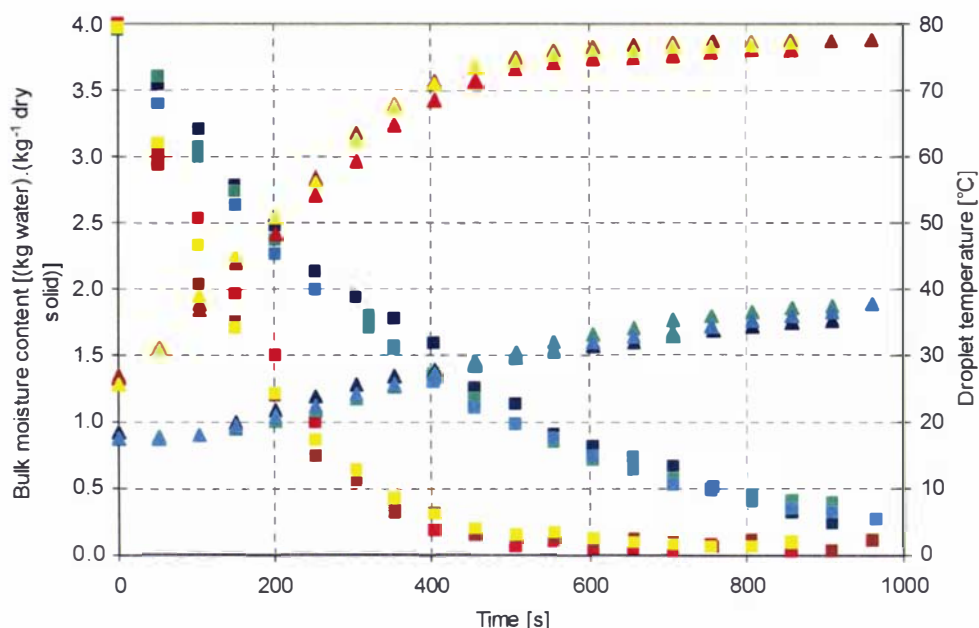


Figure 5.29: Effect of plasticisation with glycerol and maltodextrin DE18 on maltodextrin DE5 droplet drying kinetics at the 20% w/w initial solids concentration. Moisture content histories: ■ 20% w/w DE5 at 40 °C; ■ 20% w/w DE5 at 78 °C; ■ 20% w/w (3:1) DE5:glycerol at 40 °C; ■ 20% w/w (3:1) DE5:glycerol at 78 °C; ■ 20% w/w (3:1) DE5:DE18; ■ 20% w/w (3:1) DE5:DE18 at 78 °C. **Temperature histories:** ▲ 20% w/w DE5 at 40 °C; ▲ 20% w/w DE5 at 78 °C; ▲ 20% w/w (3:1) DE5:glycerol at 40 °C; ▲ 20% w/w (3:1) DE5:glycerol at 78 °C; ▲ 20% w/w (3:1) DE5:DE18; ▲ 20% w/w (3:1) DE5:DE18 at 78 °C.

Figure 5.29 shows that the effect of plasticiser addition on the drying rate, regardless of the plasticiser type, was minimal at either temperature for the 20% w/w initial solids concentration. However, inspection of the droplet surface character (finger and thumb test) showed that plasticisation of the surface may have occurred. Droplets containing only maltodextrin DE5 produced a dry, brittle and non-sticky surface at both temperatures. All the plasticisation trials produced relatively strong droplets and, although almost completely dry, their surfaces were a little bit tacky.

Figure 5.30 shows the droplet drying kinetics of the maltodextrin DE5 plasticised trials at a 40% w/w initial solids concentration at 40 and 78 °C.

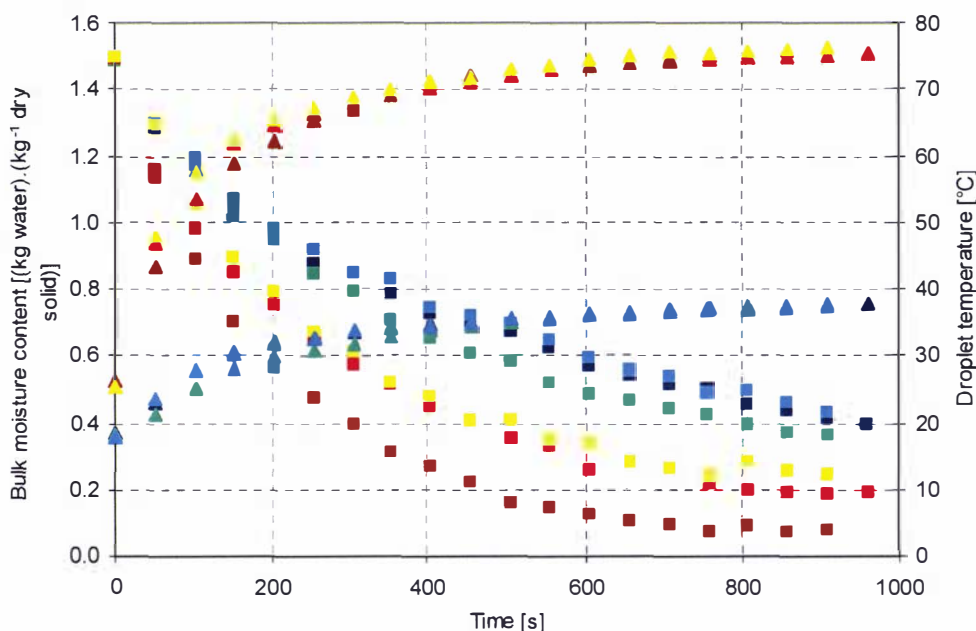


Figure 5.30: Effect of plasticisation with glycerol and maltodextrin DE18 on maltodextrin DE5 droplet drying kinetics at the 40% w/w initial solids concentration. Moisture content histories: ■ 40% w/w DE5 at 40 °C; ■ 40% w/w DE5 at 78 °C; ■ 40% w/w (3:1) DE5:glycerol at 40 °C; ■ 40% w/w (3:1) DE5:glycerol at 78 °C; ■ 40% w/w (3:1) DE5:DE18; ■ 40% w/w (3:1) DE5:DE18 at 78 °C. **Temperature histories:** ▲ 40% w/w DE5 at 40 °C; ▲ 40% w/w DE5 at 78 °C; ▲ 40% w/w (3:1) DE5:glycerol at 40 °C; ▲ 40% w/w (3:1) DE5:glycerol at 78 °C; ▲ 40% w/w (3:1) DE5:DE18; ▲ 40% w/w (3:1) DE5:DE18 at 78 °C.

Again there was little difference in the drying rate between maltodextrin DE5 alone at both air temperatures and that of maltodextrin DE5 plasticised with maltodextrin DE18. However, the addition of glycerol as a plasticiser substantially increased the drying rate, particularly at 78 °C. The reason is because glycerol (99.5% minimum assay, boiling point range 288–292 °C) is a liquid at room temperature and is not able to form a skin like maltodextrin DE18. This means greater permeability to moisture through a maltodextrin DE5–glycerol plasticised skin compared to a maltodextrin DE5–maltodextrin DE18 plasticised skin.

5.13.2 Whey protein isolate plasticisation

Whey protein isolate produced brittle droplets so some degree of plasticisation was warranted. The effect of plasticiser type on the drying kinetics was minimal at the 20% w/w initial solids concentration for the maltodextrin DE5 plasticisation trials, so only the 40% w/w initial solids concentration was investigated for whey protein isolate plasticised with either glycerol or maltodextrin DE18.

Figure 5.31 shows the droplet drying kinetics of the whey protein isolate plasticisation trials for droplets at a 40% w/w initial solids concentration and drying air temperatures of 40 and 78 °C.

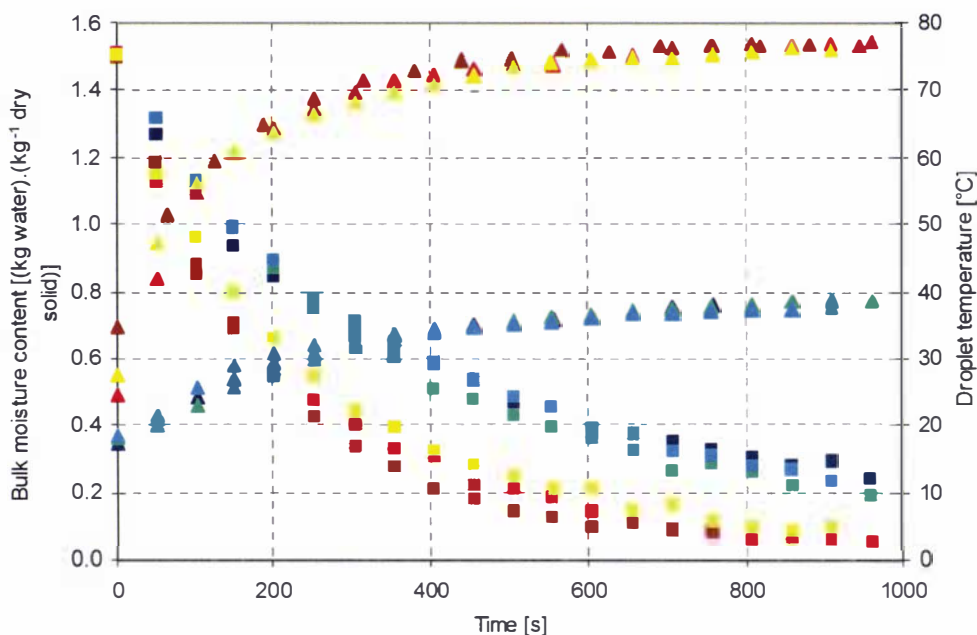


Figure 5.31: Effect of plasticisation with glycerol and maltodextrin DE18 on whey protein isolate droplet drying kinetics at the 40% w/w initial solids concentration. Moisture content histories: ■ 40% w/w WPI at 40 °C; ■ 40% w/w WPI at 78 °C; ■ 40% w/w (3:1) WPI:glycerol at 40 °C; ■ 40% w/w (3:1) WPI:glycerol at 78 °C; ■ 40% w/w (3:1) WPI:DE18; ■ 40% w/w (3:1) WPI:DE18 at 78 °C. **Temperature histories:** ▲ 40% w/w WPI at 40 °C; ▲ 40% w/w WPI at 78 °C; ▲ 40% w/w (3:1) WPI:glycerol at 40 °C; ▲ 40% w/w (3:1) WPI:glycerol at 78 °C; ▲ 40% w/w (3:1) WPI:DE18; ▲ 40% w/w (3:1) WPI:DE18 at 78 °C.

At 40 °C the drying kinetics were not affected by the addition of either plasticiser to whey protein isolate. At 78 °C maltodextrin DE18 addition decreased the initial evaporation rate slightly, which may be explained because plasticisation eliminated cracks and fissures, which can serve as a source for preferential moisture transport and a subsequent increased evaporation rate. Alternatively, maltodextrin DE18 may form its own rate-limiting skin at the surface. Glycerol, being a liquid, was able to plasticise the surface but because diffusion is faster through a liquid than a solid, it did not provide as effective a moisture barrier as maltodextrin DE18; consequently it showed an increased evaporation rate. The addition of glycerol at the drying air temperature of 78 °C did not increase the evaporation rate to the same extent for whey protein isolate as it did for maltodextrin DE5. This is explained by the more glassy and brittle nature of the whey protein isolate droplet surface (refer to Figure 5.33).

5.13.3 Conclusions

From a final microencapsulated or coated product point of view, some degree of plasticisation is recommended so that coatings are less brittle and therefore will not disintegrate during handling or allow an unhindered transport path for volatile compounds out of the particle matrix and oxygen into the particle matrix. The ratio of polymer to plasticiser as well as the plasticiser type will affect the drying rate. In particular, the polymer type should be carefully considered. Maltodextrin DE18 has a lower molecular mass and glass transition temperature than both maltodextrin DE5 and whey protein isolate and is able in principle to plasticise the surface, although this was not directly measured. With increased plasticisation comes increased permeability to mass transfer. However, this could also reduce mass transfer during drying if the plasticiser reduces skin cracking to limit preferential and hence increased

moisture transfer. Additionally, maltodextrin DE18 also forms a skin but this occurs later in the drying process than for the DE5 and DE10 maltodextrins. Hence, in the early stages of skin formation, maltodextrin DE18 can act to relieve the stresses during skin formation and then seal mass transfer later in the drying process. Glycerol is not able to do this because it is a liquid at room temperature.

5.14 MORPHOLOGICAL DEVELOPMENT

During the course of a drying experiment, marked changes in the surface character, particularly surface wrinkling and surface stickiness (thumb and finger), were observed, which were coupled to surface skin formation. Figure 5.32 presents images of selected droplets as they dried for comparison of their morphological development.

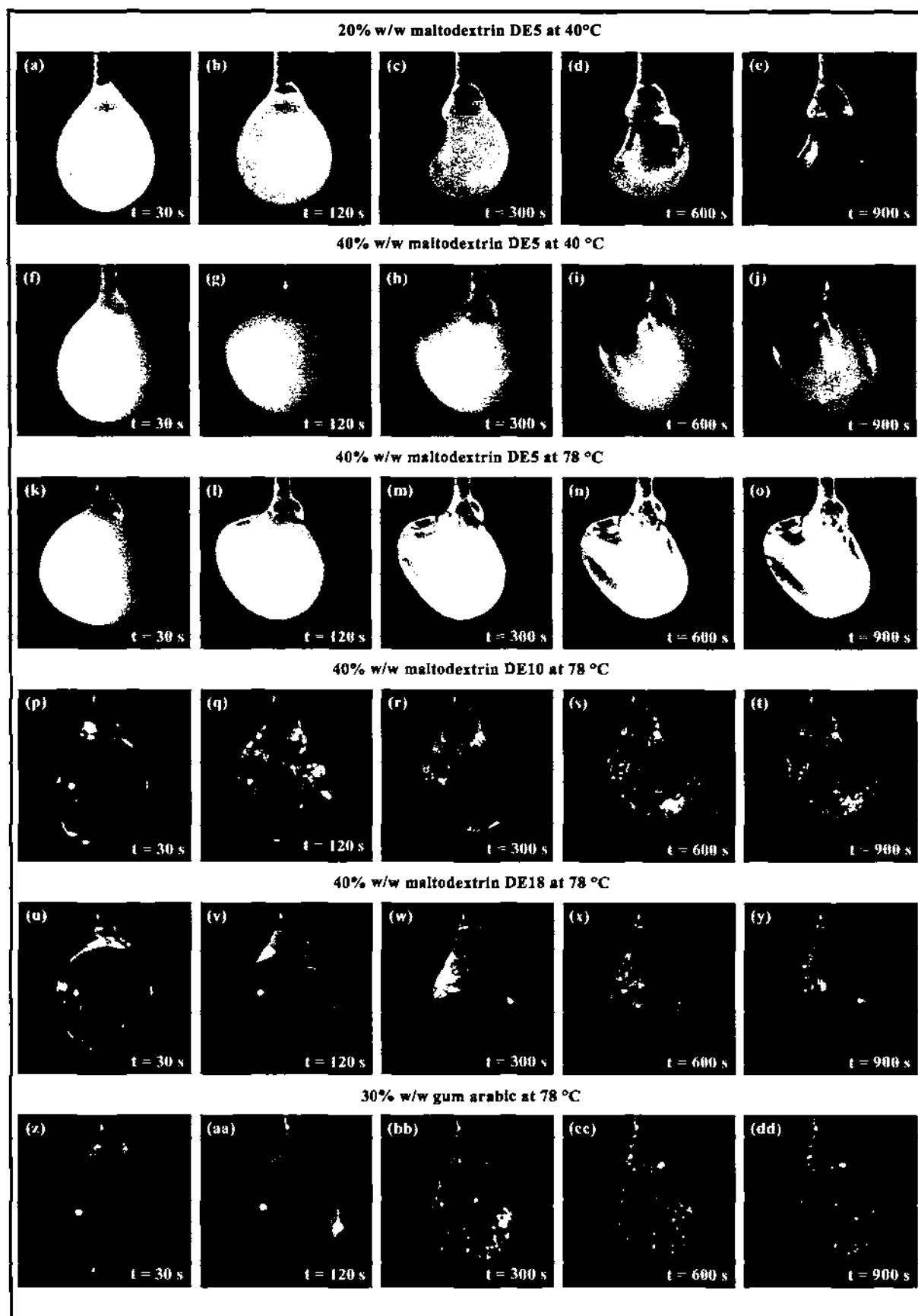


Figure 5.32: Morphological development in selected drying droplets. The drying air velocity was 0.30 m.s^{-1} . The drying air impinged the right-hand side of the images and flowed around the droplet. Note: the glass filament has an approximate diameter of 0.2 mm.

From the morphological observations and inspection of the samples after 15 min of drying time, it was clear that the droplets (especially at high initial solids concentration and air temperature) formed a skin almost immediately, and that the thickness grew inwards towards the liquid core of the evaporating droplet. The majority of the 40% w/w initial solids concentration droplets still retained a viscous solution at the centre after 15 min drying time, whereas the centres of the 20% w/w initial solids concentration droplets were almost completely dry. Inspection of the whey protein isolate droplets showed a dense surface skin–porous crumb structure (which broke easily between finger and thumb) which is in agreement with the two layer droplet structure described by Achanta and Okos (1995) and Hassan and Mumford (1996). Gum arabic on the other hand, produced dense and strong droplet skins that were difficult to remove from the filament.

There was little morphological difference between the 20 and 40% w/w maltodextrin DE5 initial solids concentration droplets at the drying air temperature of 40 °C (Figure 5.32(a–e) and Figure 5.32(f–j) respectively). However, when the drying air temperature was raised to 78 °C for the 40% w/w initial solids concentration droplets, the skin became very dry, warped and brittle. At 40% w/w initial solids concentration and 78 °C, the maltodextrin DE10 and DE18 droplets also showed signs of extreme warping and wrinkling. The wrinkles could substantially increase the droplet surface area, and decrease the distance for moisture diffusion, both leading to increasing evaporation rates. Alternatively, these wrinkles could cause stress fractures, allowing preferential moisture transfer to the surface, giving a mass loss that would be a mixture of drying kinetics driven by constant rate evaporation and internal moisture diffusion. However, in general, the higher DE maltodextrin droplets were less brittle than the maltodextrin DE5 droplets.

In industrial coating, it is imperative for product storage stability, that the coatings are dried to very low moisture contents. Currently spray-dried dairy powders are dried to moisture levels of 3–4% w/w [D. L. Pearce, Fonterra Palmerston North, personal communication, 19 March, 2004]. For coated products, the low moisture diffusivity could have implications in terms of the final coated product. While the coated product may not feel moist or sticky to touch, it may have a high moisture content layer just beneath the surface of the coating if it is not dried for long enough. This trapped moisture could present problems during storage if it migrates through the coating in either direction (air–coating surface or coating–powder surface) and have detrimental affects, such as sticking, caking and deleterious chemical reactions.

The materials showed varying degrees of stickiness as they dried. Recently, Adhikari (2002) used a probe tack test to assess the stickiness of model fruit juice droplets as they dried, noting that the skin-forming nature of maltodextrin DE6 was responsible for the reduction in surface stickiness. A reduction in the surface stickiness as a result of skin formation is desirable for the coated substrate because inter-particle agglomeration can occur readily in a Würster coater, resulting in out-of-specification product and process shut-down. In contrast, the formation of a skin on spray droplets may prevent them from adhering to the substrate on impact, resulting in decreased process efficiency (e.g. increased raw material costs and processing time). From a stickiness viewpoint, there will be a trade-off between optimising the droplet surface moisture content (and stickiness) for good droplet–substrate adherence and limiting subsequent inter-particle agglomeration.

The appearance of a skin has also been noted to aid volatile (flavour and aroma) retention during drying [Kerkhof and Thijssen (1974); Bangs and Reineccius (1981); Furuta *et al.* (1984); Reineccius (1991)]. The ‘selective diffusion’ theory presented by Brooks (1965) and Rulkens and Thijssen (1972) indicates that losses of volatile compounds occur until sufficient

water is lost from the surface to enable skin formation. This represents a significant opportunity for the production of high intensity flavoured powders, because the volatile flavour compounds can be incorporated in the coating formulation during application to the powder. A coating operation would be run at much lower air temperatures than a spray drier, hence the volatilisation of these high value compounds will not be as severe as if they were incorporated into the spray drying formulation. Currently, a large excess of volatile flavouring is required in the spray drying formulation to account for volatile flavour losses during the spray drying production of high intensity flavoured powders. For example, the wet formulation concentration of acetic acid is at least twice that actually retained in the final dry powder [R. H. Archer, Massey University, personal communication, 17 March, 2004].

The skin forming nature of the maltodextrins may also explain the differences between the retention of volatile compounds and barrier protection observed in the spray drying microencapsulation literature (as discussed in the Section 4.2.3). Consistent with the 'selective diffusion' theory and the observations in this study, skins forming earlier in the drying process for lower DE maltodextrins (and higher initial solids concentrations and air temperatures) would supposedly 'lock in' the volatile compounds, but it was seen in this study that the skins cracked towards the end of the drying process. Hence, when these same powders are subjected to storage studies, the volatile compounds leach more rapidly over time, as found by Anandaraman and Reineccius (1986) and Reineccius (1991). Higher DE maltodextrins are not as good at retaining volatile compounds, but they do not contain as many imperfections after drying and are less likely to crack. Therefore, the overall diffusion rate is likely to be dominated by morphological effects rather than binary moisture diffusion coefficient effects.

It is clear that the droplet drying kinetics and the associated skin-forming behaviour are important to the retention of volatile compounds during drying, to the stickiness potential during a coating operation and ultimately to the economics of drying and coating. Skin formation and stickiness is the focus of the following chapter.

Figure 5.33 presents images of the droplets as they dried, for comparison of morphological development for the plasticisation trials, in which maltodextrin DE5 and whey protein isolate were each plasticised with glycerol and maltodextrin DE18.

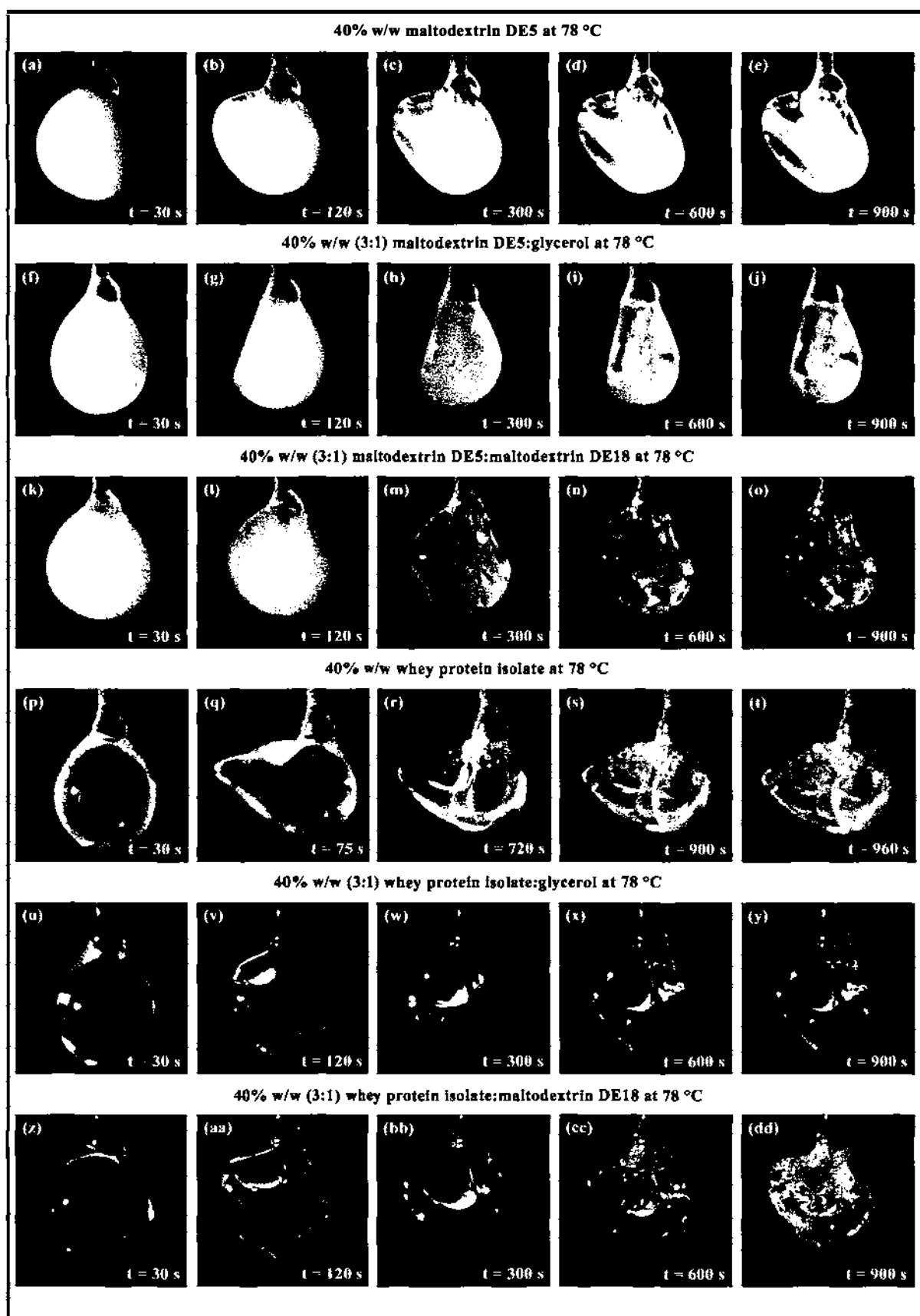


Figure 5.33: Morphological development in selected drying droplets from the plasticisation trials. The drying air velocity was 0.30 m.s^{-1} . The drying air impinged the right-hand side of the images and flowed around the droplet. Note: the glass filament has an approximate diameter of 0.2 mm.

The most notable morphological feature in Figure 5.33 is the appearance of a protrusion on the leeward side of the drying whey protein isolate droplets, particularly the 40% w/w initial solids concentration droplets at 78 °C (Figure 5.33(p–t)). This resulted from uneven drying because the air impinged the droplet from one side which is a well noted limitation of the technique (Section 5.5). Cheong *et al.* (1986) stated that a crust commences forming from a preferential site, usually the point of maximum mass transfer and spreads around the droplet. As the droplet sheltered its leeward side from the drying air, this would explain this prominent feature. When cracks began to appear in the whey protein isolate droplets, they would propagate rapidly (usually within 90 s), resulting in complete fracture and subsequent falling from the filament. In the majority of cases, the higher temperatures produced more severely distorted droplets.

Addition of glycerol as a plasticiser reduced the wrinkling and the appearance of cracks in both the maltodextrin DE5 droplets and the whey protein isolate droplets at the 40% w/w initial solids concentration and 78 °C. However, maltodextrin DE18 did not produce the same effect; cracks and fissures were still apparent but slightly reduced in severity. In both cases, the incorporation of a plasticiser increased the stickiness of the droplet surface.

In summary, plasticisers are an important formulation ingredient to reduce cracking of the surface film that forms during the drying of high molecular weight solutions. However, their use results in a qualitative increase in surface stickiness. This leads to the need for further studies into the development of surface stickiness, not only for the successful adherence of droplets and powder particles in secondary coating but also for subsequent inter-particle agglomeration, which may or may not be desirable depending on the application.

5.15 CONCLUSIONS AND RECOMMENDATIONS

The drying kinetics were collected for maltodextrins DE5, DE10 and DE18, whey protein isolate and gum arabic on a single droplet drying apparatus. The following useful guidelines were established to optimise formulation and operating conditions to control droplet drying:

- The two key variables for controlling droplet drying were the droplet initial solids concentration and the drying air temperature. Skin formation was rapid at higher initial solids concentrations and at higher air temperatures. The use of higher initial solids content sprays will result in a longer required time to dry the droplets.
- Operating at higher air temperatures did not increase the drying rate substantially. Only a slight increase in the drying rate resulted from the dependence of the binary moisture diffusion coefficient on temperature.
- Increasing the air velocity after a skin has formed did not increase the drying rate (via an increased external mass transfer) substantially. This would only serve to raise the droplet temperature (marginally) through increased heat transfer.
- Significant morphological changes in the droplet surface occur during skin development. The drying kinetics of the different materials were not markedly different when the droplets were dried at the same initial solids concentration or air temperature. This was attributed to the rapid skin-forming nature of the materials investigated and the subsequent internal mass transfer limitation that the skin imposed on the drying process. The majority of the difference in the evaporation rates is likely to be because of the different morphological character of the materials.
- Plasticisation was required for maltodextrin DE5 and whey protein isolate materials because these formed brittle skins. In most circumstances, an increase in drying rate was

observed upon plasticiser addition. It was also noted that surface plasticisation led to a qualitative increase in the surface stickiness of the droplets.

A mathematical model was selected and developed (Appendix A2) to predict the droplet drying kinetics. The model successfully predicted the drying kinetics of maltodextrin DE5 under various drying conditions. However, late in the drying process when skin morphological development becomes significant the model under-predicted the evaporation rate. To account for the increased surface area resulting from the skin arresting the droplet radius contraction, a critical surface condition (when the critical $X = (T - T_g) = 20\text{ }^{\circ}\text{C}$) was used to fix the droplet radius during the simulations. This resulted in much more accurate predictions late in the drying process. Two new calculation schemes were proposed; one, to deliver a 'dense skin-porous crumb' structure which has been observed in the literature; and two, to deliver a 'collapsed shell' structure which accounts for the severe warping also observed in the literature. These models represent extremes, so expected behaviour is somewhere in between. The model was used to draw conclusions on the design and operation of an industrial-scale Würster coater using the critical X concept and, its relationship to observed stickiness, to set critical distances to ensure successful droplet adherence during impact with the substrate particle and prevent inter-particle agglomeration.

CHAPTER 6

DEVELOPMENT OF DROPLET STICKINESS DURING DRYING

6.1 INTRODUCTION

Examination of the drying droplets in Chapter 5 showed marked differences in morphological character, particularly skin formation and associated 'stickiness' (observed by thumb and finger tests). Adhikari (2002) noted that the skin-forming nature of maltodextrin DE6 was responsible for the reduction in surface stickiness. A reduction in the surface stickiness as a result of skin formation is desirable for the coated substrate because inter-particle agglomeration can occur readily in a Würster coater, resulting in out-of-specification product and process shut-down. In contrast, the formation of a skin on spray droplets may prevent them from adhering to the substrate on impact, resulting in decreased process efficiency.

Although the evaluation of the tack properties of coating formulations is essential for solving some of the processing problems during film coating, only a limited amount of study in this area has been reported [Chopera and Tawashi (1982, 1984, 1985); Wan and Lai (1992a,b)]. In particular, little is known of the relationship between the tackiness of the coating formulation and process performance [Wan and Lai (1992b)]. In addition, according to Russo (1984) and Mehta (1988) [both cited in Wan and Lai (1992b)], coating tackiness is often the rate-limiting factor in coating small particles.

This chapter reviews skin formation and stickiness mechanisms and identifies an appropriate test method to characterise stickiness development during drying. Using the test method, the effects of formulation and drying variables are investigated.

6.2 SKIN FORMATION

The appearance of skin formation or crusts has been observed by numerous researchers [Achanta and Okos (1995); Räderer (2001)] during the drying of solute containing droplets and was observed in every trial conducted in the single droplet drying study. There is no conformity in the nature and time of skin formation among skin forming materials [Adhikari (2002)] because skin formation depends on the nature of the material and drying conditions [Hassan and Mumford (1996)]. This section of the chapter reviews skin formation and mechanisms.

6.2.1 Skin formation mechanisms

Hassan and Mumford (1993a,b,c) and Hassan and Mumford (1996) comprehensively studied skin and crust forming materials during drying and classified them into three categories:

- Type I – forms a skin due to granule swelling or gelatinisation at high temperatures. At low temperatures no skin formation is observed and a normal porous crust develops. Typical of suspensions of starch or custard.
- Type II – regardless of drying conditions a skin forms immediately unless the solids concentration is too low. Typical of gelatine and gum arabic.
- Type III – the skin appears at a certain stage of the drying process under any conditions. Typical of skim milk and sucrose.

Kim *et al.* (2003) identified 3 different scenarios about the surface formation on a spray-dried droplet. The first scenario, first suggested by Charlesworth and Marshall Jr (1960), is where surface skin or crust formation occurs because the rate of moisture transfer to the surface of the drying droplet becomes too slow to maintain saturated boundary layer conditions. The viscosity increases such that the solution near the surface becomes supersaturated and precipitates into a solid phase which immobilizes the droplet surface to become a moisture diffusion barrier. This would suggest that low solubility substances with low moisture diffusivities in their solid state will dominate the surface material.

The second scenario, suggested by Meerdink (1993), is where component segregation occurs due to surface evaporation, component concentration and a range of solute diffusivities in multicomponent droplet mixtures. The surface is expected to contain the component with the smallest diffusion coefficient.

The third scenario was suggested by Fäldt (1995) [as cited in Kim *et al.* (2003)]. Surface active components such as proteins adsorb preferentially to the air–liquid interface during atomisation and remain there during drying.

Using electron spectroscopy for chemical analysis (ESCA), Kim *et al.* (2003) concluded that a layer of milkfat followed by subsequent layers of protein (whey and casein proteins) and then carbohydrate (lactose) was found to exist at the surface of industrial spray-dried skim and whole milk powders. This initially suggests that the surface forms predominantly by the third, or solute segregation scenario for spray-dried dairy powders, but possibly a combination of all three.

In this work, a fourth scenario causes skin formation where as drying proceeds the viscosity increases rapidly and an amorphous structure forms. Adhikari (2002), in similar work, argues that this is consistent with glass transition theory in which a rubbery–glassy transition occurs and the surface of the droplet turns glassy while the core remains rubbery, leading to skin formation. This is supported by observation; most of the drying trials conducted in this chapter resulted in a dry skin and moist core.

6.2.2 Controlling skin formation

According to Achanta and Okos (1995), the thickness of the skin/crust that forms is a function of the drying process conditions and a material (single solute/solvent system), which is initially homogenous and dried rapidly, is transformed to a composite material with two layers, a dense skin and a porous crumb. The faster the drying rate, the thinner the crust. This phenomenon was well observed with whey protein isolate in the single droplet drying trials (Chapter 5), which showed a brittle morphology (especially the 20% w/w, 78 °C case). In contrast, drying above the glass transition temperature (explained later) will result in a product with a thick crust [Achanta and Okos (1995)]. Hence, crust formation may be

inhibited by operating under mild conditions that employ low air velocities, low drying air temperatures and high relative humidities.

Surface morphological changes are difficult to account for in a mathematical model because the mathematics behind these surface modifications such as folding, wrinkling and fissures is complex and to date has not been modelled. Achanta and Okos (1995) conclude that more research is required to develop a crust thickness predictor and to understand stress development and breakage during drying.

6.2.3 Conclusions

It is clear there is a complex interplay between the rate of drying and the thickness and appearance of the crust that forms. Whilst there is a definite link between skin formation and surface stickiness [Adhikari (2002)], knowledge of attributes such as skin formation time and thickness does not, however, give any information on the point at which it becomes sticky, for how long it remains sticky, nor how stickiness varies with time. As a result, stickiness was reviewed below.

6.3 STICKINESS

6.3.1 Defining stickiness

The definition of tack or stickiness is not yet standardised and tack has different meanings in different industries [Wan and Lai (1992a)]. This is because tack is not a fundamental physical property such as elastic modulus, viscosity or surface tension, and is likely to be a composite function of these material parameters, if not more [Wan and Lai (1992a)]. As early as 1941, Green (1941) defined tack as a pull resistance exerted by a film adhering between two surfaces that are separating at a definite rate with a known area of contact and a known initial film thickness. Tack was stated to be a function of the material adhesive, cohesive, surface tension, viscosity and yield value properties and the instrument measuring tack itself.

Tack and stickiness are used interchangeably in the literature. In adhesion science, stickiness, termed 'pressure-sensitive adhesion' or 'tack' refers to the spontaneous adhesion of an adhesive to another surface that is chemically dissimilar [Adhikari *et al.* (2001)]. This study uses the term 'stickiness' because of its more common use with reference to food systems. Stickiness is a commonly observed phenomenon in food science that reflects the tendency of some materials to agglomerate and/or adhere to contact surfaces [Kudra (2002)]. This study aims to use stickiness as a measure to provide insight into optimising two key micro-level processes; maximising the success of droplet adhesion on to a dairy powder surface and minimising the agglomeration between coated but sticky particles.

6.3.2 Stickiness theory and characterisation

Numerous theories to explain the interactions between the adhesive and the adherend (or substrate) have been proposed, including mechanical interlocking, electrostatic adhesion, chemical adhesion, diffusion, wetting and thermodynamic adsorption, rheological and tack character and polymer structure–function relationships [Saunders *et al.* (1992); Michalski *et al.* (1997)]. Although a great amount of effort has been made to determine mechanisms controlling adhesion in the adhesive industry, little is known about the mechanisms controlling food adhesion [Saunders *et al.* (1992)]. No single theory correctly predicts

adhesive behaviour in all situations. This is particularly true in foodstuffs because of their complex nature.

Although the exact mechanism for food stickiness is still not known, the causative factors of food stickiness, its quantification and methods of minimisation have been the subject of many reviews [Papadakis and Bahu (1992); Saunders *et al.* (1992); Bhandari *et al.* (1997a); Michalski *et al.* (1997); Adhikari *et al.* (2001); Adhikari (2002)]. These reviews have typically focused on the stickiness of powders under moisture adsorption conditions. The aim of these studies was to determine temperature and relative humidity conditions under which the powder agglomerates and cakes under storage or during post-processing. However, these conditions are not directly applicable to drying where desorption rather than adsorption is the important process through which stickiness develops during the manufacture of these powders. Furthermore, the moisture content range for the sorption studies are very low (typically 0.3 (kg water).(kg⁻¹ dry solid) for maltodextrin DE5 [Roos and Karel (1991a)]) compared to a drying spray droplet in a coating application (approximately 4 (kg water).(kg⁻¹ dry solid)). Then there is the additional complication of sorption/desorption hysteresis.

Given that an *a priori* knowledge of adhesion and stickiness cannot be established from a single theory, it is necessary to characterise stickiness experimentally. Pressure sensitive tack has been found to be a composite response of the surface chemistry of both the adhesive and substrate and the adhesive rheological properties [Hammond (1989); Saunders *et al.* (1992)]. Furthermore, according to Saunders *et al.* (1992), food scientists studying adhesion of dough to processing equipment have recognised the influence of surface energy [Andrianov *et al.* (1968) as cited in Saunders *et al.* (1992)] and viscoelasticity [Rudolph and Tscheuschner (1979) and Dhaliwal *et al.* (1990) as cited in Saunders *et al.* (1992)] on stickiness measurements and the cohesive strength of dough. Hence, knowledge of the surface energies of the materials and the rheological properties of the droplets as they dry will be important. The following sections discuss these further.

6.3.2.1 Wetting and thermodynamic adsorption

Wettability and surface energies have an important contribution to adhesion [Kilcast and Roberts (1998)]. Thermodynamic adsorption has been described by Young's force equation and Dupre's energy equation [Michalski *et al.* (1997)]. The relationships are derived considering an interfacial tension balance over a droplet on a flat, solid surface as shown in Figure 6.1.

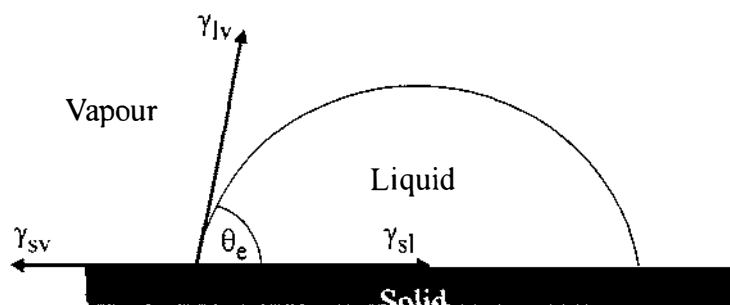


Figure 6.1: Interfacial tensions around a liquid droplet on a flat, solid surface.

Young's equation (Equation (6.1)) [from Adhikari *et al.* (2001)] relates the solid–vapour, γ_{sv} [N.m⁻¹], liquid–vapour, γ_{lv} [N.m⁻¹], and solid–liquid, γ_{sl} [N.m⁻¹], interfacial tensions and the droplet equilibrium contact angle, θ_e [°], at the solid–liquid–vapour triple line. Dupre's

equation relates adhesive and substrate surface tensions to the work of adhesion, W_a [N.m^{-1} or J.m^{-2}], in Equation (6.2) [from Adhikari *et al.* (2001)].

$$\gamma_{sv} = \gamma_{lv} \cos \theta_e + \gamma_{sl} \quad (6.1)$$

$$W_a = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} \quad (6.2)$$

The extent of film adhesion to a substrate is dependent upon the area of contact as well as the intrinsic adhesive bonding [Aulton (1995) as cited in Oh and Luner (1999)]. The adhesion of fluids (in this case spray droplets) or semi-solid foods (in this case droplets with partial skin formation) to dissimilar surfaces (in this case fat coated powder particles) is not possible unless they have good wettability (and subsequent spreadability) to the substrate [Oh and Luner (1999); Adhikari *et al.* (2001)]. Good wettability means the substrate powder and the polymer droplet have a strong mutual affinity and are likely to adhere well [Michalski *et al.* (1997)]. Spreading occurs after wetting and reflects whether a liquid droplet will spread on an initially dry surface as a continuous film or, conversely, retract as one or several droplets. The spreading coefficient, S_{LS} [N.m^{-1}], indicates, from a thermodynamic perspective, whether a given liquid–solid system will be wetting or non-wetting and is defined as the difference between the work of adhesion and cohesion [Myers (1999)].

$$S_{L/S} = \gamma_{sv} - \gamma_{lv} - \gamma_{sl} = \gamma_{lv} (\cos \theta_e - 1) \quad (6.3)$$

The closer the spreading coefficient is to zero, the more energetically favourable spreading of the film on the substrate becomes and the stronger the film adheres. Oh and Luner (1999) used the spreading coefficient as an indicator of film adhesion, while Rowe (1989), used both the spreading coefficient and the work of adhesion to study binder–substrate interactions in granulations. Spreading is dealt with in Chapter 7.

From a practical perspective, Link and Schlünder (1997), using their single nucleus coating apparatus found that the addition of the surfactant Texapon K12-96 (96% sodium lauryl sulphate, Henkel, KGaA) to a 16% w/w lactose solution increased wettability leading to faster particle coating rates. However, this could have also resulted from a higher droplet surface moisture content and subsequent increased tack due to the lower drying rates of surfactant-containing droplets (as found in Section 5.9.4). In a study of granulation, Iveson *et al.* (2001) proposed that lower surface tensions should make particle coalescence easier and increase granule growth rates. However, they said that this would also reduce the liquid bond strength between two colliding particles decreasing the likelihood of permanent coalescence and reducing granule strength. It could be speculated that a spray droplet that spreads to give a thinner coating layer would dry faster and be less likely to cause inter-particle agglomeration.

In coating, a complex trade-off is required between lowering droplet surface tension to increase droplet adhesion (maximising droplet–substrate adhesion efficiency) and achieving greater spreading extents (maximising coating coverage) while, at the same time, minimising inter-particle agglomeration. Therefore, addition of wetting agents becomes an important formulation parameter in the spreading and sticking behaviour of polymer droplets during impact and drying.

6.3.2.2 Stickiness and sample rheology

Rheology is also important to stickiness because the time taken by a fluid or semi-solid food to wet the surface is influenced by viscosity; increased viscosity leads to increased wetting times. In the case of adhesive–substrate interactions this may influence tack [Hammond (1989)]. From a practical perspective, binder viscosity has been recognised as an important parameter in controlling granulation behaviour because it directly influences energy dissipation between colliding particles [Ennis *et al.* (1990); Ennis *et al.* (1991)]. Link and Schlünder (1997) found a super-proportional (power law) increase in coating growth rate as a function of coating droplet viscosity which was thought to result from the lower chance of droplet splashing.

de Crevoisier *et al.* (1999) stated that for good contact to be established between two surfaces, some softness in the material is essential and that stickiness is related to the balance between softness and ability to dissipate energy. This suggests that the relationship between stickiness and skin formation is important. If a dry and robust skin forms on a spray droplet surface in flight before impact on the target substrate, then deformation and subsequent flow and adherence might not occur. Understanding this is important to ensure maximum droplet impingement and sticking efficiency. Furthermore, after droplet impact and spreading, continued drying may reform a skin. Low droplet viscosity is important for spreading, and subsequent rapid viscosity increase with drying is important to avoid inter-particle agglomeration. This implies that knowledge of the surface moisture content is valuable in terms of prediction of droplet adhesion and inter-particle agglomeration.

6.3.3 Conclusions

The definition of tack and stickiness remains elusive. It is not a true physical property but a composite of several physical observations, parameters and concepts. Although it has a broad and somewhat qualitative meaning, it is very useful in practice. For practical purposes, it is simply the resistance to separation and consists of two stages; wetting and debonding. The first stage, wetting is controlled by true physical properties such as surface tension and viscosity, whilst the second stage, debonding is controlled by the rheological properties of the adhesive.

Surface tension and viscosity are the key formulation properties affecting droplet stickiness and subsequently droplet–substrate adherence efficiency and inter-particle agglomeration. In order to study the effect of these formulation properties on stickiness it is important to determine how these properties are affected by surface moisture during drying. This necessarily requires accurate experimental methods and modelling for drying as described in Chapter 5, and the experimental method described below for stickiness characterisation.

6.4 EXPERIMENTAL METHOD SELECTION

Food and adhesion scientists have independently developed similar testing methodology to characterise tack [Saunders *et al.* (1992)]. The diversity in the types of objective test methods for characterising the stickiness of food products arises because the characterisation of food stickiness has been product specific [Adhikari (2002)]. A distinction must be made between ‘fundamental’ and ‘practical’ adhesion. According to Mittal (1980), ‘fundamental’ or ‘true’ adhesion refers to the intermolecular interactions between the polymer and the substrate [as cited in Felton and McGinity (1999)]. According to Packham (1992), ‘practical’ or ‘measured’ adhesion refers to the numerical value that results from a variety of testing

methods including shear and tensile tests [as cited in Felton and McGinity (1999)]. However, none of the methods used to quantify polymer adhesion can be directly used to measure fundamental adhesion [Felton and McGinity (1999)]. In addition to the interfacial interactions, other factors, such as stresses in the film and the adhesion measurement technique, will influence measured adhesion [Rowe (1981)]. This chapter does not intend to elucidate the fundamental mechanism of stickiness but rather to characterise the development of stickiness and to provide insight as to how to control this development. From this viewpoint, the study is interested in practical adhesion (i.e. stickiness) of the potential coating materials to provide a relative comparison between various formulations.

Adhikari *et al.* (2001) presents a comprehensive review of various test methods employed for characterisation of food stickiness. Methods include the shear cell, sticky-point temperature, probe tack method, peel methods, blow test and glass transition temperature methods. Three methods stood out for use in this study and are briefly discussed below.

6.4.1 Glass transition temperature

The glass transition temperature, T_g [$^{\circ}\text{C}$], is recognised as a fundamental parameter to explain stickiness [Adhikari (2002)] in amorphous and semi-crystalline low molecular weight sugars and carbohydrates. T_g is a second-order phase transition that occurs over a temperature range at which amorphous solid materials are transformed into the viscous, liquid state and results in dramatic changes in the free volume, molecular mobility and physical properties of the material [Roos (1995)]. The transition is usually described as a 'glassy' to 'rubbery' state.

Many substances, including alcohols, fats, protein solutions, sugars and sugar solutions can be converted into amorphous glasses [White and Cakebread (1966)]. An amorphous food is formed at non-equilibrium conditions by rapid removal of the dispersing medium (such as water in spray drying), or from the melt by rapid supercooling. The spray droplets in the single droplet drying studies and in industrial coating processes are all likely to exist in an amorphous state. An amorphous material is not in thermodynamic equilibrium, and is therefore unstable relative to the crystalline form. It behaves as an extremely viscous glass having a typical viscosity above 10^{12} Pa.s. In the 'glassy' state, molecular movement is highly limited, which is necessary for an orderly alignment of molecules to crystallise. Nevertheless, the glass is in a metastable state and will tend to convert to the crystalline form eventually, with a rate dependent on temperature and moisture content [Flink (1983); Bhandari and Howes (1999)] albeit many years for low temperature, low moisture conditions. When the temperature or moisture content of the glass (10^{12-14} Pa.s) is increased the material changes to a 'rubbery' state with a viscosity ranging from 10^6 – 10^8 Pa.s [Downton *et al.* (1982)]. The reduced viscosity greatly enhances the molecular mobility of the system which is linked to stickiness and adhesion. The lowered viscosity and subsequent softening is also linked to the liquid and solid bridges that cause agglomeration and caking in food particulate systems [Papadakis and Bahu (1992); Peleg (1993)].

High molecular weight ingredients such as carbohydrates and proteins have high glass transition temperatures because T_g increases with increasing molecular weight [Fox Jr and Flory (1950); Roos and Karel (1991a)] and generally do not show sticky behaviour. Hence, addition of ingredients such as high molecular weight (low dextrose equivalent) maltodextrins is recommended in drying [Bhandari *et al.* (1997b)] to minimise stickiness. This attribute has been a major criterion in the selection of the coating materials in this study.

According to Le Meste *et al.* (2002), the glass transition temperature may be relevant, once the correlation with the phenomenon of interest has been demonstrated, i.e. stickiness measured by the probe tack test.

6.4.2 Sticky-point temperature and the critical X concept

The sticky-point temperature devices exploit a definition of the sticky-point as the temperature at which the force necessary to turn an impeller in a powdered material sample with defined moisture content increases dramatically [Kudra (2002)]. Originally designed by Lazar *et al.* (1956), the method (along with subsequent modifications) has been employed frequently in relation to spray-dried food powders by numerous researchers [Downton *et al.* (1982); Wallack and King (1988); Zogzas and Maroulis (1996); Lockemann (1999); Hennigs *et al.* (2001)].

Historically, the stickiness curve represents a sharp boundary between the sticky region above and the non-sticky region below. The literature values of sticky-point temperature and glass transition temperature for numerous materials run almost parallel to each other as a function of moisture content. As a result, researchers [Downton *et al.* (1982); Wallack and King (1988); Hennigs *et al.* (2001)] have attempted to correlate the process temperature at which the onset of stickiness is observed, T [°C] relative to the material glass transition temperature and typically define a critical $X = (T - T_g)$ value. Using this knowledge, many researchers have used the critical X value to determine ‘safe powder condition’ maps from the stickiness curves [Lazar *et al.* (1956); Downton *et al.* (1982); Wallack and King (1988); Lockemann (1999); Fanshawe (2001); Hennigs *et al.* (2001)]. An example of such a map is shown for maltodextrin DE5 in Figure 6.2. A critical X value of 20 °C has been arbitrarily chosen to represent the sticky-point temperature of maltodextrin DE5.

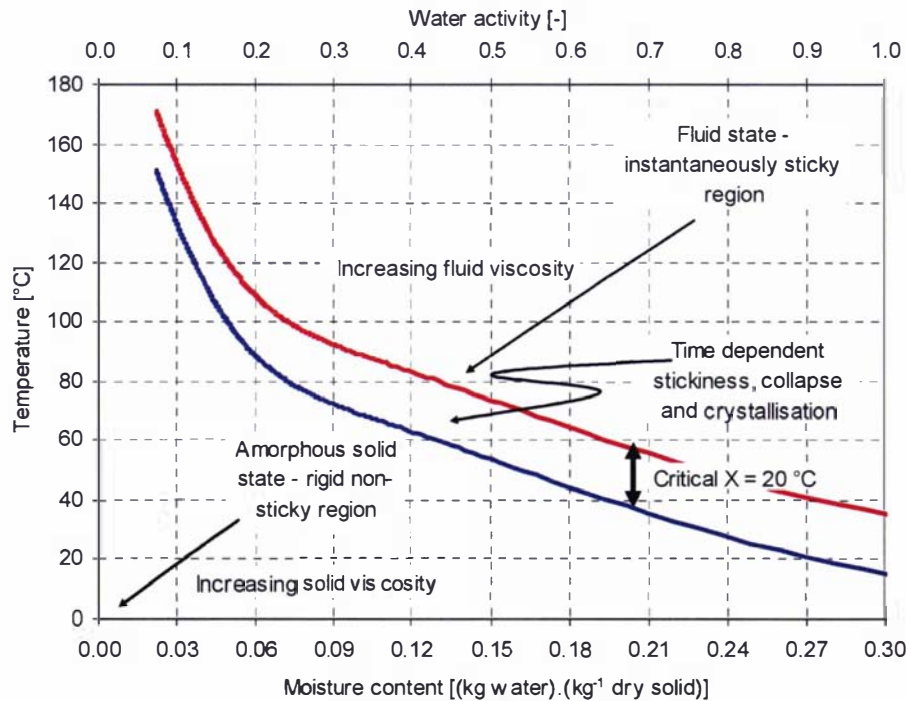


Figure 6.2: Example of a state diagram showing the glass transition temperature and assumed sticky-point temperature for maltodextrin DE5: — glass transition temperature; — sticky-point temperature.

These ‘safe powder condition’ maps or state diagrams are generated from studies in which an amorphous powder is subjected to a range of temperature and humidity conditions and the subsequent flowability or stickiness of the powder is measured. Downton *et al.* (1982) determined that the critical viscosity for stickiness of a dehydrated sucrose/fructose (7:1) mixture was independent of moisture content being 10^6 – 10^8 Pa.s [Roos and Karel (1993)]. This corresponded to a temperature 10–20 °C higher than the glass transition temperature [Roos and Karel (1993)], however, stickiness has been reported at values as low as 10 °C above T_g but not lower than T_g itself. Work conducted at Massey University [Crofskey (2000); Keir (2001); Foster (2002); Chatterjee (2003); Zuo (2004)] shows that some dairy powders do not exhibit stickiness until 25–40 °C above their T_g . Their work has shown the strong dependence of formulation ingredients with low molecular weight amorphous materials, particularly lactose, showing significant dominance over others. The literature variation in the critical X at which stickiness occurs can be partially accounted for by the different experimental methods used. According to Kudra (2002), such discrepancies could also be the result from a stickiness transition region rather than the sharp boundary represented by the stickiness curves.

However, as Kudra (2002) correctly pointed out, the sticky-point temperature determined for powders might not provide a true picture of the stickiness history of a basically irreversible drying process, which progresses in the opposite direction, viz. from the viscous liquid to the dry particulate material. As a result, this method is not appropriate for the drying of polymer droplets.

The sticky-point temperature method was not used in this work, but the state diagram shown in Figure 6.2 can be used to illustrate the scenario of interest from a drying perspective. In the humidification studies employed by researchers investigating powder stickiness, the point of interest is the conditions at which a dry, non-sticky powder first shows signs of stickiness. These conditions can then be used to set an upper processing or storage condition for the powder. In contrast, the study here is interested in the point at which the droplet surface approaches and then passes through its glass transition temperature from the reverse direction (drying), first exhibiting a ‘rubbery’ (10^6 – 10^8 Pa.s) and hence ‘sticky’ and malleable character, to then exhibit a ‘glassy’ rigid structure, above 10^8 Pa.s. If the surface moisture content and surface temperature are known (or at least predicted) then they can be plotted on such a diagram to reveal the surface state of the droplet/product (i.e. solution, semi-solid, glass) which can aid the design and optimisation of the coating process.

6.4.3 Probe tack test

The probe tack tests are intended to mimic the feel when the human finger touches a sticky surface [Hammond (1989)]. The essential feature of the probe tack test is to bring a probe in contact with an adhesive under a light contact pressure for a short time and to pull away with a fixed speed [Adhikari (2002)]. The peak tensile force is the measure of tack or stickiness [Kambe and Kamagata (1969); Hammond (1989); Adhikari *et al.* (2003)] and is dependent on the device and method specifications.

One of the earliest probe tack testers was used to study the tackiness of ink [Green (1941)]. Modified versions of the probe tack test have been widely used in work on pressure-sensitive adhesives [Zosel (1985); Hammond (1989); Ondarçuhu (1997)]. Recently, the probe tack method has been successfully adapted to measure the stickiness of food systems such as wheat dough [Chen and Hoseney (1995)], candy [Kilcast and Roberts (1998)] and sucrose/corn syrup glasses [Nowakowski and Hartel (2002)]. Saunders *et al.* (1992) tabulated

probe tack test parameters used to determine tack for various food systems. Figure 6.3 shows a schematic of a simple probe tack tester. It comprises a test plate and a probe, which is used to measure the 'pull force' as the probe is made to contact and then withdraw from the sample surface.

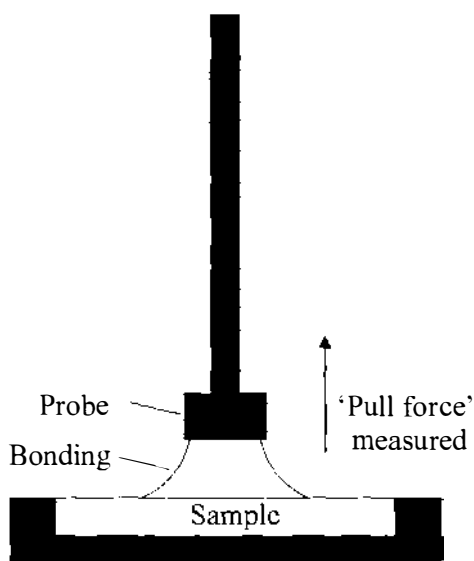


Figure 6.3: Schematic of a simple probe tack tester.

According to Wan and Lai (1992b), the change in tack behaviour as the coating film is transformed from a low viscosity liquid to a highly viscous gel (semi-solid), and then eventually to a completely dried solid state, is believed to play a major role in the particle growth mechanism during fluidised bed coating. Chopra and Tawashi (1982), Chopra and Tawashi (1984), Chopra and Tawashi (1985) and Wan and Lai (1992a) used the probe tack test to study the tackiness of various coating solutions. Although the investigations found that tackiness increased with increasing initial viscosity, these studies were on solutions of latexes, which may not be directly relevant to the aqueous soluble coating materials used in this study.

Recently, Adhikari (2002) used a probe tack test to investigate the effect of high molecular weight additives (maltodextrin DE6) on the stickiness of model fruit juice droplets (fructose, glucose, sucrose, citric acid and their mixtures) as they dried with a view to minimising agglomeration in spray drying applications through the development of 'safe drying' maps. Adhikari found that as it dried, the stickiness of maltodextrin DE6 alone rose rapidly to pass through a peak tensile force then drop away to a state of non-adhesion. It was proposed that this state of non-adhesion is responsible for the common use of high molecular weight maltodextrins being employed as drying aids. Interestingly, whilst high molecular weight maltodextrins have found use as drying aids Adhikari's work showed that the maximum tensile pressure was larger than common low molecular weight sugars such as sucrose and fructose which are considered to be extremely difficult to spray dry because of their stickiness. On average these have lower peak tensile pressures but are sticky for the entire drying period (to bulk average moisture contents as low as 0.1 (kg water).(kg⁻¹ dry solid) at 63 °C) whereas the maltodextrins are not since the skin allows the surface to dry to a moisture content low enough that the surface T_g is much higher than 63 °C at 0.1 (kg water).(kg⁻¹ dry solid) resulting in the observed state of non-adhesion.

Adhikari's findings pose two important questions for which their answers could serve useful for coater design as well as operation and formulation guidelines. The first is, 'How sticky

does the droplet become?', tempered with the additional question, 'Does this degree of stickiness really have an influence in the desired application?' Stickiness may be acceptable if the inter-particle forces in the fluid bed are much greater. If the stickiness is unacceptable, the coater should be run under more dilute air-particle volume ratios and increasingly turbulent airflow. Knowledge of stickiness can be also used to set the atomiser parameters (outlet velocity, position relative to particle flow) to ensure maximum impingement efficiency. A third question is 'How long is the droplet sticky for?' If it is sticky for a long period of time one might increase the height of the Würster insert to ensure it has dried before it circulates to the fluid bed region. Alternatively, it may be so sticky that even for a very short period of time it has a detrimental effect on the process and product.

The probe tack testing device and associated drying rig were developed by Adhikari (2002) and were available for use in this study. It was selected based on this availability, its acceptance for measuring foodstuff stickiness and because little work had been done with coating formulations.

6.4.4 Relating probe tack measurements to glass transition temperature

Although, the glass transition cannot be considered as an absolute threshold for molecular mobility, for processes such as stickiness, collapse, caking, crystallisation as well as drying, T_g data and Williams-Landel-Ferry (WLF) [Williams *et al.* (1955)] kinetics have good predictive value with regards to the effects of temperature and water content [Le Meste *et al.* (2002)]. Hence, the use of T_g is considered as a predictor in the processes of drying and adhesion/stickiness.

Past research has shown varied success with relating T_g to tack measurements. The most closely related study (with the exception of Adhikari (2002)) is that of Nowakowski and Hartel (2002). They used a texture analyser (TA.XT2, Texture Technologies Corp., Scarsdale, NY, USA) to correlate surface tack of sugar (sucrose/corn syrup) glasses with T_g as the samples adsorbed moisture (reverse of the process of drying). Although some important information was able to be extracted from the tests regarding formulation properties of the glass, the results were limited by the fact that the correlations were based on a bulk moisture content whereas the probe tests measured the surface stickiness which was at a higher moisture content. Since T_g was based on the bulk sample moisture content it did not represent the actual T_g at the surface which was at a higher moisture content (subjectively observed) and subsequently a lower T_g .

Other workers also note a possible correlation. Heddleson *et al.* (1994) noticed that increasing temperature and moisture content had the same effect on increasing sample tack for wheat dough. Rudolph and Tscheuschner (1979) [as cited in Nowakowski and Hartel (2002)] noted that both modes of failure (adhesive and cohesive explained later in Section 6.7.5) in the tack tests were apparent in the T_g zone for dough. It is generally agreed that the transition from cohesive to adhesive failure takes place when one moves toward the phase transition from liquid-like viscous to rubber-like elastic behaviour [Satas (1989)]. That said, using multiple regression analysis, Brennan and Mohamed (1984) found that subjective stickiness of commercial sugar syrup solutions was best predicted by viscosity and to a lesser extent surface tension and not by probe tack test measurements.

In summary, relating the glass transition temperature to probe tack tests for food systems is not new. Although it is well known that stickiness is a surface phenomenon, no attempt has

been made to relate the probe tack tests to surface T_g . This is a possible reason for the varied success of T_g as an indicator for foodstuff stickiness behaviour to date.

6.5 EXPERIMENTAL SET-UP

The experimental set-up used to collect the stickiness profiles of drying droplets described below was designed, built and resides at the School of Engineering at The University of Queensland (UQ), St. Lucia, Australia. Below is a brief description of the apparatus. A detailed description can be found in Adhikari (2002).

6.5.1 Set-up overview

The apparatus to deliver air and house the drying droplet along with the datalogging system and image acquisition system were the same as that described to collect the single droplet drying kinetics in Chapter 5. Figure 6.4 is a photograph of the main drying chamber showing the two key additions, an actuator assembly with droplet holder (item F and E) respectively) and a stainless steel probe (item D) which enter the bottom and top ports of the main drying chamber respectively. Various additional components are also shown.

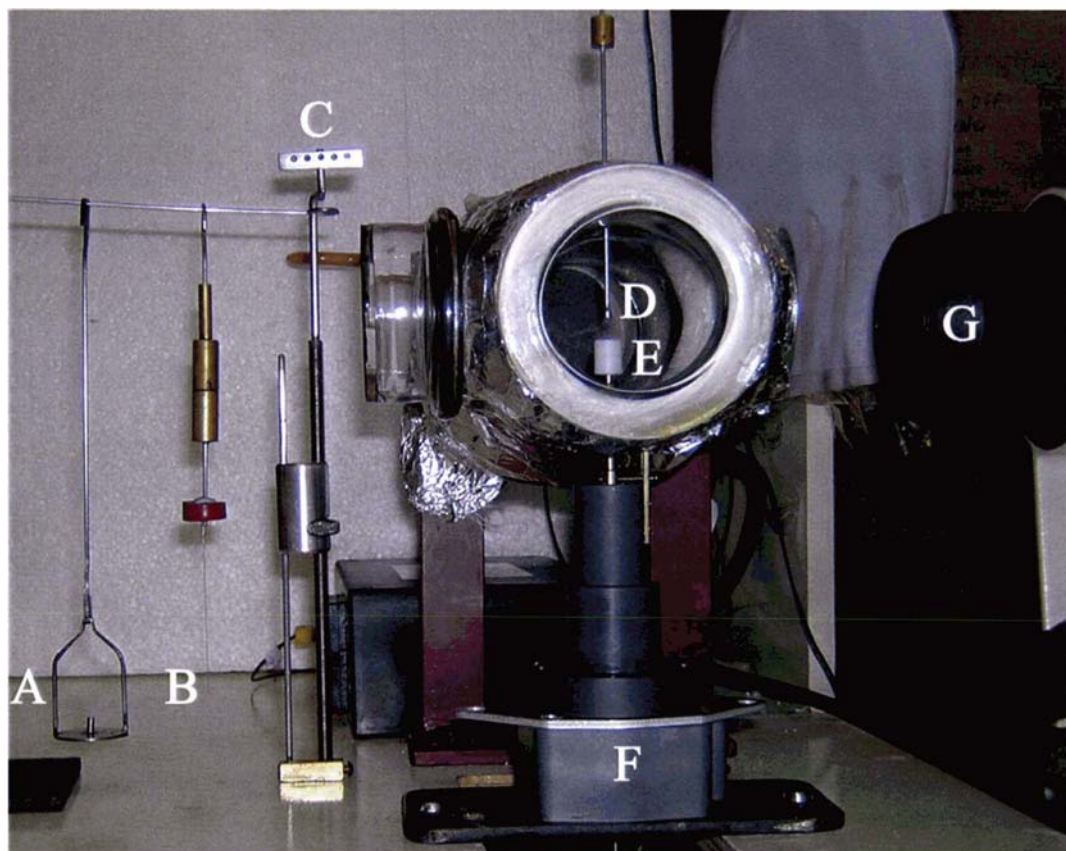


Figure 6.4: Front-end (air outlet) photograph of the single droplet drying chamber along with probe tack test device: A = droplet suspension system for stickiness test moisture content histories; B = droplet suspension system for single droplet moisture content histories; C = tool for positioning wire thermocouple in the single droplet drying tests; D = stickiness testing probe; E = Teflon® droplet holder for stickiness tests; F = actuator assembly to drive droplet holder; G = stereomicroscope.

6.5.2 Actuator assembly with droplet holder

Items (E) and (F) in Figure 6.4 show the actuator assembly with a droplet holder, respectively. A detailed description of the actuator assembly can be found in Adhikari (2002). It is briefly restated here. A unipolar, 4 phase stepper motor (RS 318-711, RS Components Australia Ltd) having a step size of 0.025 mm, step accuracy of ± 0.005 mm and repetition accuracy of ± 0.01 mm was used to drive the droplet holder up and down for contact and withdrawal with the suspended probe. A threaded armature (rotor) and a lead screw (225 mm long with travel up to 170 mm) translate the rotary motion to a linear motion. To decouple the rotary and linear motion to provide for smooth contact without torsion affect on the droplet the rotary component was prevented with the aid of a retaining pin bored into the guide shaft. The pin led to a capture-plate in which it was allowed to travel up and down along a trough (20 mm long and 2.5 mm wide) effectively blocking the circular component of the lead screw motion.

At the top of the actuator assembly was a 11 mm (height) $\times$ 8 mm (diameter) Teflon® cylinder with a fine recess (0.5 mm depth) to give a 7 mm circular walled flat-top to retain the droplet. Teflon® was selected as the droplet holder material due to its low thermal conductivity ($0.34 \text{ W.m}^{-1}.\text{°C}^{-1}$ at 27 °C) thus minimising the amount of heat conducted to the sample.

A driver board (RSSM2, RS Components Australia Ltd) was used to control the actuator actions (start/stop, speed, half or full step and direction). The start/stop operation was controlled manually through a panel mount switch along with a potentiometer to set the stepper motor speed. A digital button in a custom program developed using VisiDAQ software (Version 3.11, Advantech Co., Ltd, Taiwan) was used to control the actuator direction. VisiDAQ software was also used to log the temperatures (droplet and air), mass balance readings (during drying and contact/withdrawal) and actuator direction.

6.5.3 Probe

Item (D) in Figure 6.4 shows the stickiness testing probe. Probe material selection was a key decision. Different types of adhesives have different degrees of adhesion to different surfaces [Chen and Hosney (1995); Hosney and Smewing (1999)]. Ideally, a milkfat surface (representative of the powders of interest, discussed in Section 7.6.1) and a surface of the same material as the droplet being dried would be the surfaces of choice for such an investigation. However, in the limited time available on the UQ rig and the modifications necessary it was not possible to do so. Instead the stainless steel probe provided was used. Stainless steel would represent well the sticking potential of a coated particle on a clean coater wall which represents raw material and product losses rather than the sticking potential between a droplet and a substrate particle. However, it does allow relative comparisons between the polymers and presents a well standardised surface. Figure 6.5 shows a schematic of the stickiness probe and droplet holder.

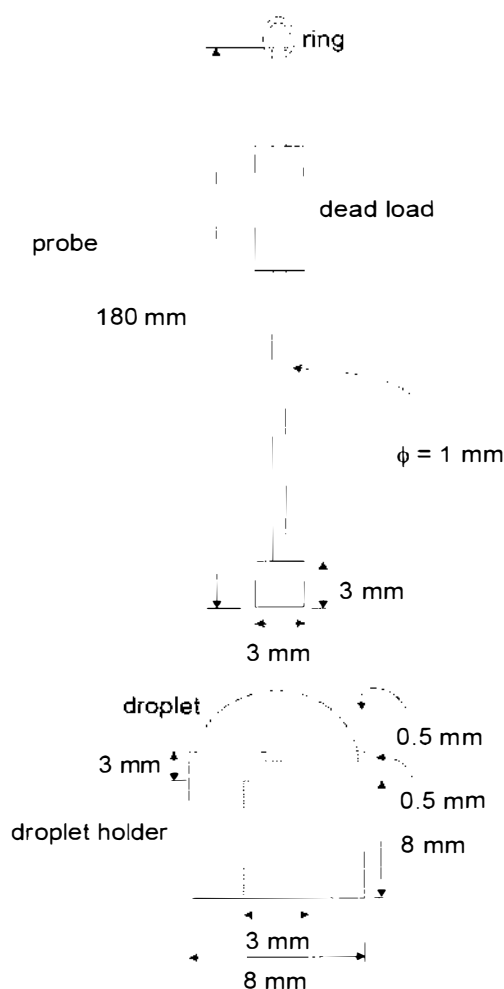


Figure 6.5: Schematic of the stickiness probe and droplet holder.

The probe was a 3 mm (diameter) $\times$ 3 mm (height) stainless steel rod welded with a 1 mm (diameter) $\times$ 177 mm (height) stainless steel cylindrical rod. A cylindrical hollow brass rod was attached to it as a dead load. This dead load provides sufficient contact pressure to exceed 100 g.cm^{-2} (10 kPa) on the droplet surface of $\approx 7 \text{ mm}^2$ (probe surface area) which is a recommended standard according Hammond (1989). The dead load also prevented excess swinging of the probe when it was subjected to the air flow environment. A ring was coupled to the free end of the rod to allow coupling to a flattened hook which hung from the bottom of the mass balance (HM-202, A&D Company Ltd, Tokyo, Japan).

6.5.4 Moisture content history monitoring system

Item (A) in Figure 6.4 shows the droplet suspension system for collecting the drying kinetic data for the stickiness tests. It was comprised of a 25 mm (diameter) $\times$ 1 mm (thickness) stainless steel disc with a 2.5 mm (diameter) $\times$ 5 mm (height) stainless steel pin welded at its centre to fix the sample holder and the sample stably in place during drying. A flattened wire hook coupled the suspension system to a second hook attached to the bottom of the micro-balance (HM-202, A&D Company Ltd, Tokyo, Japan). The mass readings from the balance were continuously logged (via RS-232 serial port) to the personal computer (Compaq, Presario).

6.5.5 Temperature history monitoring system

The temperature history of a drying droplet was monitored through a wire thermocouple (70 μm wire diameter, K-type, Omega Engineering, Inc., Stamford, CT, USA). A Teflon® tube carried the thermocouple in from the top port and was positioned using the camera and software so that the thermocouple junction remained in the centre of the drying droplet.

6.6 EXPERIMENTAL PROTOCOL

6.6.1 Key variable and level selection

The skin formation and the stickiness of the relatively high molecular weight food grade materials will be governed by the formulation and the drying conditions. The same variables and levels as used in the single droplet drying tests were of interest here. These were the droplet initial solids concentration, drying air temperature, air velocity, relative humidity, plasticiser addition, and wetting agent addition. The only difference is that 100 μl droplets were employed here compared to 6 μl earlier.

It was not possible to investigate the effects of RH, for reasons already outlined in Chapter 5. RH is crucial to surface stickiness measurements on dry powders, because water has a strong plasticising effect on amorphous polymers and because the equilibrium moisture content at the surface is dependent on the RH. For these reasons control of RH in an industrial coater is likely to be crucial.

The effect of surface tension on stickiness (wetting agent addition) was not studied experimentally due to time constraints. Chen and Hosney (1995) found a decrease in dough stickiness with lowering of the water fraction surface tension. Wan and Lai (1992a) found the tack of methylcellulose/Tween 80 solutions to diminish with decreasing surface tension although viscosity remained the dominant factor.

Standard conditions were as follows: initial solids concentrations of 20 and 40% w/w; air temperatures of 40 and 78 °C; drying air velocity of 0.30 m.s^{-1} ; relative humidities from 0.5% (at 78 °C) to 4% (at 40 °C). The additions of maltodextrin DE18 and glycerol as plasticisers to maltodextrin DE5 and whey protein isolate were made at levels outlined in Section 6.12. The solutions were made up as already described for the single droplet drying tests (Section 5.7.2).

6.6.2 Stickiness tests

The following procedure was followed for the stickiness tests. The drying chamber along with probe were heated until steady-state was reached. The drying air was quickly swung out to atmosphere to bypass the chamber using valves V2 and V3 in Figure 5.4 and a $100 \pm 1 \mu\text{l}$ droplet produced at the tip of a 100 μl gas-tight micro-syringe (Hamilton Company, Reno, NV, USA) was transferred to the droplet holder that resided on top of the actuator assembly. The drying air was immediately swung back into the drying chamber. At predetermined times during the course of the drying the actuator assembly was driven upwards until the droplet contacted the probe that was suspended from above. The time at which this was done was noted to allow time interpolation to obtain the moisture content (from moisture content history data) at which the stickiness test was performed. Tests were carried out until the point of non-adhesion was identified with enough intermediary measurements taken to get a full

characteristic curve of the stickiness. Between stickiness tests the probe was washed with water (MilliQ) and dried with lint free tissue paper. Section 6.7 discusses the standardised procedure required to get reproducible results.

6.6.3 Moisture content and temperature history data collection

Kinetic data had to be collected in order to determine the concentration at which a stickiness test was performed. It was not possible to collect the temperature and moisture histories simultaneously for the same reasons as outlined in the droplet drying tests (Section 5.6.4). The procedure for their collection was the same as that for a stickiness test but the probe was substituted for the suspension system (item A in Figure 6.4). Solutions were prepared as outlined in Section 5.7.2. The drying time of the 100 μl sample was up to 3 h depending on conditions. As a result, only a single moisture content and temperature history were collected. In all cases, stickiness runs were carried out first until the point of non-adhesion was determined and then the kinetics were collected up to that point. This reduced experimental time but meant that the ability to calculate a standard and therefore comparative drying efficiency (time to dry to a particular moisture content) was lost. Mass balance readings were converted to bulk moisture content.

6.7 PRELIMINARY RIG TESTING

Before any experiments were performed the consistency of experimental conditions was investigated.

6.7.1 Drying air conditions

Since the same air delivery system was used in this apparatus and the same drying air levels were to be investigated as used in the drying kinetics studies, the same degree of consistency in air velocity, air temperature and relative humidity was achieved here.

6.7.2 Droplet suspension system

As was done in the drying kinetics chapter (Section 5.8.4) a sensitivity study of the droplet suspension system was required to ensure accurate and reliable mass data was collected. A comprehensive study of the mass balance sensitivity found no evidence of an offset. Once the mass balance was zeroed, the effect of drag on the suspension system was essentially factored out of the calculations as no systematic error could be found.

6.7.3 Drying kinetics

It was evident from the droplet drying kinetic studies that small differences in the initial mass delivered to the suspension system and the time taken to load the sample significantly affect the results, in particular the moisture content profiles of the droplets for high initial solids concentrations in which rapid skin formation occurs very early in the drying process. Figure 6.6 shows the mass histories of a triplicate run using the 'same sized' droplets under the same experimental conditions.

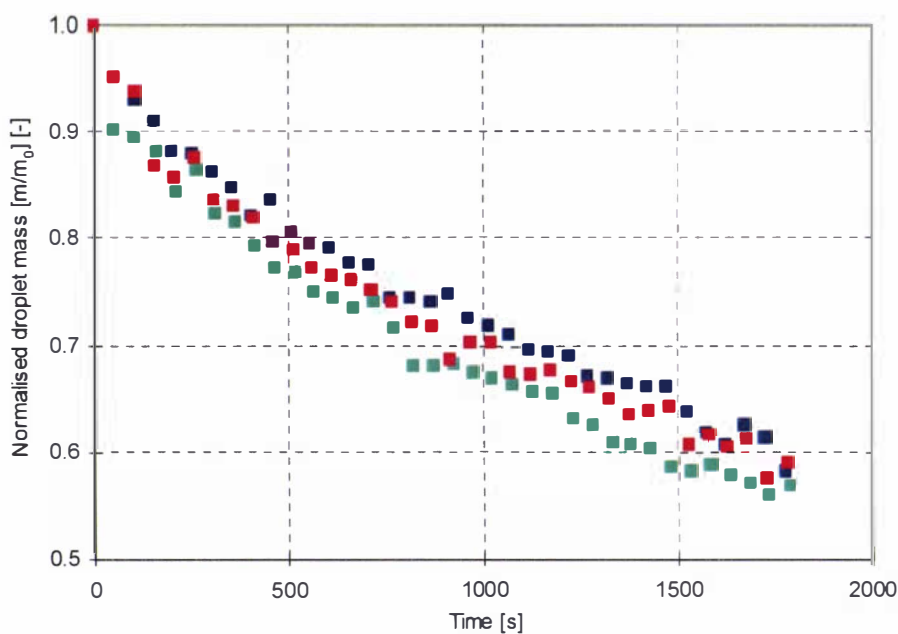


Figure 6.6: Reproducibility of mass history data for 100 µl 40% w/w maltodextrin DE5 droplets drying at 78 °C: ■ trial 1; ■ trial 2; ■ trial 3. Data was collected by John Edwards, Institute of Technology and Engineering, Massey University, New Zealand.

It is clear that the evaporation rates are similar suggesting good reproducibility which enabled a single drying run to be used as a case for interpolating droplet moisture content and temperature with time. Figure 6.7 shows a typical moisture content and temperature history for a 20% w/w maltodextrin DE5 droplet drying at an air temperature of 78 °C.

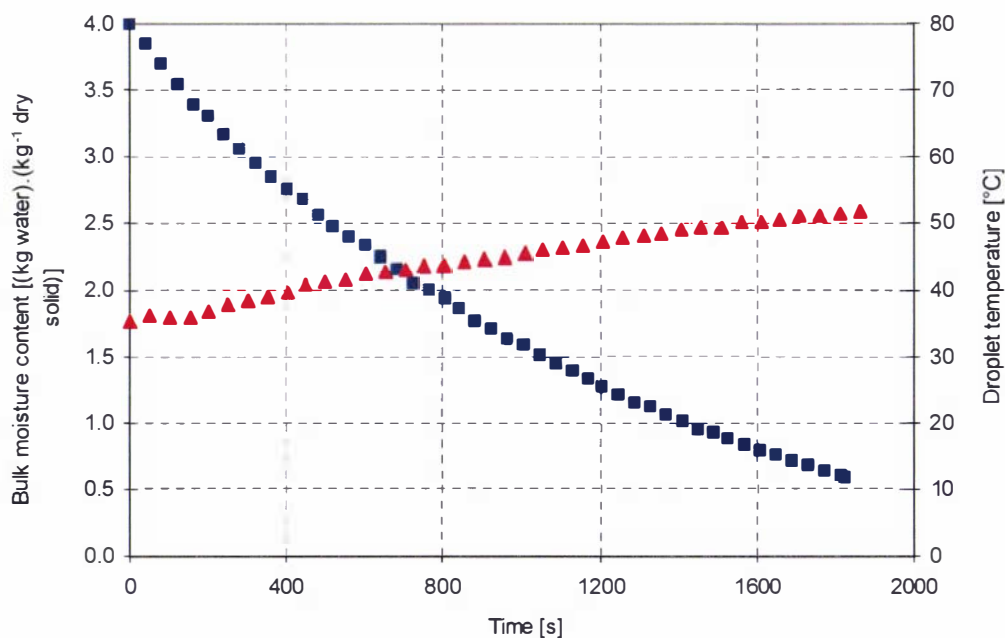


Figure 6.7: Moisture content and temperature histories of a 100 µl 20% w/w maltodextrin DE5 droplet drying at 78 °C: ■ moisture content history; ▲ temperature history.

All moisture content and temperature histories obtained in these experiments showed similar features to those observed in single droplet drying experiments, but with the expected longer

drying time and the larger temperature deviation between the droplet and the air at the end of the drying process. In all cases, the cross-sectional area of the initially hemispherical droplet remained constant (equal to that of the droplet holder) whereas the height shrank continuously as the drying progressed. This was probably due to contact angle pinning, and the fact that skin formation progressed from the base of the droplet (gum arabic most notably). Because of this and the greater weight force of the larger sized droplets, the droplets looked more like a slab or a slab with a slightly curved surface.

Figure 6.8 shows the moisture content histories for 40% w/w maltodextrin DE5, DE10 and DE18 droplets drying at an air temperature of 78 °C.

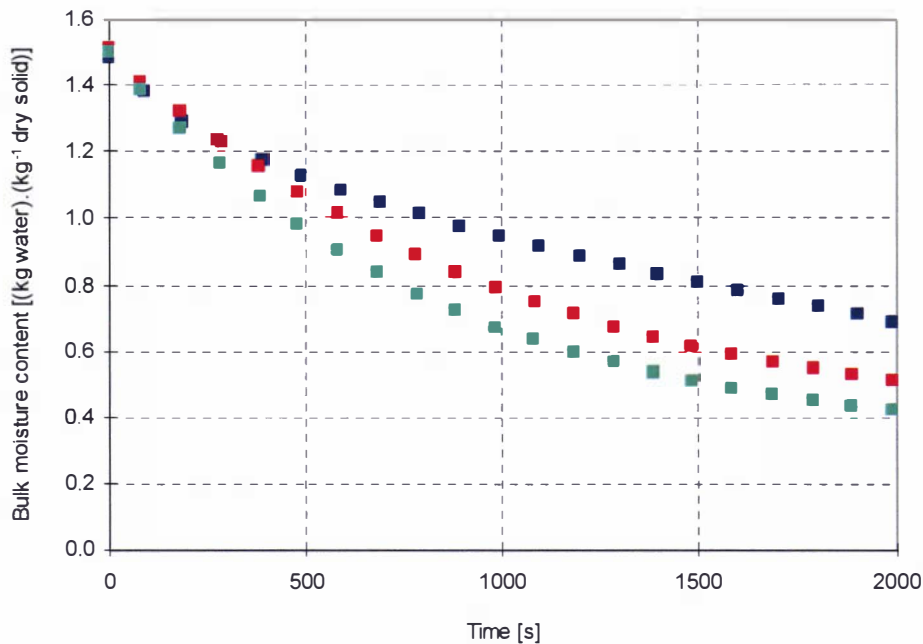


Figure 6.8: Comparison of moisture content history data for 100 µl 40% w/w maltodextrin DE5, DE10 and DE18 droplets drying at 78 °C: ■ maltodextrin DE5; ■ maltodextrin DE10; ■ maltodextrin DE18.

The drying rate increases with increasing DE. This is similar to that found in the single droplet drying tests in Chapter 5 except the difference in drying rates is more pronounced with the larger droplets employed in the stickiness tests.

6.7.4 Standardisation of probe-associated variables

The probe tack test has limits that are acknowledged in the literature. No single tack value can characterise stickiness because of differences in bond formation under different pressures, times, substrate surface roughnesses, and compositions [Hammond (1989)]. With respect to this work, these variables need to be set at levels expected to occur in the coating zone of an industrial coater, which are difficult to quantify. Despite these limitations, the test is commonly employed throughout the adhesives and, more recently, food literature to provide a relevant comparison with base formulation changes. The contact and withdrawal of the probe and the droplet surface introduce many variables and their effects need to be quantified. A series of reproducibility experiments were conducted on a 100 µl droplet containing 40% w/w maltodextrin DE5 under ambient laboratory conditions (still air, 24 °C, 50% RH).

6.7.4.1 Stickiness calculation

Figure 6.9 shows a typical pressure curve generated from probe contact and withdrawal with a 100 μl water droplet at 24 °C.

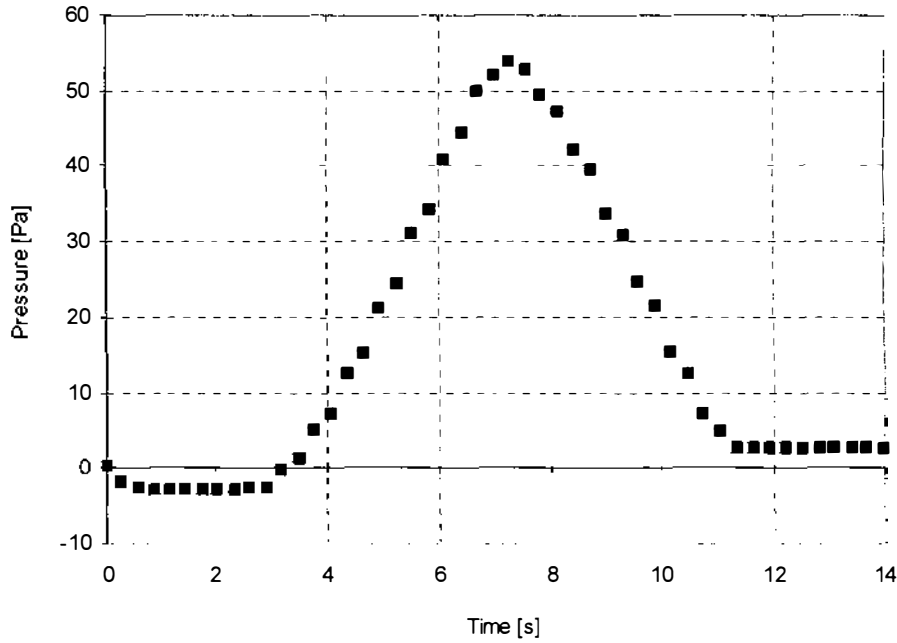


Figure 6.9: Probe tack test pressure curve for a 100 μl pure water droplet at 24 ± 0.5 °C and a probe speed of 30 $\text{mm}\cdot\text{min}^{-1}$. A contact pressure of 2 Pa was realised and yielded a peak tensile pressure of 54 Pa at 7.5 s. The peak tensile pressure was taken as the measure of stickiness.

The readings from the balance were logged every 250 ms during probe approach/contact/withdrawal. The initial mass of the probe was subtracted from each reading to obtain the net change in mass during compression (contact) and tension (withdrawal). The net change in mass was converted to weight force ($m\cdot g$) and then to pressure noting that the diameter of the probe surface was 3 mm. The full contact pressure (≥ 10 kPa) could not to be realised (approximately 2 Pa from Figure 6.9) as droplet rupture would occur and the resulting stickiness force would not be representative of the surface alone. A peak tensile pressure of 54 Pa was obtained. Assuming that stickiness is a function of surface tension alone (surface tension of water being $72 \text{ mN}\cdot\text{m}^{-1}$ at 25 °C [Rahman (1995)]) and that this force acts on the perimeter of the probe, the tensile pressure expected for water is given by Equation (6.4).

$$\frac{72 \times 10^{-3} (\pi D_{\text{probe}})}{(\pi D_{\text{probe}}^2 / 4)} = 96 \text{ Pa} \quad (6.4)$$

The measured value was almost 50% lower than the theoretical value. However, the simple calculation assumed a zero contact angle, considered only the static forces involved during the bonding and debonding process and did not account for the complicating dynamics of viscous dissipation and capillary effects during fluid necking. Despite this, the reproducibility of the tests was good (54 ± 0.9 Pa, 95% confidence interval (CI), $n = 9$ or a coefficient of variation (COV) of 2.2%) and provided for a simple comparative measure of the stickiness of different coating formulations. It is shown in Section 6.7.4.4 that attempts to extract meaningful tensile pressures are further complicated by incomplete bonding resulting from dramatic changes in

surface morphology. Others [Chopra and Tawashi (1982); Heddleson *et al.* (1994)] have measured tack in terms of the energy of separation per unit area of interface, rather than maximum debonding stress. However, in the current experimental set-up, there was no way to ensure complete bonding or to measure the amount of bonding for such a calculation. To draw comparisons, the peak tensile pressure (stress) was taken as the measure of stickiness in all subsequent trials.

6.7.4.2 Effect of solids

The dissolved solids (40% w/w maltodextrin DE5) in the droplet increased the average of the peak tensile pressure to 63 Pa compared with 54 Pa for water, both at ambient temperature. This was an expected result given that the increased viscosity of the maltodextrin DE5 solution was able to dissipate more energy until the bond was ruptured.

6.7.4.3 Effect of probe speed

A 5 mm (height) stainless steel rod was used to set the gap between the sample holder and the probe surface. The time for the stepper motor to drive the sample holder this distance was recorded five times to give an average linear velocity. A range of approach/withdrawal speeds between 12 and 180 mm.min⁻¹ were available. Speeds below 25 mm.min⁻¹ showed noticeable unevenness in motion while speeds above 50 mm.min⁻¹ did not allow enough response time to ensure good contact and withdrawal control on the sample. This range of speeds encompassed those most commonly used in polymer probe tack tests [Zosel (1985); Ondarçuhu (1997)].

It is the characteristic of probe tack tests that higher tack values are obtained with higher probe speeds [Hammond (1989); Wan and Lai (1992a); Chen and Hosney (1995); Ondarçuhu (1997)] until a plateau (saturation) is reached [Chopra and Tawashi (1982)]. This study, using a 40% w/w droplet containing maltodextrin DE5 at ambient temperature, resulted in 40 Pa for 56 mm.min⁻¹ compared with 63 Pa for 30 mm.min⁻¹. This was in direct contrast to the expected trend. The reason for this result is not known but Erb and Hanson (1960) and Bikerman (1968), suggested that low tack values at higher rates of separation may be due to viscoelastic effects [both cited in Chopra and Tawashi (1982)]. Although the solution was slightly shear thinning, it would not account for this difference. Hammond (1989) demonstrated only a slight increase in tack values with increasing rate of separation for a roughed adhesive surface. As a comparison, Adhikari (2002) found only a 5% increase in tack for a 60% increase in speed (from 30 to 48 mm.min⁻¹) with a pure water droplet; a result not statistically significantly different considering the scatter in replicate data. It is possible (although not tested) that the separation rate used in this study was above the critical separation rate at which an increasing dependence of peak force was seen with increasing separation rate. Also of note is that fast separation of the surfaces favours adhesive failure, whereas slow separation of the surfaces favours the cohesive failure [Kambe and Kamagata (1969); Ondarçuhu (1997)]. A probe speed of 30 mm.min⁻¹ was selected for this study, as it gave a smooth action and provided enough reaction time to ensure good contact and withdrawal control with the sample.

6.7.4.4 Effect of contact pressure

Foods are pressure sensitive and may behave in a similar manner to pressure-sensitive adhesives. Hosney and Smewing (1999) stated that, the greater the contact force between the probe and the food, the greater will be the tackiness. One problem with the experimental

set-up of the probe tack test was that mass data could not be plotted in real time (PC data acquisition limitation). This meant that it was difficult to maintain a constant contact force for each approach. However, after significant practice and careful observation of the video images, an operator-subjective, yet reproducible, technique was developed.

The technique relied on carefully assessing the intrusion depth. For a 40% w/w maltodextrin DE5 droplet, in the early stages of drying before a skin formed, the intrusion depth was varied qualitatively from shallow, to medium to deep. This yielded peak tensile pressures of 63 Pa for the shallow depth and 67 Pa for the deeper depths. In later stages of drying, obtaining 100% contact between the surface of the probe and the sample was difficult. Skin formation and subsequently wrinkling and warping as drying proceeded meant that, in some instances, it was not possible to achieve 100% contact without droplet rupture resulting in flow of the viscous fluid through the ruptured skin to the probe surface. These results were discarded as they were not indicative of the surface stickiness. Therefore, a qualitative approach was taken. The actuator was raised until 100% contact was achieved, unless significant wrinkling of the skin had occurred. In these cases, lower contact areas were accepted in order to measure the stickiness. However, this meant that the peak tensile pressure between trials could not be directly compared because of the lower surface area of contact, which was not quantifiable with the current experimental set-up. This limitation should be considered when drawing conclusions from the magnitude of the tensile pressures.

6.7.4.5 Effect of contact time

Viscosity will ensure that it takes a certain time for a polymer to wet all the asperities on the probe surface. As a result, the increase in tensile pressure could be interpreted as an increase in the real contact area [Ondaçuhu (1997)]. Wan and Lai (1992a) found a significant increase in tack force with increasing contact time, followed by a plateau. In this study, there was no significant difference in the peak tensile force with contact times ranging between 1 and 3 s (63 Pa) whereas a slightly higher result (71 Pa) was obtained for a contact time of 10 s. Therefore, a contact time of 3 s was used to ensure good contact.

6.7.4.6 Effect of multiple contacts

Because of the destructive nature of the probe tack test, multiple contacts on the same droplet could not be made.

6.7.5 Modes of failure

The standardisation of probe-associated variables to determine the reproducibility of the stickiness measurements were made on droplets that had not yet formed a surface skin. Three types of bonding failure can be identified during adhesion tests: cohesive, cohesive–adhesive and adhesive. Figure 6.10 shows a time series of five digital images of the bonding and debonding process for five different polymer droplets as they dried and depicts the three modes of failure. Six digital videos depicting the 40% w/w maltodextrin DE5 droplets drying at 78 °C undergoing probe tack test measurements produced in .AVI format have been compressed using the DivX codec and are contained on the CD inside the back cover of the thesis. The modes of bonding failure are described below.

6.7.5.1 Cohesive failure

The cohesive mode of failure is one in which bond rupture takes place within the droplet itself because the adhesive strength at the droplet–probe interface is stronger than the cohesive strength of the droplet. Figure 6.10(c) and Figure 6.10(d) show the liquid bond thinning during withdrawal until finally, upon separation, the probe surface remains completely covered with the residue material (but need not be covered with the entire residue from the droplet holder). This mode of failure occurred only before the appearance of a skin on the droplet surface. Regardless of polymer type, cohesive bond failure resulted in peak tensile pressures close to that of the water tests (54 Pa).

6.7.5.2 Adhesive failure

Adhesive failure takes place at the droplet–probe interface because the cohesive strength of the droplet exceeds the bonding strength of the droplet–probe interface. Figure 6.10(p–t) and (u–y) show the time series of events taking place during adhesive failure. The former series is referred to as adhesive failure, which can be described in most cases as ‘spot tack’. ‘Spot tack’ is a subset of adhesive failure and refers to the cases of adhesive failure where the initial bonding between the probe and the droplet surface is less than 30% despite close to 100% contact with the surface. This occurred (particularly during the plasticisation trials, Section 6.12) and results from an inhomogeneity in the surface moisture content. During withdrawal, the droplet surface ‘peeled’ away to leave the probe surface with little or no residue and the surface of the droplet with an ‘inflected up’ portion. Adhikari *et al.* (2003) found similar results. Although no transfer of material to the probe surface takes place (i.e. no skin rupture) the peak tensile pressure values are comparable with the cohesive–adhesive failure results and are included as such because they do represent a stickiness state, albeit very low in potential for droplet adhesion or inter-particle agglomeration. ‘Spot tack’ appears somewhere between 2 and 5 min of drying time prior to a complete state of non-adhesion, as shown in Figure 6.10(u–y). In this instance, the skin on the surface of the droplet is so dry that no deformation or flow of fluid can occur to form a bond. In some cases, much of the droplet moisture content still remains but exists below the skin surface in the viscous bulk.

6.7.5.3 Cohesive–adhesive failure beneath the skin

According to Adhikari (2002), cohesive–adhesive failure occurs when cohesive and adhesive failure modes exist together. Adhikari (2002) further classified the cohesive–adhesive failure into three sub-classes: cohesive dominance, equal dominance and adhesive dominance, all based on the amount of probe surface that the material covers after withdrawal. These transitional stage modes were probably observed on the lower molecular weight polymers employed by Adhikari (2002), such as fructose, sucrose and their mixtures, which did not form skins. These sub-classes were not observed in the trials carried out in this study because all polymers formed a skin at some point during the drying process. The skin would usually adhere to the probe surface and would separate from the viscous bulk of the droplet during withdrawal. For this study, the cohesive–adhesive bond failure occurred beneath the skin. It could be argued that this was simple cohesive failure because the adhesive forces of the skin surface were stronger than the viscous bulk cohesive forces, but the term cohesive–adhesive failure was retained because of the varying degree of adhesive contact area occupied by the droplet on the probe surface, indicating some balance between the mechanisms. Figure 6.10(f–j) and Figure 6.10(k–o) show the cohesive–adhesive failure beneath the thin malleable skin of a 30% w/w gum arabic, 78 °C, 0.30 m.s⁻¹ droplet, and the more rigid skin of a 40% w/w (3:1) whey protein isolate:glycerol, 78 °C, 0.30 m.s⁻¹ droplet respectively. Satas (1989)

stated that the transition from cohesive to adhesive failure is generally associated with the transition from liquid-like viscous to rubber-like elastic behaviour. However, this transition is difficult to determine using the probe tack test because the peak force measures the mechanical failure of the skin as it ruptures away from the fluid beneath.

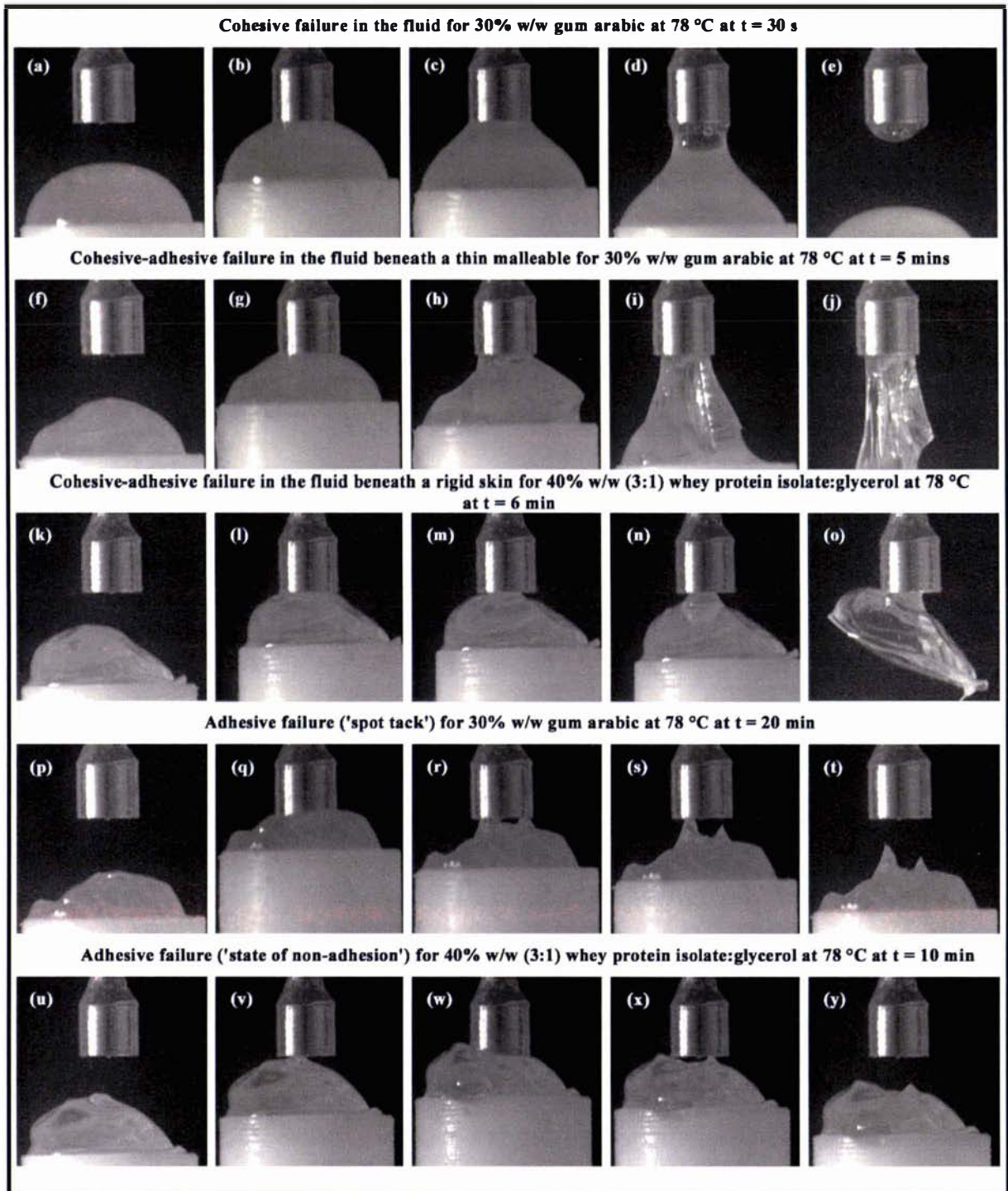


Figure 6.10: Bonding and debonding behaviour identified from the probe tack measurements for the drying of droplets that form an amorphous skin. Note: the drying air velocity was 0.30 m.s^{-1} . Each row of images contains in chronological order, an approach, initial contact, initial withdrawal, withdrawal at a later instant and final separation image. Note: image (w) is a subsequent contact image to ensure 100% droplet–probe surface contact. The probe remained fixed while the droplet holder moved up and down. The probe diameter was 3 mm.

6.7.6 Reproducibility of stickiness measurement

Stickiness is a difficult attribute to measure [Hoseney and Smewing (1999)]. The reproducibility of tack measurements in the general literature is poor. According to Wan and Lai (1992a), the degree of scatter for individual tack data points is an inherent problem in measuring tack because tack, like other parameters characterising the cohesive strength failure of materials, is exceedingly difficult to measure with even a fair degree of reproducibility, in contrast to the remarkable constancy in measurements of properties such as viscosity and elasticity. The reasons for this difficulty are varied, but they all stem from the fact that bond rupture involves a physical discontinuity of stress, of extension and of the material under study.

For water, the reproducibility was high, i.e. 54 ± 0.9 Pa (95% CI, $n = 9$) or a COV of 2.2%. The reproducibility during cohesive fluid failure for a 40% w/w maltodextrin DE5 droplet under ambient stagnant air conditions was also high, i.e. 63 ± 3 Pa (95% CI, $n = 3$) or a COV of 3.4%. Wan and Lai (1992a) and Chen and Hoseney (1995) found that the COV decreased with increasing viscosity and stickiness respectively, but their work was not complicated by skin formation found in this study, which leads to different bonding contact areas. As a result of skin formation, this study had peak tensile pressure reproducibility of up to $\pm 25\%$. Because of the skin formation and the uncertain probe contact area as a result of wrinkling, it is difficult to draw quantitative comparisons between the degree of stickiness of polymers. In addition, the time, and hence the bulk moisture content at which the state of non-adhesion and the peak tensile pressure occur are only estimates because of the discrete nature of the data collected. Because of the constrained time for the use of the probe tack tester and the fact that only one measurement could be made on a single droplet, it was not possible to hone in on the concentration at which these points of interest occurred. The collection of only one stickiness profile was considered to be warranted. The trends alone are of significant importance and, with further method development, more accurate data and reproducibility could be attained. That said, the moisture content at which non-adhesion occurred was very reproducible ($\pm 5\%$). This point was of primary interest to the study.

6.7.7 Interpretation of results

Two points are of primary interest: the point of non-adhesion and the point of maximum tensile pressure. The point of non-adhesion represents a non-sticky spray droplet or coating surface. Knowledge of this point is useful for optimising the drying conditions so that the coated particles become non-sticky before they are recycled to the fluidised bed of particles in a Würster coater. The peak tensile pressure represents the best point at which an atomised droplet should impinge the powder substrate to achieve maximum adherence efficiency.

6.7.8 Conclusions

A reproducible method and standardised conditions were established with careful attention being paid to contact quality and the mode of bond failure. Although the standardised parameters such as separation rate, contact load and contact time were not representative of those occurring in a real situation, it was the intention to characterise the behaviour of the polymers on a comparative basis and to make deductions from these on how the polymers would behave in an industrial-scale Würster coating process. The remainder of this chapter characterises the development of stickiness of various coating formulations under different drying conditions.

6.8 STICKINESS OF MALTODEXTRINS

The stickiness profiles for the maltodextrin materials were characterised as a function of initial solids concentration and drying air temperature.

6.8.1 Maltodextrin DE18

Figure 6.11 presents the characteristic stickiness profiles for maltodextrin DE18 at the two drying temperatures and initial solids concentrations.

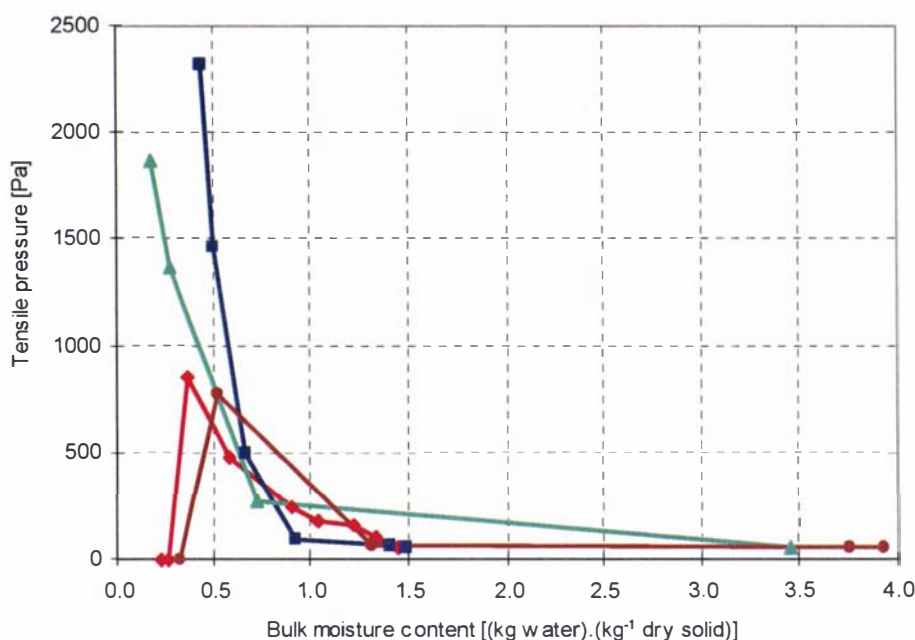


Figure 6.11: Stickiness of 100 μ l maltodextrin DE18 droplets during drying: $\bullet$ 20% w/w, 40 °C; $\blacktriangle$ 20% w/w, 78 °C; $\blacksquare$ 40% w/w, 40 °C; $\blacklozenge$ 40% w/w, 78 °C.

Whether the initial solids concentration is 20% w/w (4 (kg water).(kg⁻¹ dry solid)) or 40% w/w (1.5 (kg water).(kg⁻¹ dry solid)) the stickiness of the droplet could tentatively be said to rise at about 1.5 kg.kg⁻¹. The immediate conclusion to draw, regarding the onset of stickiness, is that the surface had a surface moisture content (and hence viscosity) low enough to allow the wetting of the probe surface and subsequent polymer flow necessary for bonding to occur. This implies the surface temperature was significantly above the glass transition temperature, T_g .

The 20% w/w, 40 °C trial passed through a peak tensile pressure of around 800 Pa at a bulk moisture content of 0.5 kg.kg⁻¹ and then reached a state of non-adhesion at about 0.35 kg.kg⁻¹ suggesting skin formation and its subsequent drying. In contrast, the 20% w/w, 78 °C trial showed an increasing stickiness below 0.25 kg.kg⁻¹ (no further data points were taken). This implies that the 20% w/w, 40 °C trial acquires a surface viscosity high enough to prevent wetting of the probe and subsequent bond formation.

The rate of drying is also important, because it affects the rate of skin formation. One might expect the 40% w/w droplet at 78 °C to develop a skin faster and become non-adhesive earlier in the drying process than the 20% w/w, 40 °C trial because of the larger driving force for drying. This was not observed as the 40% w/w, 78 °C trial followed a similar profile as the

20% w/w, 40 °C trial. Again this could be related to the glass transition temperature. In the 78 °C tests, the surface temperature was high enough to exceed the surface T_g to remain sticky down to a lower bulk moisture content (although when plotted against time it appears sticky for far less time). Prediction of skin formation then becomes important since it is the rate of skin formation and its growth with time that will determine the surface moisture content and surface temperature. Without knowledge of the surface moisture content and temperature it is difficult to predict whether a droplet will be sticky based on its proximity to the surface glass transition temperature of the droplet.

6.8.2 Maltodextrin DE10

Figure 6.12 presents the characteristic stickiness profiles of maltodextrin DE10 at the two standard drying temperatures and initial solids concentrations.

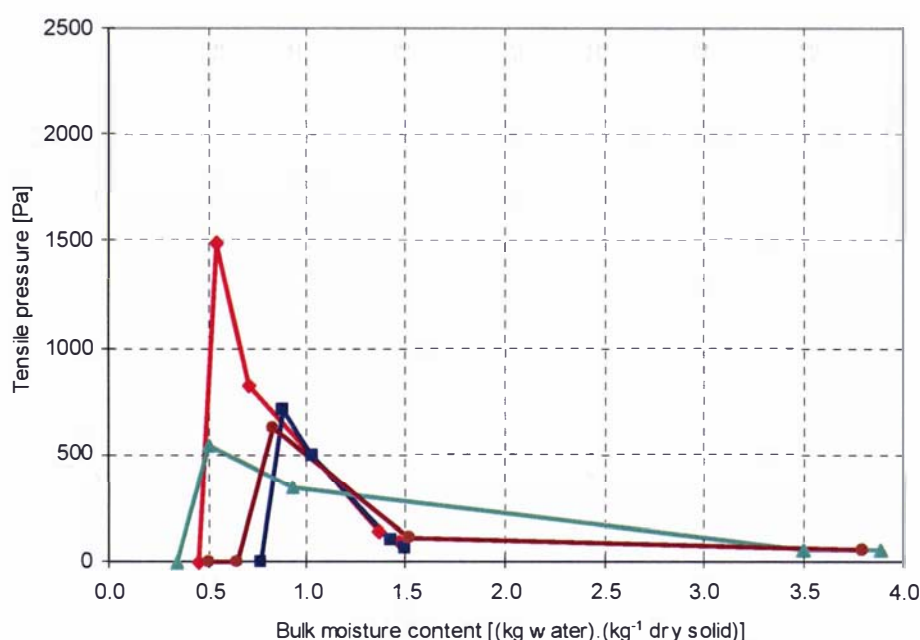


Figure 6.12: Stickiness of 100 µl maltodextrin DE10 droplets during drying: ● 20% w/w, 40 °C; ▲ 20% w/w, 78 °C; ■ 40% w/w, 40 °C; ◆ 40% w/w, 78 °C.

The first point of interest is that the state of non-adhesion for the maltodextrin DE10 droplets was reached at higher bulk moisture contents (0.5 kg.kg^{-1} and 0.75 kg.kg^{-1} for 78 °C cases) than the maltodextrin DE18 counterparts (0.35 kg.kg^{-1}). The moisture content history profiles (Figure 6.8) show that maltodextrin DE18 dries faster than maltodextrin DE10. Therefore, one would expect a drier surface at any point in time during the drying process for the maltodextrin DE18 droplet, but this is not necessarily so, because as the skin forms it acts as a diffusion barrier; the maltodextrin DE10 skin acts as a more effective barrier resulting in a slower drying rate. Therefore, the maltodextrin DE10 droplet (having a higher molecular weight) actually has a drier surface at similar bulk moisture contents to the maltodextrin DE18 droplets. In addition, maltodextrin DE18 has a lower glass transition temperature in the dry state and so remains sticky to lower moisture contents at elevated temperatures, as observed.

The bulk moisture content at which the peak tensile pressure and the state of non-adhesion occur was no different between the maltodextrin DE10 and maltodextrin DE18 trials (within the experimental accuracy of the data). However, both the peak stickiness and state of non-

adhesion are shifted to lower bulk moisture contents with increasing temperature in agreement with the findings of Adhikari (2002). Again, this could be a viscosity effect as represented by the temperature approach to the glass transition temperature. For example, at higher temperatures the droplet surface temperature remained above the glass transition temperature and sticky-point viscosity of the material and hence remains more malleable allowing more moisture to escape. This proceeds until the surface moisture content is dry enough for the skin or crust to fully develop and inhibit further moisture transfer resulting in the state of non-adhesion.

6.8.3 Maltodextrin DE5

Figure 6.13 presents the characteristic stickiness profiles of maltodextrin DE5 at the two standard drying temperatures and initial solids concentrations.

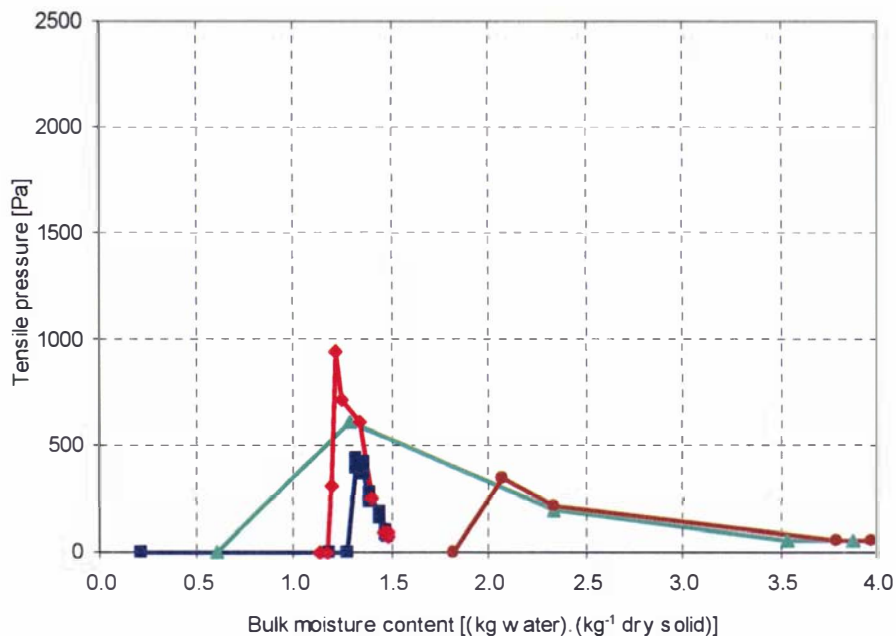


Figure 6.13: Stickiness of 100 μ l maltodextrin DE5 droplets during drying: $\bullet$ 20% w/w, 40 $^{\circ}$ C; $\blacktriangle$ 20% w/w, 78 $^{\circ}$ C; $\bullet$ 40% w/w, 40 $^{\circ}$ C; $\blacklozenge$ 40% w/w, 78 $^{\circ}$ C.

The most striking feature of the maltodextrin DE5 profiles was the very narrow bulk moisture content range in which the 40% w/w initial solids concentration maltodextrin DE5 droplets were sticky. A skin formed early on in these droplets, giving peak tensile pressures that were at least six times that of water (which is at around 60 Pa) at the same temperature. Because drying was so rapid, the time for which the droplet was sticky was very short.

Similarly, to the maltodextrin DE18 and maltodextrin DE10 trials, a shift was seen in the peak tensile pressure to lower bulk moisture contents with increasing temperature. It should be noted that the 20% w/w, 78 $^{\circ}$ C maltodextrin DE5 trial produced a cavity on the lee-side during drying, which made its concentrations erroneous as the droplet was not uniform in structure.

6.8.4 Discussion

According to Nowakowski and Hartel (2002), the probe tack test measures the response of viscosity changes of the amorphous surface layer as it dries. Figure 6.14 shows the tensile

pressures for the maltodextrins as a function of initial droplet viscosity (taken from the Grain Processing Corporation, Maltrin® brochure, 1999).

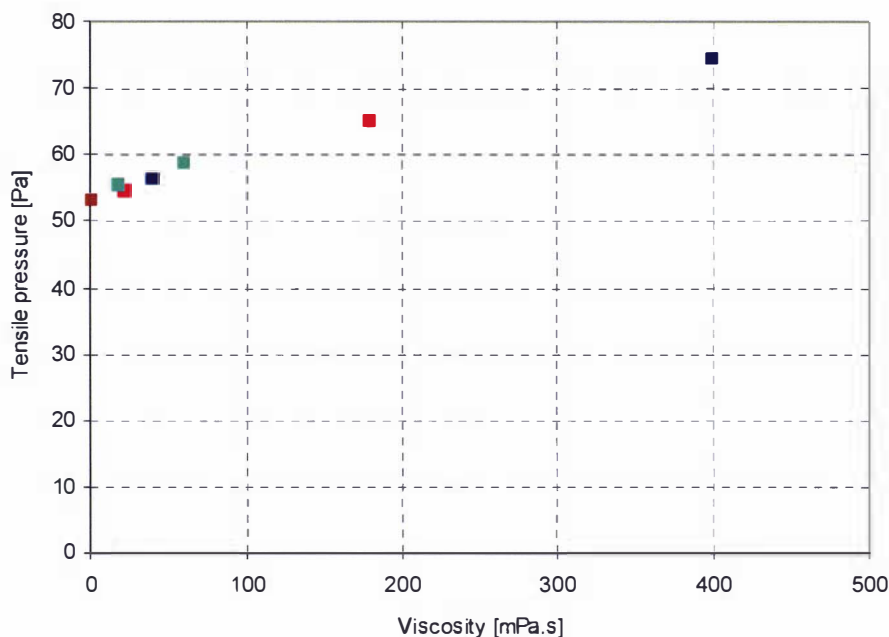


Figure 6.14: Tensile pressure as a function of maltodextrin viscosity. ■ water; ■ maltodextrin DE5; ■ maltodextrin DE10; ■ maltodextrin DE18.

In agreement with Nowakowski and Hartel (2002), there is an increase in stickiness with increasing viscosity prior to skin formation. After skin formation, the increase in stickiness was up to 10 times greater than that shown in Figure 6.14. The actual surface viscosity is not known but the stickiness is not likely to be dependent on viscosity alone. In addition, the surface tension of pure water and of 40% w/w maltodextrin DE5 solution droplets in this work ranged from 72.5 to 66.9 mN.m⁻¹ respectively (see Section 7.5.2). Such a small change in surface tension with concentration (during drying) is unlikely to be responsible for the changes seen in the droplet stickiness before skin formation. However, the surface tension of droplet solids concentrations above 40% w/w and during skin formation is not known. It is also unknown what the effects might be at surface tensions as low as 30 mN.m⁻¹ which can be attained with the addition of lecithin wetting agents (see Section 7.5.2). The single droplet drying tests showed that these wetting agents accumulate at the droplet surface and will likely be in competition with skin formation. Their effect will only be pronounced during the early stages of drying before skin formation. After this time, it is likely that they will be incorporated into the skin as a solid and may not act to lower surface tension but could plasticise the skin surface by lowering the surface glass transition temperature. Surfactant addition is worthy of future investigation.

Therefore, it is clear that viscosity or surface tension alone cannot be used to explain probe tack measurements of surface stickiness. The exact mechanism behind surface stickiness in skin forming materials remains unclear and, until the mechanism is understood the prediction of surface stickiness during the drying of foodstuffs will remain elusive.

6.8.5 Conclusions

It was shown from the trials above that in most cases the maltodextrins (DE5, DE10 and DE18) passed through a peak tensile pressure before reaching a state of non-adhesion. This was similar to that found by Adhikari (2002) for maltodextrin DE6. It is the skin-forming property of maltodextrins and the fact that they pass through to this state on non-adhesion that make them successful drying aids. The peak stickiness and state of non-adhesion were shifted to lower bulk moisture contents with increasing temperature in agreement with the findings of Adhikari (2002). The higher the molecular weight (i.e. lower DE) of the maltodextrin, the narrower the concentration range it was sticky for. The time duration for which the droplet remains in this sticky state is set by the diffusion rate through the skin and the evaporation rate from the surface. In these trials there was a clear trend in the time it takes the droplet to reach the point of non-adhesion with maltodextrin DE5 becoming non-sticky the fastest. However, without a measurement or predictive technique to confirm the moisture content and temperature of the droplet surface, the prediction of stickiness cannot be made.

6.9 RELATIONSHIP BETWEEN PROBE TACK TEST STICKINESS AND SURFACE GLASS TRANSITION TEMPERATURE

Some researchers consider that drying begins in the inner tube of a Würster coater; others consider that particles are still sticky at the exit of this tube [Guignon *et al.* (2002)]. The stickiness curves collected in this study show that differences in formulation and drying conditions probably account for these discrepancies. In fact, these curves could aid design of operation and formulation conditions as well as coating equipment design, particularly the atomiser distance from the bed of particles and the length of the Würster insert as demonstrated in Section 5.11. It was of interest to determine if a common critical X value exists for the maximum stickiness and the point of non-adhesion on the stickiness curves for the different materials and under the various conditions. However, the current experimental set-up limited the reliability of the data and seriously complicated the mathematical prediction of the drying kinetics. Consequently, predictions were not made. The relationship between the surface glass transition temperature and the probe tack test stickiness measurements is worthy of future investigation. The following is a brief discussion on the appropriate modifications to the experimental set-up required to investigate this relationship.

6.9.1.1 Glass transition data

Poor accuracy in the glass transition data limits the ability to draw a relationship between the probe stickiness measurements and the surface glass transition temperature. For example, the T_g in the literature for lactose can vary with 10 °C [Foster (2002)] dependent on the method and the sample preparation. The maltodextrins used in the thesis contained a relatively large molecular weight range, having been hydrolysed, which led to broad peaks which, in some cases, were undetectable. Predictions should improve with more accurate glass transition temperature data.

6.9.1.2 Non-continuous data and lack of replicates

The data collected was non-continuous in nature so it is difficult to pinpoint the actual peak tensile pressure or onset of non-adhesion. This primarily resulted from a time constraint. Future work should collect more data around these key points of interest and more replicates should be taken to increase the statistical significance of the measurements.

6.9.1.3 Morphological development

The use of the large 100 μ l hemispherical droplets and drying from one side imposed the most serious constraints to the stickiness test method. This led to non-uniform drying and resulted in significant morphological changes. The morphological variability is difficult to account for mathematically which introduces error into the prediction of the drying kinetics and hence surface conditions at the time the probe makes contact. During the drying of the 20% w/w initial solids concentration maltodextrin DE5 droplet at 78 °C, a large cavity appeared on the lee-side which most likely allowed preferential moisture transfer to occur. In some instances, particularly the glycerol plasticised droplets, the droplet centre collapsed under its own weight to give a crater. These morphological developments inevitably led to inhomogeneities on the droplet surface with some points showing significant stickiness whereas other parts were dry. Since a model does not account for local moisture content inhomogeneities on the droplet surface it is difficult to draw definitive conclusions on the overall stickiness of the droplet surface. Non-uniform drying also resulted in a non-constant contact area during probe approach and withdrawal which makes it difficult to draw quantitative conclusions about the degree of stickiness between formulations. Ultimately, it is the morphological development that limits the stickiness test method. However, the test does point out that surface inhomogeneities may exist in an industrial-scale spray droplet and lead to a probabilistic distribution of stickiness.

Morphological variability during stickiness testing may be minimised by using a thin film drying technique common in the modelling and drying kinetics literature [e.g. Yamamoto (1999); Räderer (2001); Adhikari (2002)]. A possible option would be to use a circular disc, 50 mm in diameter and 1 mm in depth. The disc should lie horizontal in a drying chamber and the drying air should impinge the top surface of the film to give even drying. The disc could enable multiple contacts on the same sample to reduce experimental time. It may also enable the collection of the moisture content history simultaneously with the stickiness measurements. An identical disc and solution could be placed beside the primary disc for the stickiness/moisture content history data collection and used simultaneously to collect the temperature history of the thin film. The disc should have a thin bottom and be made of aluminium so it provides an evenly distributed and constant heating rate to make the modelling easier. The walls of the disc should also be thin to minimise the peripheral heating of the thin film so it is a simple one dimensional modelling problem. The disc could then be simply mounted to the actuator assembly on the current experimental set-up.

It is believed that these modifications will significantly enhance the ease of collection, the accuracy and reliability of future data to investigate a possible relationship between the surface glass transition temperature and the stickiness measured by the probe tack test.

6.10 STICKINESS OF WHEY PROTEIN ISOLATE

It is the skin-forming property of maltodextrins and the fact that they reach a state of non-adhesion that make them successful drying aids. It was of interest to see whether the other high molecular weight potential coating materials would also exhibit the same behaviour. As mentioned in Chapter 4, the glass transition temperature for whey proteins is difficult to determine since protein denaturation occurs at a temperature (approximately 78 °C) prior to the glass transition temperature. The probe tack test would then represent an alternative method to assess stickiness of whey protein-based coating materials in the absence of a suitable method to measure T_g data. Figure 6.15 presents the characteristic stickiness profiles

of whey protein isolate (WPI) at the two standard drying temperatures and initial concentrations.

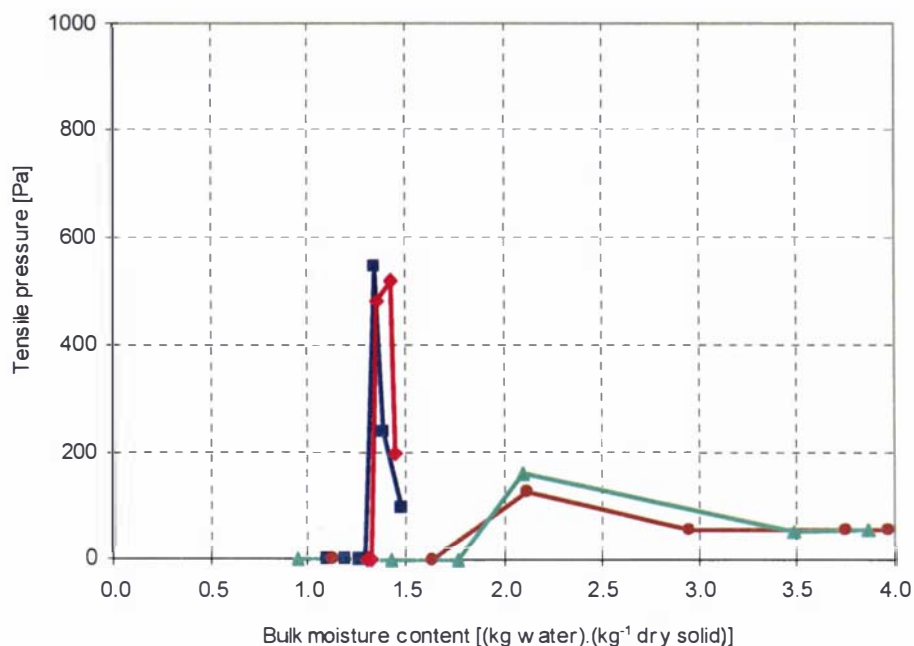


Figure 6.15: Stickiness of 100 µl whey protein isolate droplets during drying: ◆ 20% w/w, 40 °C; ▲ 20% w/w, 78 °C; ■ 40% w/w, 40 °C; ◆ 40% w/w, 78 °C.

The 40% w/w WPI stickiness profiles showed a rapid transition to a non-sticky surface which is similar to that found for 40% w/w maltodextrin DE5. However, there was no temperature dependence as shown in the maltodextrin DE5 trials. WPI appeared to be less sticky than maltodextrin DE5. Although the 20% w/w WPI droplets appeared to be sticky for a significant duration, they were only about twice as sticky as water (120 Pa compared with 54 Pa).

WPI dries faster than maltodextrin DE5 (see Section 5.12) so one would assume WPI to have a higher moisture content at the surface early on in the drying process and remain sticky for a little longer than it has done compared to maltodextrin DE5. However, there were significant differences between the single droplet drying tests and stickiness tests for WPI. The droplets were brittle and fractured easily and so it could be expected that preferential moisture transfer through these cracks occurs resulting in a drier surface than expected. In contrast, the stickiness tests yielded smooth, non porous skins which showed no sign of residual tack. This is likely a result of the larger droplet having a much lower drying rate which results in the outside surface becoming very strong in agreement with that stated earlier by Achanta and Okos (1995), that slower drying rates above the glass transition temperature leads to less porous crusts with viscous solution inside. This was the case with the WPI stickiness trials.

6.11 STICKINESS OF GUM ARABIC

Figure 6.16 presents the characteristic stickiness profiles of gum arabic at the two standard drying temperatures and initial concentrations of 20 and 30% w/w.

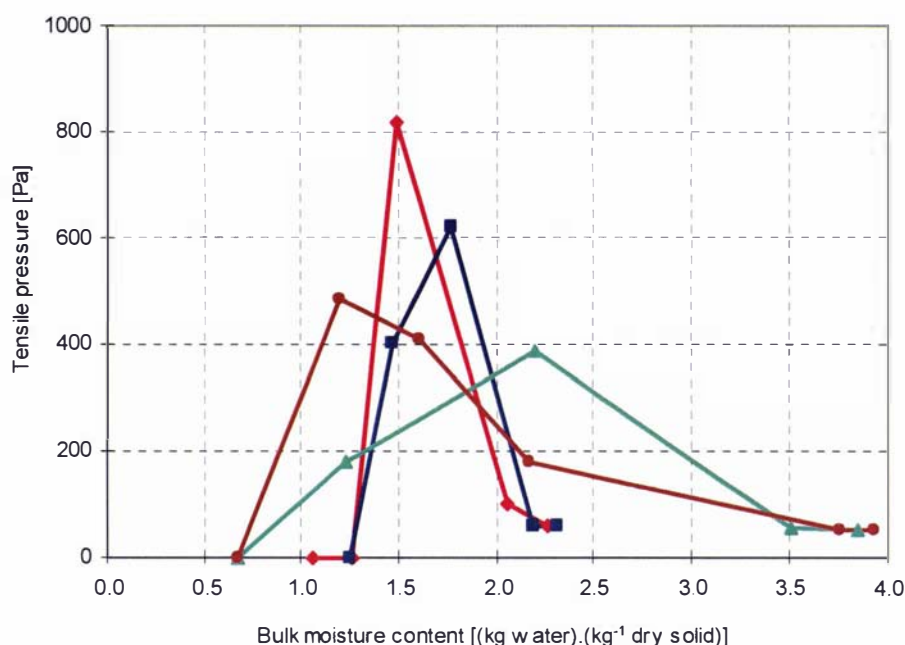


Figure 6.16: Stickiness of 100 μ l gum arabic droplets during drying: $\bullet$ 20% w/w, 40 °C; $\blacktriangle$ 20% w/w, 78 °C; $\blacksquare$ 30% w/w, 40 °C; $\blacklozenge$ 30% w/w, 78 °C.

Gum arabic remained sticky over a larger bulk moisture content range compared to maltodextrin DE5 and WPI. There was no significant difference in the point of non-adhesion with drying air temperature which is similar to the WPI trial at the higher initial solids concentration (in this case 30% w/w not 40% w/w). The skin formation did not appear to occur as quickly as in the maltodextrin DE5 or WPI trials (contrary to the Type II material described by Hassan and Mumford (1996)) possibly because of different initial concentration. However, the point of non-adhesion appeared at bulk moisture content of 1.2 kg.kg^{-1} , which was similar to that of maltodextrin DE5 ($1.2\text{--}1.3 \text{ kg.kg}^{-1}$) but was slightly lower than that of WPI, which occurred at 1.4 kg.kg^{-1} .

As with the WPI trial, the lower initial solids concentration (20% w/w) showed no temperature dependence on the point of non-adhesion (both occurred at around 0.7 kg.kg^{-1}), although a few more data points are required to confirm this. However, there did appear to be a slight effect on the point of maximum stickiness, which occurred at 2.2 kg.kg^{-1} for the 78 °C case and 1.25 kg.kg^{-1} for the 40 °C case. It also appeared that gum arabic showed signs of stickiness early on in the drying process and remained sticky for some time, which was similar to the 20% w/w maltodextrin DE5 concentration trials. This coincides with observations of a very thin and fragile skin forming on the surface (refer to Figure 6.10(k-o)) and hence many of the contacts ruptured the skin and the stickiness force was a result of the viscous fluid beneath the skin. It also showed tensile pressures similar to those found in the 20% w/w maltodextrin DE5 trials.

6.12 PLASTICISATION OF MALTODEXTRIN DE5 AND WHEY PROTEIN ISOLATE

Both maltodextrin DE5 and WPI represent good coating materials in terms of storage stability (based on their relatively high glass transition temperatures and low moisture sorption isotherms) and their good degree of resistance to oxygen diffusion. WPI also represents a material that can be tailored to produce both water-soluble and water-insoluble coatings for

controlled release applications. From the base case results presented above, it was clear that the skin formation in both maltodextrin DE5 and WPI at 40% w/w initial solids concentration was very rapid, leading to surfaces that became non-sticky over very narrow bulk moisture content ranges. Thus, these materials represent ideal coating materials because they limit the agglomeration potential in spray coating applications. However, the window for successful droplet adherence upon substrate impact is very narrow. Consequently, it is recommended that, when using these materials, the spray nozzle should be close enough to the bed of particles to ensure that the droplets impinge with significant surface moisture content to allow them to stick.

The single droplet drying tests in Chapter 5 revealed that these same materials (particularly WPI) were brittle under certain conditions. Plasticisers were found to reduce crack formation but in most cases led to a qualitative increase (finger and thumb) in the surface stickiness of the droplets. It is believed that plasticiser addition will lead to a widening of the characteristic curves and thus provide a useful means to tailor the stickiness of the droplets and coatings. Trials employing 40% w/w initial solute concentration at a plasticiser level of 3:1 were carried out at the two standard drying temperatures. The plasticisers were again glycerol and maltodextrin DE18. Figure 6.17 shows the effect of plasticiser addition on the stickiness of maltodextrin DE5.

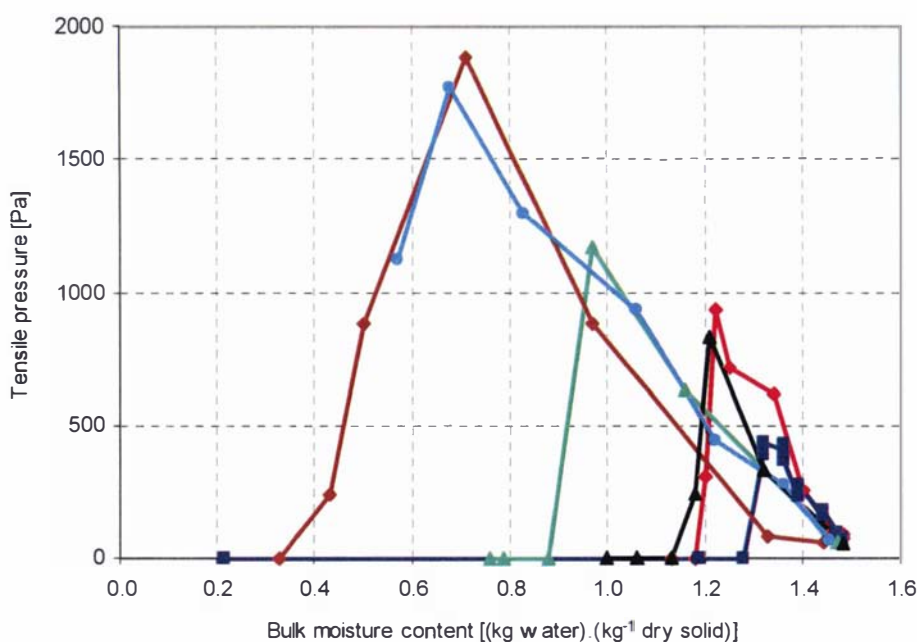


Figure 6.17: Effect of plasticiser addition on the stickiness of 100 μ l maltodextrin DE5 droplets during drying: ■ 40% w/w, 40 °C; ◆ 40% w/w, 78 °C; ▲ 40% w/w DE5:glycerol, 40 °C; ● 40% w/w DE5:glycerol, 78 °C; ▲ 40% w/w DE5:DE18, 40 °C; ● 40% w/w DE5:DE18, 78 °C.

All maltodextrin DE5 plasticisation trials resulted in wider stickiness profiles. It was found that, in all the maltodextrin DE5 plasticisation trials, the nature of the stickiness bond appeared to show far greater ‘spot tack’ character (i.e. $\approx$ 10% bonding) and careful consideration had to be given to the point of non-adhesion as being representative of the majority of the sample surface.

The onset of stickiness remained unchanged with the addition of either plasticiser to maltodextrin DE5. The addition of glycerol or maltodextrin DE18 at 78 °C had the same

plasticising effect on 40% w/w maltodextrin DE5, shifting the point of non-adhesion from 1.2 kg.kg^{-1} to approximately 0.4 kg.kg^{-1} . At 40°C , maltodextrin DE18 showed a lower plasticisation ability as a state of non-adhesion occurred earlier at a bulk moisture content of approximately 1.2 kg.kg^{-1} , as opposed to around 0.9 kg.kg^{-1} for glycerol. In the high temperature case, the maximum tensile pressure was almost twice as high as that for maltodextrin DE5 alone (notwithstanding the reliability of drawing comparisons between trials based on tensile pressure, as mentioned earlier). This suggests that, in all cases, the lower molecular weight compounds in the formulation were present at the surface to plasticise the skin as it formed, possibly slowing the thickness development of the skin. However, as it heads toward the non-adhesive state at around 0.75 kg.kg^{-1} the appearance of maltodextrin DE5 at the surface must also be significant because, if it was dominated solely by maltodextrin DE18, the non-adhesive state should not appear until at least a bulk moisture content of 0.5 kg.kg^{-1} (see Figure 6.11). In general, the peak tensile pressures for the plasticised droplets were higher than that of the unplasticised droplets. This is in agreement with Felton and McGinity (1999) who found that stronger adhesion occurred when the T_g of the film was lower.

Without knowing the properties of the surface, it is unclear why the larger peak tensile pressures resulted for the higher temperature cases. It is possible that, because of the lower rigidity of the surface skin, more bonding contact area can occur, leading to increased bond strength and larger peak tensile pressures. This points to the complicating skin development that makes interpretation and prediction of stickiness in film-forming materials difficult.

Interestingly, the maltodextrin DE5 droplet plasticised using maltodextrin DE18 at 40°C showed a similar profile to that of maltodextrin DE5 alone at 78°C . This would enable drying at lower process temperatures while achieving the same degree of stickiness. This may prove to be economically beneficial in a coating process. Figure 6.18 shows the effect of plasticiser addition on the stickiness of WPI.

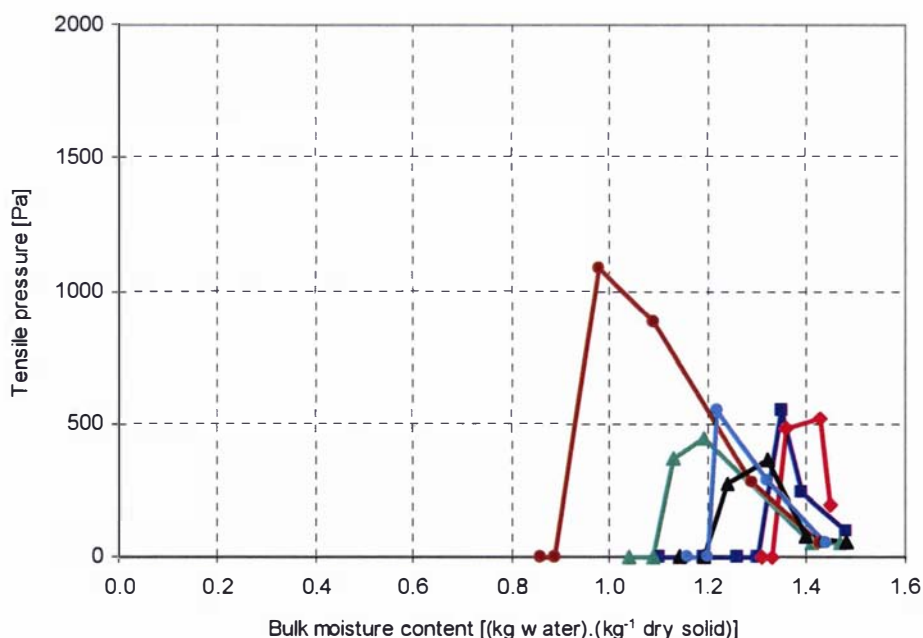


Figure 6.18: Effect of plasticiser addition on the stickiness of $100 \mu\text{l}$ whey protein isolate droplets during drying: ■ 40% w/w, 40°C ; ◆ 40% w/w, 78°C ; ▲ 40% w/w WPI:glycerol, 40°C ; ● 40% w/w WPI:glycerol, 78°C ; ▴ 40% w/w WPI:DE18, 40°C ; ◆ 40% w/w WPI:DE18, 78°C .

Similar to the maltodextrin DE5 trials, glycerol had a far greater plasticising effect than maltodextrin DE18 for the WPI/plasticiser stickiness profiles. However, maltodextrin DE18 and glycerol did not plasticise the surface to the same extent, because the point of non-adhesion occurred above a bulk moisture content of 0.8 kg.kg^{-1} for all trials. The shift in the point of non-adhesion was again evident with increasing temperature when glycerol was added but not with maltodextrin DE18 as it had the same point of non-adhesion at around 1.2 kg.kg^{-1} . There was little difference in the maltodextrin DE18 plasticiser trials. There appeared to be a difference in the plasticising effect between glycerol and maltodextrin DE18 at 78°C , with the latter showing a point of non-adhesion at 1.2 kg.kg^{-1} as opposed to 0.9 kg.kg^{-1} . The reason for this is unclear. In general, the plasticisers had a greater effect on maltodextrin DE5 than they did on WPI, probably because they show a greater chemical similarity to maltodextrin DE5. It would appear that rapid skin formation (as is the case for WPI) will result in a lower degree of stickiness control achieved by the plasticisers at their current levels.

Plasticiser levels as low as 25% w/w (considering that many industrial operations use them at around 50% w/w dry basis) can markedly affect the stickiness characteristics of a coating formulation droplet during drying, giving added flexibility to the formulator. Hence, the probe tack test is a useful tool to tailor coating formulations prior to pilot-scale coating trials.

6.13 CONCLUSIONS AND RECOMMENDATIONS

The probe tack test was used to map the level of stickiness of droplets of different coating materials as they dried. Stickiness can be maximised to increase droplet adhesion efficiency on to the substrate or it can be minimised to decrease the likelihood of inter-particle agglomeration once impinged upon the substrate. The probe tack test provided the following useful guidelines to optimise formulation and operating conditions to control formulation stickiness:

- Surface stickiness occurred during drying. As skin formation progressed, the stickiness passed through a maximum, in most cases to arrive at a point at which the droplet was no longer sticky at all (non-adhesive state).
- The time it took for the sticky transition to begin and to traverse to the non-adhesive state was dependent on both the formulation and the drying air conditions.
- The only consistent trend throughout the majority of the trials was that of a temperature shift, which saw higher temperature systems having maximum tensile pressures (stickiness) and the state of non-adhesion occurring at lower bulk moisture contents.
- Lower DE (higher molecular weight) maltodextrins had sharper stickiness profiles which meant the droplet was sticky for less time.
- Gum arabic had a broad stickiness profile, which is consistent with a much thinner skin forming on the surface.
- Whey protein isolate has a similar characteristic stickiness curve to maltodextrin DE5 suggesting it would also be a good drying aid although many times more expensive. However, it represents an excellent potential coating candidate as it can provide coatings that are both water-soluble and water-insoluble when processed below or above the protein denaturation temperature.
- The addition of glycerol and maltodextrin DE18 as plasticisers (to tailor coating properties) resulted in the broadening of the stickiness curves.

The above guidelines present a qualitative understanding of the stickiness of droplets as they dry and provides a few rules of thumb. With further modifications, in particular, the use of a thin film drying sample, the probe tack test could be a quick, quantitative and reproducible evaluation system for comparison of the stickiness of coating formulations. This would enable the formulator to screen a large number of potential formulations quickly and at less expense to running laboratory-scale coating trials. Future work should investigate a possible relationship between the predicted surface glass transition temperature and the stickiness measured by the probe tack test.

CHAPTER 7

DROPLET IMPACT AND SPREADING

7.1 INTRODUCTION

The impact and spreading of coating droplets on the surface of a dairy powder particle is a key micro-level process that affects coating quality parameters such as coating thickness and coating coverage. In air-suspension particle coating, it is desirable to optimise the formulation and the process conditions to achieve a maximum droplet spread diameter that does not splash or rebound. It is believed that good droplet spreading will lead to tighter control of the film thickness and more coherent coatings. This chapter sets out to develop an understanding of the impact and spreading micro-level process with respect to dairy powder applications. Firstly, a brief background to the theory of droplet impact and spreading is presented to compliment that found in the ‘focused literature review’ (Chapter 3). Secondly, an experimental set-up for investigating key formulation and operating parameters that control droplet impact and spreading is described. Thirdly, formulation and operating guidelines are established to maximise the droplet spread diameter in an industrial-scale Würster coating operation.

7.2 DROPLET IMPACT AND SPREADING

7.2.1 Phenomenological explanation of droplet impact and spreading

Figure 7.1 shows the impact, maximum spreading and recoil positions of a droplet on a smooth, flat surface.

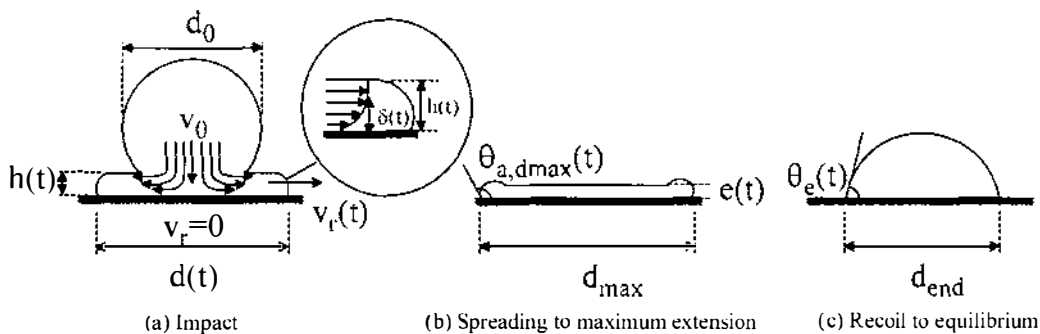


Figure 7.1: Schematic of the impact of a droplet on a smooth, flat surface: d_0 = initial droplet diameter [m]; $d(t)$ = droplet diameter in contact with the substrate surface [m]; d_{max} = maximum spread diameter [m]; v_0 = initial impact velocity [m.s^{-1}]; $v_r(t)$ = radial spreading velocity [m.s^{-1}]; $\delta(t)$ = droplet boundary layer thickness [m]; $h(t)$ = spread film height; $e(t)$ = thickness of flattened middle droplet zone [m]; $\theta_{a,dmax}(t)$ = advancing contact angle at d_{max} [°]; $\theta_e(t)$ = equilibrium (receding) contact angle after recoil [°]. (t) denotes that the variable is a function of time [adapted from Mourougou-Candoni *et al.* (1999)].

Droplet impact and spreading has been described by a normalising ‘spread factor’, $\xi(t)$ [–], which is the ratio of the droplet spread diameter, $d(t)$ [m] (with respect to time), on the substrate surface to the initial droplet diameter, d_0 [m], prior to impact, represented by Equation (7.1).

$$\xi(t) = d(t)/d_0 \quad (7.1)$$

Two key values are determined from Equation (7.1): the maximum spread factor, ξ_{max} [–], and the final spread factor, ξ_{end} [–], which simply replace $d(t)$ with the maximum spread diameter, d_{max} [m], and the final spread diameter, d_{end} [m], respectively. Figure 7.2 shows the evolution of the spread factor for a water droplet impinging on a flat, dry glass surface.

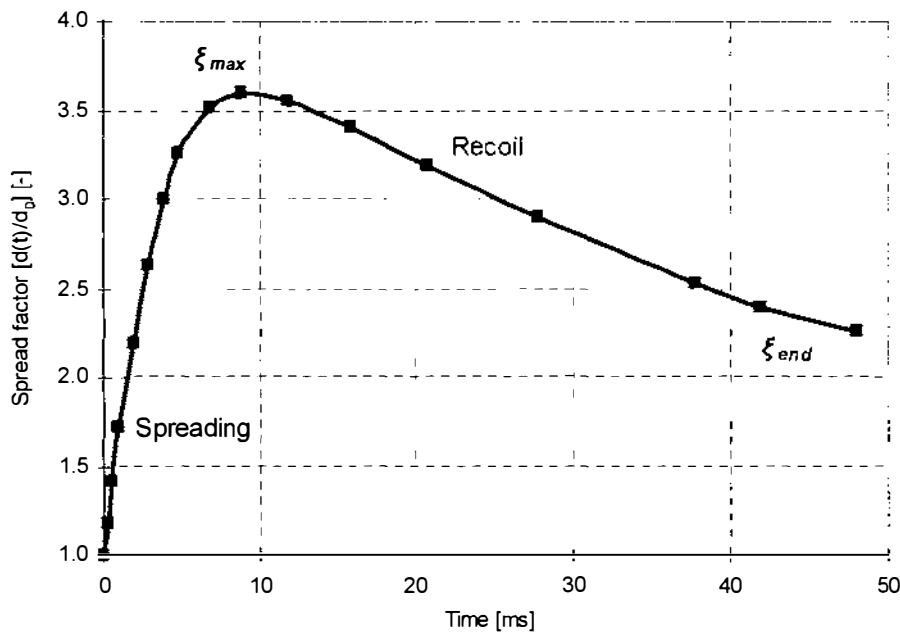


Figure 7.2: Evolution of the spread factor for a water droplet of diameter 3.4 mm impinging at 1.5 m.s^{-1} on to a flat, dry, glass surface [adapted from Zhang and Basaran (1997)].

The droplet approaches the surface with kinetic energy and surface energy. As it impacts the surface, the droplet flattens and spreads across the surface to often resemble a thin disc or ‘pancake’ shape. During the flattening process, the initial impact energy is dissipated in overcoming viscous forces and creating new surface area [Crooks *et al.* (2001)]. When this initial impact energy is depleted, the droplet reaches d_{max} (or ξ_{max} in Figure 7.2) and recoils as a result of the large surface energy established from the flattened droplet and the need to reach equilibrium at the three-phase contact line, d_{end} (or ξ_{end} in Figure 7.2). The inertial forces result from the kinetic energy of the droplet, and are determined by the droplet size, density and velocity. Meanwhile, the fluid viscosity of the droplet governs the viscous dissipation, and the surface tension force establishes the energy that is required to deform the droplet. These parameters are typically used to define two dimensionless numbers that gauge the relative strength of the forces that oppose one another. The Reynolds number, Re [–], is the ratio of the inertial and viscous forces, and the Weber number, We [–], is the ratio of the inertial and surface tension forces. In other words, the inertial forces are in competition with viscous dissipation and the deformation of the droplet.

$$Re = \frac{\rho_d v_0 d_0}{\mu_d} \quad (7.2)$$

$$We = \frac{\rho_d v_0^2 d_0}{\gamma_{lv}} \quad (7.3)$$

where ρ_d , v_0 , d_0 and γ_{lv} are the droplet density [kg.m^{-3}], the initial droplet impact velocity [m.s^{-1}], the initial droplet diameter [m] and the droplet surface tension (liquid–vapour) [N.m^{-1}] respectively. The competition between the viscous and surface tension (capillary) forces can be described by a third dimensionless quantity known as the Capillary number, Ca [–]. This quantity is expressed simply as $Ca = We/Re$, the ratio of the droplet Weber and Reynolds numbers.

7.2.2 Prediction of droplet impact and spreading

The dynamics of single droplet impact have been thoroughly investigated and are reasonably well understood. Several complex (three-dimensional) numerical models [e.g. Ghafouri-Azar *et al.* (2003)], which require numerical solution of the Navier–Stokes equations have been published but are beyond the scope of this thesis for reasons explained below.

According to Pasandideh-Fard *et al.* (1996), several simple analytical models of droplet impact have been proposed, based on an energy balance that equates the initial droplet kinetic energy to the change in surface energy due to droplet deformation and the work done in overcoming liquid viscosity during impact. The three phenomena of common interest in droplet impact studies are the occurrence of splashing, the final spread diameter and the maximum spread diameter [Scheller and Bousfield (1995)]. Most of the published work is in metallurgical microfabrication and has investigated ζ_{max} in which the actual coverage area of the droplet has been set by maximum spreading due to: cooling solidification, uptake of liquid into a porous substrate, or surface roughness holding the liquid in the area of maximum spread [Scheller and Bousfield (1995)]. Thus, these simplified analytical models predict ζ_{max} [Scheller and Bousfield (1995)]. No simplified analytical models exist that describe the final spread diameter, or ζ_{end} , let alone an investigation devoted to maximising ζ_{end} .

The final spread diameter was the parameter of interest to this work. The maximum spread diameter is of less interest because droplet spreading cannot be arrested at this point during air-suspension particle coating; impact, spreading and recoil are very rapid, occurring over a few microseconds [Toivakka (2003)]. Scheller and Bousfield (1995) stated that, if the surface energy of a plastic film is constant, the final spreading should be set by the liquid surface tension and not be dependent on the impact velocity. Their experiments showed the contrary, i.e. a positive effect of the impact velocity on the final spread factor. They attributed this to the difference in the advancing and receding contact angles as a droplet spreads and then recoils. This suggests that the simple thermodynamic wetting analysis, making use of Young's equation (Equation (6.1)) to aid prediction of the extent of spreading of a droplet on powdered surfaces, does not adequately describe the full extent of spreading. Given that no simple models for ζ_{end} exist and the limited use of Young's equation, it is reasonable to make use of a simplified ζ_{max} model to guide this research. This simplified approach should then be sufficient to provide insight into control of the coating quality and coater performance as a function of key formulation and operating variables.

7.2.3 Simplified droplet impact and spreading model

Bennett and Poulikakos (1993) reviewed several simplified analytical models for droplet spreading. They pointed out that the role of surface tension was similar between the models but the treatments of the viscous energy dissipation were dissimilar. According to Bennett and Poulikakos (1993), Madejski's (1976) analytical model is the most frequently quoted and has the most published experimental support. It is considered to provide the most theoretically sound treatment of viscous energy dissipation but effectively ignores the initial surface tension energy prior to impact and the contact angle effect during spreading. Several later models have provided a better representation of the surface tension effects [Bennett and Poulikakos (1993); Pasandideh-Fard *et al.* (1996)] whilst retaining the superior description of the viscous energy dissipation provided by Madejski (1976). Pasandideh-Fard *et al.* (1996) developed a simple energy conservation model to predict the maximum spread diameter of droplets during impact [refer to Aziz and Chandra (2000)]. This model equates the droplet energy before and after impact, accounting for the energy dissipated during impact, and is represented by Equation (7.4).

$$KE_1 + SE_1 = SE_2 + W + \Delta KE \quad (7.4)$$

The initial kinetic energy, KE_1 [J], the pre-impact surface energy, SE_1 [J], and the change in kinetic energy due to solidification, ΔKE [J] (i.e. all the kinetic energy in this layer is assumed to be lost), are given by:

$$KE_1 = \left(\frac{1}{2} \rho_d v_0^2 \right) \left(\frac{\pi}{6} d_0^3 \right) \quad (7.5)$$

$$SE_1 = \pi d_0^2 \gamma_{lv} \quad (7.6)$$

$$\Delta KE = \left(\frac{1}{2} \rho_d v_0^2 \right) \left[\frac{\pi d_{max}^2}{4} s \right] \quad (7.7)$$

where ρ_d , v_0 , d_0 , d_{max} , γ_{lv} and s are the droplet density [kg.m^{-3}], the initial droplet impact velocity [m.s^{-1}], the initial droplet diameter [m], the maximum droplet spread diameter [m], the droplet surface tension (liquid–vapour) [N.m^{-1}] and the thickness of the solidified layer [m] respectively. After impact, when the droplet has reached d_{max} , its kinetic energy is zero, and the surface energy at maximum droplet extension, SE_2 [J] is:

$$SE_2 = \frac{\pi}{4} d_{max}^2 \gamma_{lv} (1 - \cos \theta_a) \quad (7.8)$$

where θ_a is the advancing liquid–solid contact angle [°]. The work done in deforming the droplet against viscosity, W [J] is given by:

$$W = \frac{\pi}{3} \rho_d v_0^2 d_0 d_{max}^2 \frac{1}{\sqrt{Re}} \quad (7.9)$$

The determination of W is subject to some key assumptions made by the Pasandideh-Fard *et al.* (1996) model, which are discussed later in this chapter. In the meantime, Equation (7.10) serves only as a guide to determining the crucial parameters rather than the actual extent of

spreading. A simple expression for ξ_{max} is obtained by using the energy conservation condition in Equation (7.4) and combining Equations (7.5)–(7.9) along with the Reynolds and Weber numbers.

$$\xi_{max} = \frac{d_{max}}{d_0} = \sqrt{\frac{We + 12}{\frac{3}{8}We s^* + 3(1 - \cos \theta_a) + 4\left(\frac{We}{\sqrt{Re}}\right)}} \quad (7.10)$$

where s^* is the dimensionless thickness [–] of the solidified layer ($= s/d_0$). The model has been shown to agree well with experiments on relatively large molten metal droplets (2.2 mm in diameter) and for low impact velocities (2.5 m.s^{-1}), whereas the droplets in most metallurgical microfabrication applications are much smaller and travel with considerably greater speeds. At least qualitatively, these models have been shown to be quite similar to real industrial applications [Ghafouri-Azar *et al.* (2003)].

Pasandideh-Fard *et al.* (1996) obtained favourable comparisons (within 15% maximum error) between predictions and the experimental results of other researchers (encompassing data with $213 < Re < 35\,339$ and $26 < We < 641$). The most relevant to this work are comparisons with the results of Ford and Furmidge (1967) for water droplets on beeswax, cellulose acetate and glass surfaces. The beeswax surface is hydrophobic and so is the milkfat used in this work. Glass is a hydrophilic surface, and is of interest in terms of a coating droplet impinging upon an already coated area. Thus, this simplified spreading model predicts well the maximum spreading diameter for a number of applications not dissimilar to that proposed in this work.

7.2.4 Controlling droplet impact and spreading

The simplified analytical model can be used to understand how to control impact and spreading outcomes. The three terms in the denominator of the right-hand side of Equation (7.10) represent the three effects that restrain droplet spreading: solidification, surface tension and viscous dissipation respectively. The model requires knowledge of the material properties of advancing liquid–substrate contact angle, density and viscosity, and knowledge of the process parameters of droplet size and velocity. The driving force for impact spreading is the kinetic energy of the droplet, whereas flow resistance is provided by the viscosity and surface tension of the liquid [Toivakka (2003)]. According to Toivakka (2003), the contact angle will either promote or resist spreading, although Toivakka found little effect on d_{max} under the conditions used in his modelling investigations. Intuitively, one would expect low contact angles to promote spreading.

Equation (7.10) (using a value of 0 for s^* , i.e. no solidification during spreading, and physical data in Table 7.1) was used to generate surface response plots in Figure 7.3 depicting the maximum spread factor as a function of both the initial droplet diameter and the impact velocity under industrially and experimentally relevant conditions. An advancing contact angle had to be carefully selected. Dynamic contact angles depend on velocity and the direction of the contact line [Mourougou-Candoni *et al.* (1999)] and are known to increase with increasing contact line velocity. For a 2 mm diameter water droplet impacting stainless steel at 1 m.s^{-1} [e.g. Pasandideh-Fard *et al.* (1996)], reveals that an initial static equilibrium contact angle of approximately 90° increases with increasing contact line velocity to a maximum of 110° . Once the droplet reached its maximum extension the spread diameter remained constant while the contact angle decreased until it reached its minimum value,

called the receding contact angle, which was 40° . The receding contact angle is lower than the advancing contact angle as the spread droplet recoils on a modified substrate surface as it leaves a very thin liquid film behind on the surface [Pasandideh-Fard *et al.* (1996)]. The static equilibrium contact angle for a water droplet on anhydrous milkfat was 67° . Measurement of the actual advancing contact angle could not be made at this time, so a value of 90° was used to construct the surface plots below.

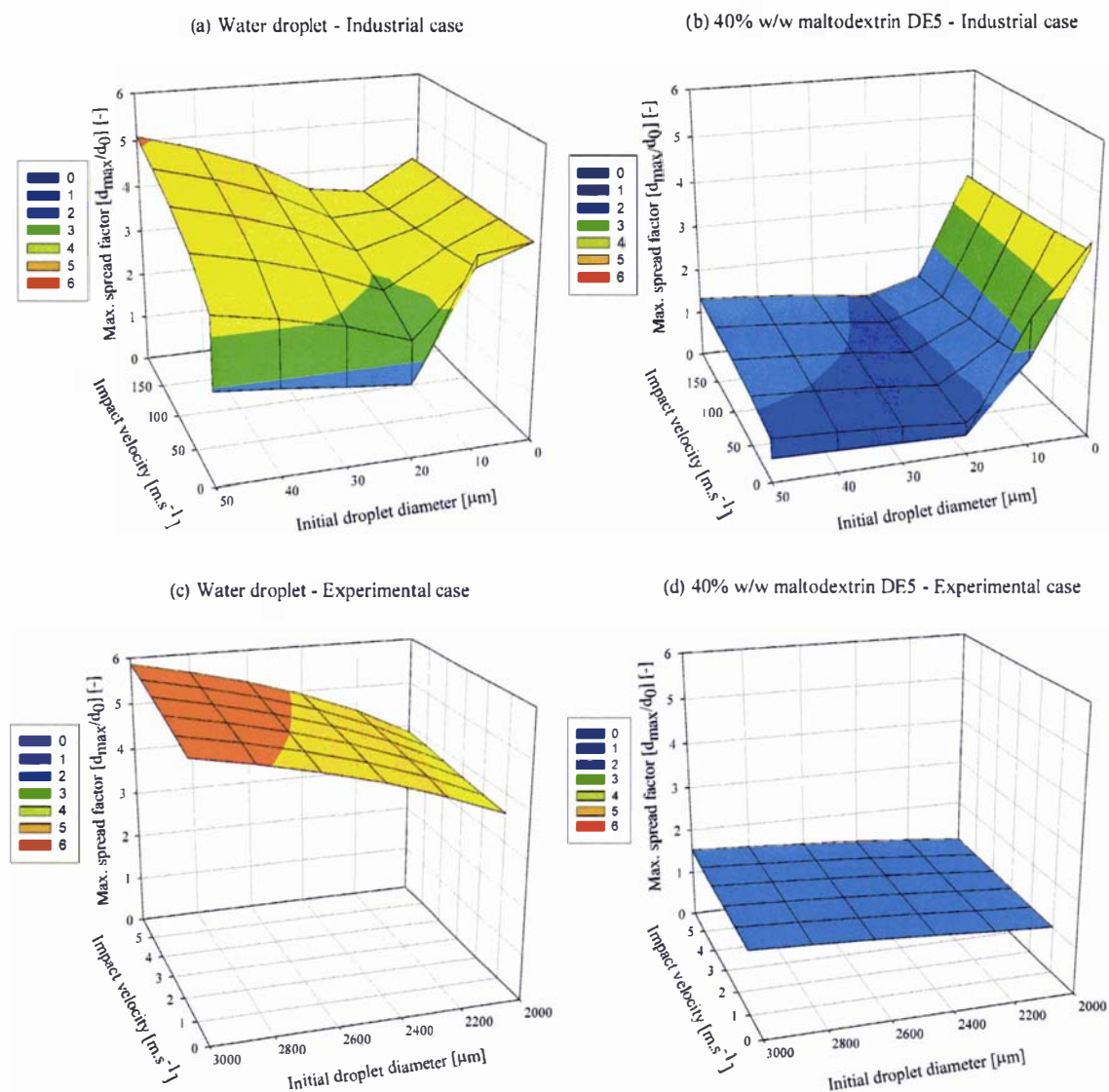


Figure 7.3: Maximum spread factor predicted by the Pasandideh-Fard *et al.* (1996) model for industrial and experimental conditions on to an anhydrous milkfat surface.

The plots above reveal some anomalies. Firstly, it can be seen in both industrial cases that a concavity occurs in the response surface at droplet diameters of $20\ \mu\text{m}$. This is not in agreement with that expected based on the larger droplets having a higher initial kinetic energy on impact to drive them to greater spreading extents. The effect of impact velocity is not as significant as one would expect, with the exception that as the impact velocity approaches $0.1\ \text{m.s}^{-1}$, the maximum spread factor drops away dramatically. Of particular note is the prediction for the 40% w/w maltodextrin DE5 industrial case at $20\ \mu\text{m}$. There are combinations yielding spread factors below unity, meaning the maximum spread diameter is below that of the initial droplet diameter, which suggests spreading does not occur at all. The model clearly does not predict that expected for 40% w/w maltodextrin DE5 droplets under

industrially relevant conditions. This incorrect prediction is likely to result from the analytical expression used in the model to determine the boundary layer thickness. This expression was made on the assumption that liquid flow in the droplet can be represented by axisymmetric stagnation point flow. The boundary layer thickness will be a function of the droplets Re number and hence prediction outside the Re numbers for which the model was developed are not likely to be accurate. As shown in Figure 7.5, both the experimental and industrial-scale Re and We numbers are well outside the range that the model has been successfully able to predict.

Although the model would not predict an industrial situation its analysis is worthwhile based on droplet sizes and velocities that would be employed in the experiments here to provide useful insight into tailoring experiments. Firstly, viscosity dramatically affects maximum spread factor, i.e. higher viscosities lead to lower spread diameters as more impact energy is dissipated in work done against viscosity. For the water case, the effect of impact velocity on maximum spread factor is not as strong as one would expect. It is unclear why this lack of effect exists. The almost linear increase in maximum spread factor with increasing initial droplet diameter is as expected because of the cylindrical surface area and spherical volume relationship.

While it is not entirely clear whether the model predictions are accurate, it suggests that viscosity is a critical variable controlling droplet impact behaviour.

7.3 METHOD SELECTION

The impact and spreading of droplets usually involves a droplet production technique and a droplet visualisation system. Studies involving the impact and spreading of molten metal droplets typically use a high pressure reservoir to deliver a droplet to the end of an orifice [e.g. Attinger *et al.* (2000)]. Droplets are usually of the order 2 mm in diameter. In the spreading and infiltration of inkjet droplets an inkjet print-head and cartridge are normally employed to give droplet diameters in the 50 μm range [e.g. Holman *et al.* (2002)]. Due to difficulties in visualising such small droplets with the available equipment along with the very low viscosity constraints in using an inkjet print-head (actually trialled) a simple syringe delivery system was opted for. This droplet production method has been used by numerous researchers [Pasandideh-Fard *et al.* (1996); Aurenty *et al.* (1997)]. Droplets produced by this method were between 2 and 3 mm in diameter. They were easy to measure, reproducible and are of the same size as those studied in the single droplet drying experiments (Chapter 5).

7.4 EXPERIMENTAL SET-UP

7.4.1 Set-up overview

Figure 7.4 is a photograph of the experimental set-up used in the droplet impact and spreading investigations.

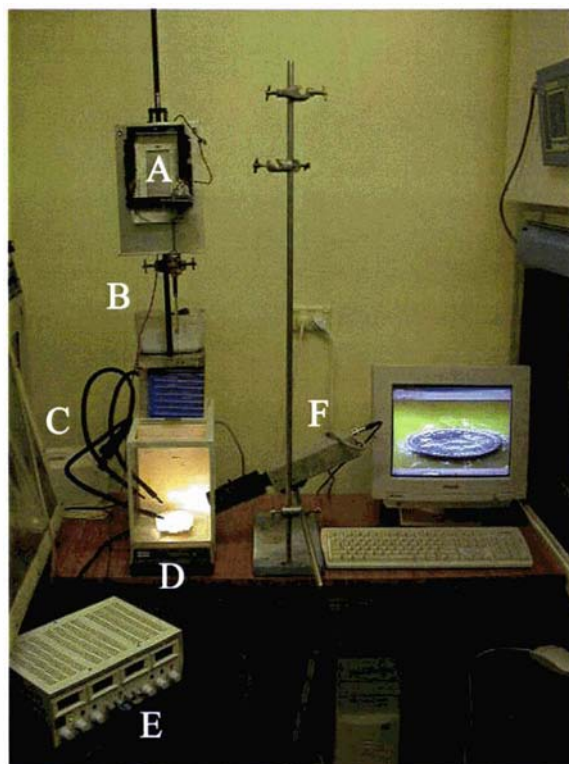


Figure 7.4: Photograph of the experimental set-up used for the droplet impact and spreading investigations: A = syringe plunger driving system; B = syringe; C = fibre optic light source; D = digital mass balance; E = power supply; F = video camera (25 and 2 475 frames per second).

The apparatus consisted of a droplet production system and an image acquisition system; they are detailed individually below.

7.4.2 Droplet production and impact velocity determination

A single droplet was allowed to form at the tip of a 100 μl gas-tight syringe (Hamilton Company, Reno, NV, USA). The syringe (B) was mounted to a stainless steel backing plate and coupled to a DC motor-driven computer CD-ROM disc drive (A) that was used to mechanically drive the syringe plunger down the syringe barrel to deliver a droplet. The speed of delivery could be manipulated by voltage control on a standard power supply (E). When the gravity force on the droplet exceeded the surface tension forces attaching the growing droplet to the end of the hypodermic needle (25 gauge, 0.26 mm internal diameter, flat end), the droplet fell over a predetermined distance towards the test surface.

The impact energy of the droplet (a function of the droplet size, density and velocity) can be varied by the choice of internal needle diameter and fall height of the droplet. The single gauge needle size was used in all the experiments. Smaller droplet sizes were not possible because the high viscosity of the 40% w/w maltodextrin DE5 solution (242.7 mPa.s) limited the needle size to gauges higher than that used here. Droplet diameters were reproducible but were dependent on the solution density and particularly the presence of surfactants. Experimental calculations were always normalised based on initial droplet diameter to account for the small variations in droplet diameters delivered. The effect of droplet size variations is discussed in Section 7.6.3.4. Hence, the only method of affecting droplet impact energy was via velocity which was manipulated by adjusting its fall height.

The impact velocity as a function of the fall height was calculated by considering a momentum balance over a falling droplet given by Equation (A2.6). Numerical integration of Equation (A2.6) gave a terminal velocity of around 8.3 m.s^{-1} for a 2.8 mm diameter water droplet which compared favourably to the terminal velocity (8.0 m.s^{-1}) calculated using the non-iterative procedure of Clift *et al.* (1978). To achieve a velocity of 8.3 m.s^{-1} , fall heights of at least 20 m are required. Such heights were not practical due to construction limitations and droplet trajectory deviations from the available field of view the camera was able to capture. For large fall heights a plastic sheath was used to isolate the droplets fall to the test plate from air flow fluctuations in the laboratory. The maximum droplet velocity attainable that gave reasonable reproducibility was 5.4 m.s^{-1} , which corresponded to a fall height of 1.9 m.

Using the high speed camera (camera system II detailed below) it was found that the impact velocity of the droplets measured just prior to the point of impact with the test surface (by considering the vertical distance travelled between a set number of frames) agreed well (-6%) with that calculated using Equation (A2.6).

7.4.3 Image acquisition and analysis

Two camera systems were used in this study. Since initial interest was to maximise the final spread diameter, camera system I (item F in Figure 7.4) utilised a standard CCD camera (TK-1281 EG colour video camera, JVC Company of America, Wayne, NJ, USA). The analogue image was captured digitally with a video capture card (WinFast TV2000 XP, Leadtek Research Inc., Taipei, Taiwan) and bundled software (Ulead VideoStudio 6 SE DVD, Taipei, Taiwan).

The initial droplet diameter prior to impact could not be captured at the standard frame rate (25 frames per second) and had to be inferred by mass and density measurements once it landed on the test plate which sat on a 4 decimal place digital mass balance (Mettler AE200, Mettler-Toledo International Inc., Columbus, OH, USA) (item D in Figure 7.4). The weighing process usually took 2–4 s to stabilise.

Camera system II was used for the dynamic series of experiments. This was a high speed camera (Mega Speed MS-1000, Canadian Photonic Labs Inc., Minnedosa, Manitoba, Canada) rented from the University of Canterbury, Christchurch, New Zealand (contact John Abrahamson). Although capable of frame rates up to 50 000 frames per second (fps), the rather large field of view required ($18 \times 18 \text{ mm}$) for the experiments, due to deviations in the impact position from deviations in the droplet trajectory and variable spread diameters, limited the highest frame rate to 2 475 fps. This gave an image resolution of 400×200 pixels. The camera comes with its own data acquisition card (National Instruments, Austin, TX, USA) that runs with the software provided by Canadian Photonic Labs Inc.

In general, a standard camera angle around $30\text{--}40^\circ$ from the horizontal plane of impact was used to observe changes in droplet diameter (primary concern) and height. However, due to differences in solution transparency, slight adjustments were required at times. This meant that a separate calibration was required each time the camera position was altered. Given the inherent scatter in the data, a simple two point calibration was carried out correlating the number of pixels occupied by a standard coin (360 pixels horizontal direction, vertical direction varies due to camera angle) to its real dimensions (diameter = 17.5 mm). The correction factor was used to scale the digital images to real dimensions. The distance (number of pixels) for calibration (and for droplet diameter measurement) was made using

image analysis software (SigmaScan® Pro 5, Statistical Solutions, Saugus, MA, USA). Measurement of the Feret mean diameter (diameter of a circle having the same measured area as an irregular shaped droplet) was not warranted given the limited increment in accuracy for the effort required. This was due to the inherent scatter, sometimes non-uniform droplet diameters and rectangular pixels (aspect ratio of 0.8). As a result, a single horizontal diameter was always taken. If the droplet was not uniform it was not measured. Eight replicate measurements (for the d_{end} experiments) were usually taken. Three replicate measurements were taken for d_{max} in the dynamic droplet impact and spreading tests.

Both cameras made use of the same Fujinon-TV zoom lens (1:12/12.5-75, H6X12.5R, Fujinon Inc., Wayne, NJ, USA). The aperture was used to good effect to help to elucidate the droplet on the highly reflective anhydrous milkfat test plate surfaces. Observations were facilitated by the use of a Schott 150 W AC cold light source (KL1500, Schott Glas, Mainz, Germany) incorporating three goose-neck-mounted fibre optic lights (item C in Figure 7.4) to enable accurate light source positioning close to the droplet and the surface. Because of the high reflectivity of the AMF surface, the light source and its placement were of crucial importance in illuminating the droplet, particularly the low solids concentration droplets, which appeared to be translucent. Typically, light angles of incidence below 40 ° were required.

7.5 EXPERIMENTAL PROTOCOL

7.5.1 Key variable and level selection

Experimental work should aim to mimic conditions likely to be encountered on the industrial-scale. The Reynolds and Weber numbers describe the relative magnitudes of the key driving forces in droplet spreading and provide a basis for scaling the experimental conditions to those expected on an industrial-scale. Figure 7.5 compares the calculated Re and We numbers achievable with the current experimental set-up (droplets of diameter 2.8 mm) with those expected under industrial conditions (droplets of diameter 10 μm). The comparison is made for both 20 and 40% w/w maltodextrin DE5 droplets at various initial droplet sizes and impact velocities on to an anhydrous milkfat surface.

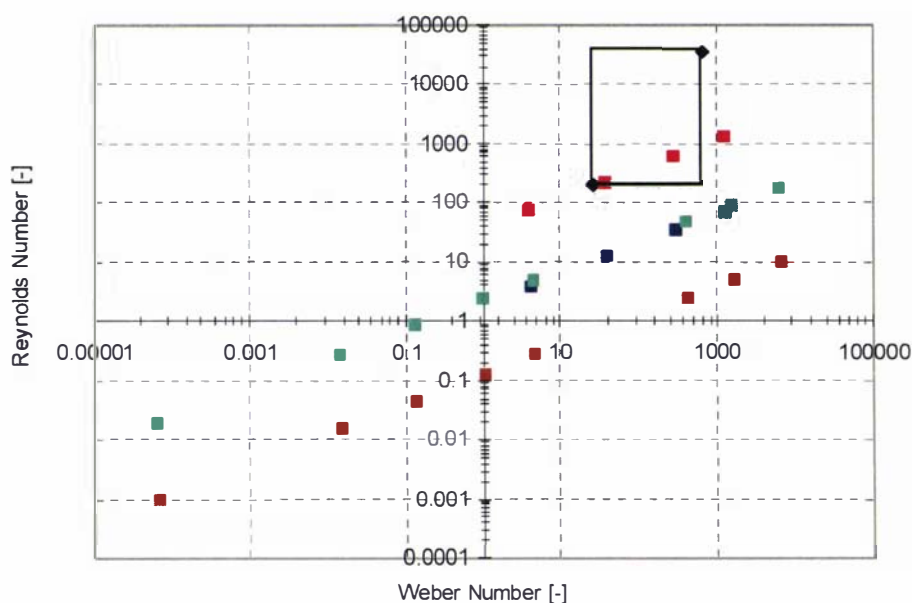


Figure 7.5: Reynolds and Weber numbers under experimental and industrial-scale conditions: ■ 20% w/w maltodextrin DE5 droplet under experimental conditions; ■ 40% w/w maltodextrin DE5 droplet under experimental conditions; ■ 20% w/w maltodextrin DE5 droplet under industrial-scale conditions; ■ 40% w/w maltodextrin DE5 droplet under industrial-scale conditions. Experimental conditions: droplet diameter 2.8 mm; impact velocities; 0.3, 0.92, 2.54, 5.31 m.s^{-1} . Industrial conditions: droplet diameter 10 μm ; impact velocities; 0.02, 0.3, 0.92, 2.54, 5.31, 8, 50, 100, 150, 200 m.s^{-1} . The boxed region encompasses the successful range of predictions for the Pasandideh-Fard et al. (1996) simplified analytical model.

The plot of Re versus We shows four parallel sets of lines (two experimental and two industrial-scale conditions). The lack of overlap means that the current experimental set-up is unable to generate data under the physical conditions likely to be experienced by industrial-scale sized droplets. Although this limitation is noted, this set-up was the only method available at the time that was able to deliver reproducible results with minimal complexity. The work here was a first step to generate valuable information regarding key formulation and control parameters. Future research should aim to scale the experimental set-up to verify the guidelines established in this work. Only the experimental conditions for the 20% w/w maltodextrin DE5 droplets fall into the Re and We ranges that the Pasandideh-Fard *et al.* (1996) model (black boxed region) has been able to predict successfully.

Due to the numerous experimental combinations and lack of understanding at this stage, it was desirable to investigate one variable at a time to elucidate the key variables. Maltodextrin DE5 was selected at the same concentrations used throughout the thesis (20 and 40% w/w). Based on a 2.8 mm diameter water droplet, impact velocities ranged from 1.7 to 4.1 m.s^{-1} to investigate droplet inertia effects. All trials were conducted under ambient laboratory conditions (22–25 $^{\circ}\text{C}$, 40–60% relative humidity).

7.5.2 Solution preparation

Solution preparation is a crucial aspect of any droplet impact and spreading study. In their study of the rheological character of solutions on impact and spreading, Crooks *et al.* (2001) carefully constructed a series of test fluids. In order to isolate and investigate one rheological feature at a time it is important to be aware that any changes in one solution property may bring about changes in another. To standardise the different formulations, their rheological

aspects, including bulk viscosity, shear thinning behaviour (during impact) and polymer elasticity, must be matched and changes to solution density, surface tension as well as component interactions (polymer–surfactant) must be considered. However, this was a probing investigation, so the considerable effort required to match the solutions exactly was not warranted and simple test solutions were prepared as shown in Table 7.1.

Each solution was made up individually on a weight basis by dissolving the maltodextrin DE5 powder at 85 °C whilst stirring in a covered beaker to minimise evaporation. Two total solids measurements were made on each solution, by oven drying at 85 °C until zero mass change, to determine the final solids content, to account for both evaporative losses and the water associated with the dissolved powder. The solutions were split into 400 ml portions and appropriate quantities of surfactant added. The solutions were stored at –18 °C to minimise microbial growth. The same solutions were used throughout the trials to avoid variations during solution preparation. Significant gelling occurred in many of the solutions containing surfactants, particularly at the 40% w/w initial solids concentration level, if left to stand between 12–24 h. The gellation resulted in a higher viscosity and a yield stress required for the solution to flow. It was also noted that significant crystallisation and settling of both the 20% w/w and 40% w/w maltodextrin DE5 solutions occurred after 24–72 h. To avoid both crystallisation and gellation effects, each day the solutions were redissolved at 85 °C and vigorously shaken to break any network formation and suspend the solid fraction. The trials were conducted as soon as the solution cooled to room temperature. The physical properties of the solutions are given in Table 7.1. Viscosity was measured using a Paar Physica Rheolab MC1 and surface tension was measured using the Wilhelmy plate technique (as outlined in Chapter 4).

Table 7.1: Viscosity and surface tension of solutions

Polymer concentration [% w/w]	Surfactant type	Surfactant concentration [% w/w]	Equilibrium surface tension [mN.m ⁻¹]	Solution density [kg.m ⁻³]	Viscosity at 1000 s ⁻¹ shear rate [mPa.s]
0	0	0	72.5	997*	0.93*
20	0	0	66.9	1085	11.9
30	0	0	68.7	1132	36.7
40	0	0	68.7	1185	242.7**
20	SDS	0.5	53.6	—	—
20	TX	0.02	42.8	—	—
20	UP	2	32.4	—	—
20	PE	2	29.1	—	—
20	YG	2	27.7	—	—
40	SDS	0.5	65.6	—	—
40	TX	0.02	45.5	—	—
40	UP	2	42.4	—	—
40	PE	2	31.4	—	—
40	YG	2	38.2	—	—

* Calculated at 24 °C from Equations (A2.19) and (A2.23) in Appendix A2; ** extrapolated from curve fit to the viscosity data; — not measured.

The viscosity of the surfactant-containing solutions was assumed to be the same or very similar as that of the standard concentration maltodextrin DE5 solutions once vigorously shaken to disrupt any potential network (gel) formation.

7.6 PLATE PREPARATION AND PRELIMINARY TESTING ON AN ANHYDROUS MILKFAT SURFACE

7.6.1 Test surface selection

Anhydrous milkfat (AMF) was chosen as the test surface to mimic an industrial dairy powder surface. The reasons for this are discussed below. Numerous researchers [Fäldt *et al.* (1993); Fäldt and Bergenståhl (1995); Fäldt and Bergenståhl (1996a); Fäldt and Bergenståhl (1996b); Chen (2001)] have investigated the surface morphology and composition of spray-dried dairy powders. There is still much debate on the surface composition, making selection of a typical model surface difficult. It is likely that the vast differences in the literature are due to different formulation and drying conditions and various techniques of analysis. The surface may be smooth or may contain pores, wrinkles and cracks. The above-mentioned studies have employed electron spectroscopy for chemical analysis (ESCA) to show that a thin layer of milkfat exists on the surface of many fat-containing powders. Consequently, lecithination is used to improve the dispersibility and wettability of whole milk powders. The high fat powders produced at Fonterra, Longburn (New Zealand) have also been found to contain a surface fat layer [Chen (2001); Kim *et al.* (2002)]. Other coating scenarios are possible. With further advances in spray drying microencapsulation it is likely that the industry will want to coat onto hydrophilic protein or carbohydrate surfaces. Also, as coating progresses, successive coating layers will be built up of the same material – in this case a maltodextrin based layer, which means a hydrophilic droplet landing on a hydrophilic surface. The hydrophobic surface was selected because current high fat powders needing coating have a fat rich surface. However, in the current scenario, if coating onto AMF cannot be achieved in the first place, continued coating onto the hydrophilic surface becomes redundant.

As noted in Chapter 3, porosity can promote spreading. However, it was decided to optimise the formulation conditions for the worst case scenario, i.e. a smooth hydrophobic surface, as any promotion of spreading by porosity would be an additional benefit in the industrial system. Preliminary tests also pointed to difficulties in producing a porous or roughened AMF surface. This is further discussed in Section 7.9.2.

7.6.2 Anhydrous milkfat plate preparation

A considerable amount of time was spent developing a method for preparing a reproducible anhydrous milkfat surface for the work. In all cases, the same standard 20 kg batch of AMF (New Zealand Milk Products) was used and sourced from Fonterra Palmerston North. The frozen AMF (−18 °C) was cut into pieces, placed in a beaker and heated in a 1.15 kW microwave until no solids remained. By careful positioning of the light source, the surface morphologies obtained using various surface preparation procedures were elucidated and are shown in Figure 7.6.



Figure 7.6: Anhydrous milkfat surface morphologies under various preparation procedures: (a) 9 °C wiped surface (smooth); (b) heat-gun-melted surface showing surface crystallisation (roughened); (c) unwiped moisture condensation after 40 min (pools of condensation); (d) wiped after 40 min (streaked); (e) bulk crystallised at room temperature (wrinkled irregular surface).

The production of these surfaces is outlined below.

7.6.2.1 Molten AMF thin film preparation

In an air-suspension particle coating operation (at temperatures greater than 40 °C) it is likely that the thin milkfat layer will be in a molten state and the coating droplet will impinge into a shallow pool. In this instance, the droplet spreads more efficiently, as the apparent surface tension is much lower, resulting in a higher Weber number [Matson *et al.* (1998)]. In addition, there will be an absence of a retarding contact angle pinning effect experienced on rough solid surfaces and inhibiting adsorption processes at the spreading front [Stoebe *et al.* (1997)]. In some instances, spreading on liquid surfaces of comparable surface energy can exceed those on a solid surface by an order of magnitude [Stoebe *et al.* (1997)].

The thickness of this surface fat layer on industrial dairy powders has not been conclusively quantified. However, surface studies employing ESCA suggest that the layer is at least 10 nm based on the depth the X-rays penetrate the sample [Fäldt *et al.* (1993)]. To complicate matters, it is possible that a droplet may also penetrate the surface to spread between the molten milkfat and the underlying solid surface, which for the Fonterra Longburn powders is expected to be a layer of protein or carbohydrate [Chen (2001)].

In the first instance, attempts were made to produce a test plate having a thin layer of molten AMF on the surface of a glass microscope slide as a flat smooth base. The hydrophilic nature of the glass surface proved problematic. Numerous methods were trialled from rubbing solid AMF, to dip coating, to pouring on a tilted slide and solidifying. In all cases the AMF would bead up and coalesce to give an irregular shaped surface. As a result, the same procedures were tried on a stainless steel (more hydrophobic, therefore less beading) plate of the same dimensions. Again non-uniform surface thickness prevented this method being adopted. To achieve uniform thickness plastic Petri dishes were opted for to provide a boundary for the AMF to reside within. In general, a flat surface was obtainable once solidified at 4 °C but it was not smooth due to a small degree of crystal formation on the surface. However, this surface layer was heated so it did not present a problem. Two heating methods were trialled to produce the thin molten AMF surface layer. The first attempt was to heat the entire plate in the oven (near 40 °C). The second method trialled was to heat the plate surface only by passing a heat gun over the surface until a visible melting occurred. Unfortunately both methods resulted in the droplets impinging into surface layers of varying depths leading to non-reproducible results. In the second case, which initially showed more promise, there was also an issue with rapid crystallisation resulting in skin formation on the surface during the course of the experiment as shown in Figure 7.6(b). It was concluded that it was not possible

at this time to produce a thin molten AMF surface. It was decided that impaction experiments would be on to solid AMF.

The compromise to use a solid surface at this stage can be rationalised in that impingement in the real system may behave as if it were impacting a solid surface if the molten fat layer is in fact very thin relative to the size of the droplet. Range and Feuillebois (1998) found that the splashing mechanism of a droplet impact on a shallow liquid layer is quite similar to that on a dry solid surface. This is possible, given that industrial sized droplets are approximately $10\text{ }\mu\text{m}$ in diameter and a particle surface fat layer of $1\text{ }\mu\text{m}$ thickness would account for approximately 13% of the fat in a $100\text{ }\mu\text{m}$ powder particle containing 30% w/w fat.

7.6.2.2 Smooth, solid, dry AMF surface at room temperature

Rapid freezing was used to solidify the AMF as a smooth, solid apparently amorphous surface. After microwaving, the liquid AMF was quickly poured into Petri dishes (referred to as plates from here on) that were acclimatised in a $-18\text{ }^{\circ}\text{C}$ freezer (30 min) room giving a final solid thickness of about 3–6 mm. Careful attention was made to ensure the plates remained level so the droplets impacted a non-sloping surface. Attempts to solidify at room temperature resulted in skin formation and the wrinkled irregular surfaces as shown in Figure 7.6(e). The plates were quickly transferred to vacuum desiccators containing silica gel, placed in a $4\text{ }^{\circ}\text{C}$ cool room and allowed to stand overnight (12 h) prior to use.

After the plates had been removed from the desiccators at $4\text{ }^{\circ}\text{C}$, they still contained a small amount of surface moisture (seen as micrometre sized condensed droplets). The moisture appeared during plate preparation in the $-18\text{ }^{\circ}\text{C}$ freezer and again when the plates were removed from the desiccators into the $4\text{ }^{\circ}\text{C}$ cool room. It would seem that, even under strong desorption conditions (silica gel with vacuum) there was still insufficient driving force to desorb the moisture from the AMF surface. As it was not practical to produce the required number of plates by any other means (i.e. under dry air conditions below the AMF plate dew point temperature), this moisture layer was accepted at this stage of the plate production process.

In early impact experiments conducted at room temperature, an additional attempt was made to remove the surface moisture by leaving the plates to stand overnight at room temperature ($24\text{ }^{\circ}\text{C}$, 40–60% RH, 12 h) to evaporate the moisture. However, this step was later abandoned since impact at velocities above 2.6 m.s^{-1} resulted in slight surface deformation of the AMF (a crater), resulting in impeded spreading. The only remaining alternative was to use the plate directly from the $4\text{ }^{\circ}\text{C}$ cool room before it had time to significantly soften.

7.6.2.3 Smooth, solid AMF plate at $4\text{ }^{\circ}\text{C}$

Using the $4\text{ }^{\circ}\text{C}$ plate at room temperature presented two potential problems. The first, is that industrially, the powder surface temperature is likely to be $10\text{--}30\text{ }^{\circ}\text{C}$ higher. However, when one considers all other sources of uncertainty, along with the deformation problems at higher temperatures, the thermodynamic temperature effect on spreading is not expected to be significant. The second problem was the condensation of moisture on the plate surface as it warmed to room temperature over each experiment. The presence of condensed moisture could either encourage spreading by promoting lower contact angles, as well as lowering the probability of contact angle pinning due to lubrication, or it may discourage spreading if the thin film provides a breaking force at the three-phase line if it needs to ‘push’ the film aside to spread the droplet on the AMF surface below.

To determine the effect of moisture condensation on spreading, a time delay between trials on the same plate was allowed. It was found that up until one hour after the plates were taken from the chiller, reproducible results could be achieved on the same plate. To ensure this was the case for all tests, during data analysis the effect of droplet size on the final spread diameter was plotted but in no case was a systematic error evident amongst the inherent scatter of the data. However, after 3–4 h on the same plate, the results were no longer reproducible. This was due to the appearance of different sized beads of moisture and their varying degrees of coalescence resulting in the appearance of moisture pools dispersed amongst dry evaporated patches of exposed AMF. These shallow pools allowed the impacted droplet to meander across the surface of the plate leaving irregular shaped droplets and poor reproducibility. Although the results were not reproducible after 3–4 h it was noted that, in general, these pools had the ability to slightly promote spreading in most cases. It was decided to exploit this observation. A series of impact trials were conducted on plates left to stand from 1–3 h in an attempt to find a relatively homogeneously moisture covered surface. Results again showed a potential increase in spreading with time, but the poor reproducibility was unacceptable. An attempt to run a thin film of water across the surface, in the hope it would be retained, was also unsuccessful because the AMF hydrophobicity caused significantly worse beading than that achieved by moisture condensation alone.

The solid, dry AMF surface experiments at room temperature, reported in Section 7.6.2.2, gave slightly lower final spread factors than these experiments which used AMF plates stored at 4 °C (the comparison was only for velocities $< 2.6 \text{ m.s}^{-1}$). This suggests the existence of a thin moisture layer (possibly monolayer) on the 4 °C plate which was not visible to the eye. This positive spreading effect of the thin moisture layer could be exploited to encourage spreading by passing the powder through a fine mist spray prior to passing the nozzle containing the coating solution. It would also encourage droplet coalescence.

7.6.3 Identification of error sources and statistical significance of the data

Having identified an appropriate surface and procedure for its production to obtain reproducible results (accuracy between trials), the scatter (precision within a trial) required quantification and minimisation by considering the potential sources of variability in experimental conditions.

7.6.3.1 Statistical significance

Inherent scatter was evident in all the data collected. The measurements of d_0 and d_{end} were relatively precise, but many variables contributed to the measurements, each having its own variability. There was a small degree of subjectivity in measuring the diameter of the droplets as they were not always perfectly circular. Eight replicates d_{end} were measured for each experimental combination. t -Tests ($n < 30$, normally distributed data, double sided) were employed to determine the 95% confidence intervals for each experimental combination, giving statistical significance to the inherently scattered data. The following sources of experimental uncertainty were considered and procedures were established to standardise data collection.

7.6.3.2 Plate use-by dates

Generally, plates were used within 2 or 3 days to ensure that potential oxidation of the surface did not alter the results. This effect was not quantified but it was found that results were

repeatable (within the experimental scatter) with up to 3 days of storage time in the cool room at 4 °C.

7.6.3.3 Solution effects

The solution preparation detailed in Section 7.5.2 was kept the same for all experiments.

7.6.3.4 Initial droplet diameter and impact variations

A variable of concern was the initial droplet mass delivered by the needle. It was found with droplets of water, that the syringe delivered a relatively narrow range of droplet masses (13.5 ± 0.11 mg at the 95% confidence interval for $n = 8$) due to small variations in laboratory air flow conditions and DC motor vibrations. However, in most cases, the solutions containing maltodextrin DE5 and surfactants resulted in droplets two thirds (8–10 mg) the size of those without surfactant (12–14 mg). It was not known whether the surfactant-containing droplets could be compared with the trials involving the larger droplets without surfactants.

The models of Pasandideh-Fard *et al.* (1996) and Toivakka (2003) found an increase in ζ_{max} with increasing initial droplet diameter. For impacting water droplets of 3.4 and 4.6 mm in diameter, Zhang and Basaran (1997) found the initial rate of spreading and ζ_{max} were only weak functions of the size of the pre-impact droplet diameter. However, in the same study Zhang and Basaran (1997) found that with Triton X-100 addition, an increase in ζ_{max} occurs with increasing pre-impact droplet diameter. This was attributed to an increase in initial kinetic energy or the increase in Weber number. The latter results from a dynamic surface tension (DST) effect (discussed in Section 7.8.2) which can reduce the surface tension at the three-phase line. Since surface dilational (expansion) rates, which effect DST values are not known at this stage, the effect of impact velocity and initial kinetic energy was investigated.

The droplet impact velocity calculation is relatively insensitive to the small variations in the set-point values for the variables of initial height, density and droplet size. However, the initial kinetic energy diminishes by a factor 8 with a halving of the initial droplet diameter. Without a relationship between ζ_{max} and ζ_{end} to check whether such an effect was significant under the experimental conditions used here, ζ_{end} was plotted as a function of initial droplet size for experiments at 20% w/w and 40% w/w maltodextrin DE5 concentrations with and without 2% w/w surfactant (Ultralec P) at an impact velocity of 2.6 m.s^{-1} . The initial droplet size was varied from 6 mg up to 20 mg by using a disposable syringe with a larger internal needle diameter. No trend was evident above the inherent scatter of the data. Therefore, it was assumed that all other test combinations also exhibit no dependence on droplet sizes delivered by the syringe.

Another source of variability in the measured spread diameters could be from slight deviations from a normal angle of incidence upon droplet impact (i.e. non-zero horizontal velocity component). This would give a different contact angle on one side of the droplet. Droplet oscillations were noted during droplet detachment from the needle. This was compounded slightly as the DC motor motion driving the syringe plunger was not entirely smooth. This would only affect droplet shape at very low impact heights. These sources of error are more difficult to quantify and minimise than the other error sources but were not expected to contribute significantly to the overall scatter of the data.

7.7 DYNAMICS OF DROPLET SPREADING

The high speed camera was used to observe droplet flow dynamics and allowed measurement of ζ_{max} in addition to ζ_{end} . It should be noted that slight differences were found in the ζ_{end} measurements collected here and those measured in the ζ_{end} experiments using camera system I. The most obvious factor is that the dynamic tests do not allow enough time for the droplet to reach the final ζ_{end} (limited by the data storage capacity of the high speed camera). However, checks after 2–4 s show that the same droplets reached a similar ζ_{end} value to that already measured in the non-dynamic ζ_{end} experiments. There are also slight differences due to scatter, but most notably slight differences in solution properties resulting from continued heating/redissolving and cooling. In general, the same trends are evident. If more accurate comparisons between tests are to be made, it is advised all experiments involved in the comparison be conducted on the same day to minimise these differences.

Figure 7.7 shows a time series of selected images that depict the spreading and recoil processes for various droplet formulations. Selected digital videos produced in .AVI format have been compressed using the DivX codec and are contained on the CD inside the back cover of the thesis. Due to the large amount of light required to capture high speed images the resulting images have had to be digitally enhanced.

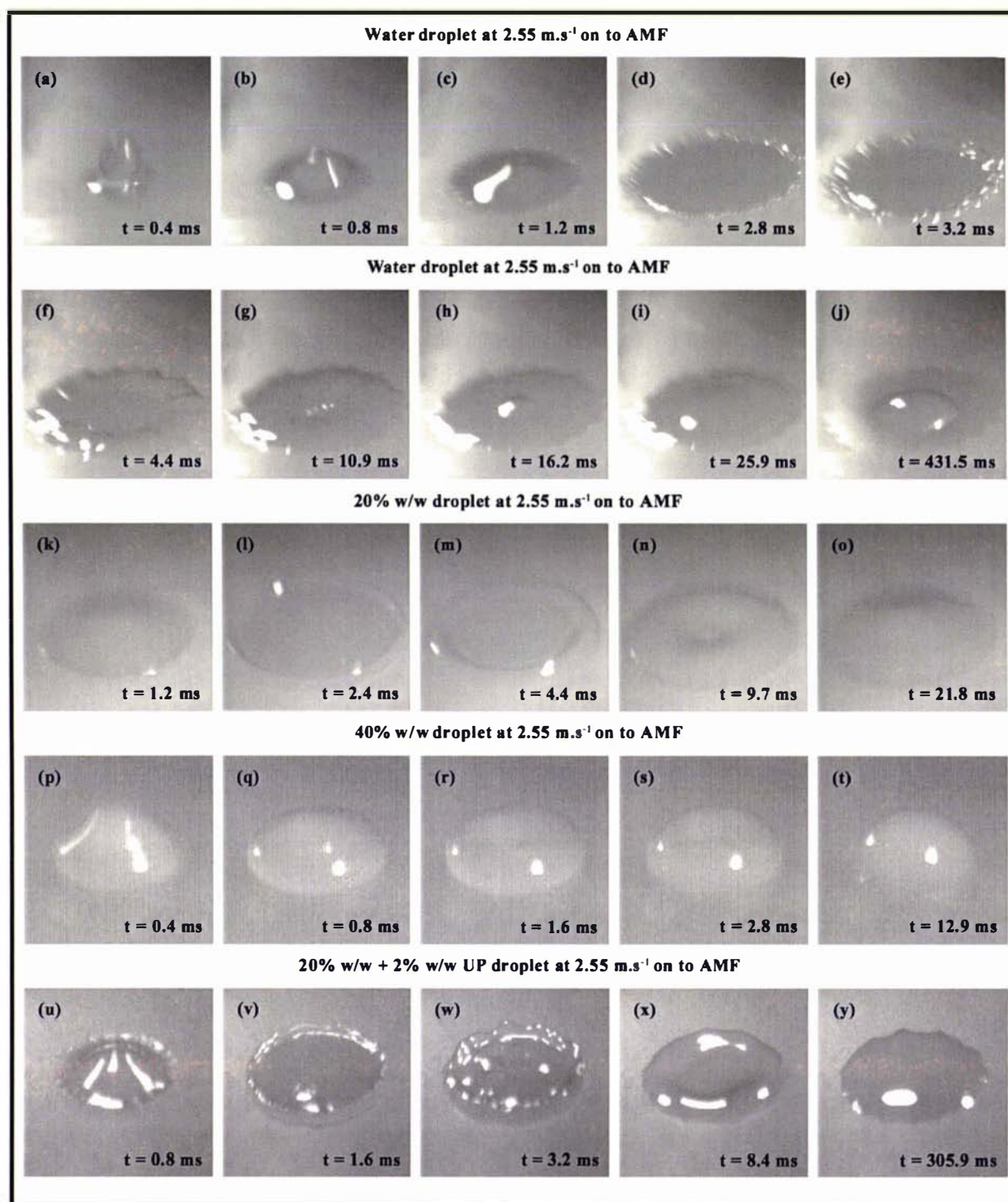


Figure 7.7: Time series of events depicting the impact, spreading and recoil of various water and maltodextrin DE5 droplet formulations on anhydrous milkfat. Only the important features for discussion are shown; thus, the full extent of spreading and recoil may not be shown in some cases. The images appear to be oblong rather than circular because of the camera angle used. Note: because different magnifications have been used for each time series, images (e, j, o, t and y) have approximate droplet diameters of 11.0, 5.8, 7.6, 4.1 and 7.0 mm respectively.

Figure 7.7(a–j) shows a time series of digital images of a water droplet impinging an AMF surface. At the moment of impact (Figure 7.7(a)), the droplet resembles a truncated sphere and a high velocity jet at the bottom shoots out as a thin film. The bulk volume of the droplet then spreads uniformly in the radial direction from the impingement point as a thin liquid film (Figure 7.7(b–d)). Now, as the droplet has spread past its equilibrium diameter (set by its

equilibrium contact angle) because of the initial kinetic energy, the three-phase line is subjected to a ‘back’ force provoked by the departure from equilibrium and the droplet therefore recoils. At ζ_{max} (Figure 7.7(d)), the contact line remains stationary while the contact angle adjusts from the advancing contact angle to the receding contact angle [Zhang and Basaran (1997)]. At this point, the peripheral rim begins to thicken at the maximum diameter with weak azimuthal undulations, called festoons (Figure 7.7(e)) at the droplet periphery [Mourougou-Candoni *et al.* (1999)]. In cases of higher impact velocity, the festoons form fingers. The fingers are progenitors of a peripheral splash droplet [Allen (1975)]. Concentric capillary waves begin to appear (Figure 7.7(f–i)) on the droplet surface as the centre of the droplet spreads to the periphery as a rolling wave to give a doughnut-shaped splat. The rolling wave (possibly waves) is reflected from the periphery to refill the central well (Figure 7.7(g)), recoiling the droplet periphery to a value less than ζ_{max} . The centre begins to rise in height (Figure 7.7(h)) and settles back out towards a final ζ_{end} value. In high impact velocity cases, the rise in height of the central liquid column can become so unstable that a droplet can separate (‘eject’) from its top as in a Rayleigh instability. The oscillations reduce in amplitude and frequency with time [Zhang and Basaran (1997)]. While the wave propagates back and forth, the droplet periphery retracts until it reaches its final ζ_{end} value (Figure 7.7(j)). The outline of the maximum spread diameter remains and is observed as a thin film left on the AMF surface (Figure 7.7(j)).

The hydrodynamic wave and the doughnut shape become less pronounced in Figure 7.7(k–o) and almost absent in Figure 7.7(p–t) with increasing viscosity because viscous dissipation reduces the droplet and rolling wave momentum.

The presence of surfactant is of particular note in Figure 7.7(u–y). Little or no recoil at all occurs, as Figure 7.7(w) and Figure 7.7(y) have approximately the same diameter, although they are over 300 ms apart. This description makes it clear that complex hydrodynamics occur, and need to be considered if predictions of droplet spread factors are to be made.

7.8 DROPLET FORMULATION EFFECTS

7.8.1 Inertia and viscosity effects

The model presented by Pasandideh-Fard *et al.* (1996) shows viscosity to be critical to ζ_{max} but does not give insight into ζ_{end} . Intuition tells us that slow-moving, highly viscous droplets, which have low Reynolds and Weber numbers, can dissipate all their kinetic energy on impact, leaving nothing to propel them to greater spreading extents. For example, a drop of honey will not spread far because it is viscous. If, instead, the viscous droplet is fast moving and the inertial energy is sufficient to cause good spreading, it could be argued that the subsequent recoil of the droplet due to surface tension gradients may not be able to overcome the viscous dissipative forces, thus encouraging an ζ_{end} similar to ζ_{max} . With these hypotheses in mind, a series of experiments was conducted to determine whether inertia and viscosity can be tailored to achieve greater ζ_{end} values. Although the impact of droplets has been studied intensively, the research on viscous liquids is limited to under 10 mPa.s [Zhang and Basaran (1997)], except for the work of Scheller and Bousfield (1995) which provided data of comparable viscosities (up to 300 mPa.s) to those used in this work.

Figure 7.8 shows the ζ_{end} results of a series of experiments employing droplets containing 0, 20, 30 and 40% w/w maltodextrin DE5 on a 4 °C smooth AMF surface at impact velocities of 1.7, 2.6, 4.1 m.s⁻¹. Droplet splashing was found to occur at 5.4 m.s⁻¹ for the 0, 20 and 30%

w/w concentrations and are not shown. Splashing did not occur for the 40% w/w droplet at this impact velocity as the compression wave is attenuated by viscosity and cannot overtake the contact line velocity to cause droplet splashing [Scheller and Bousfield (1995)].

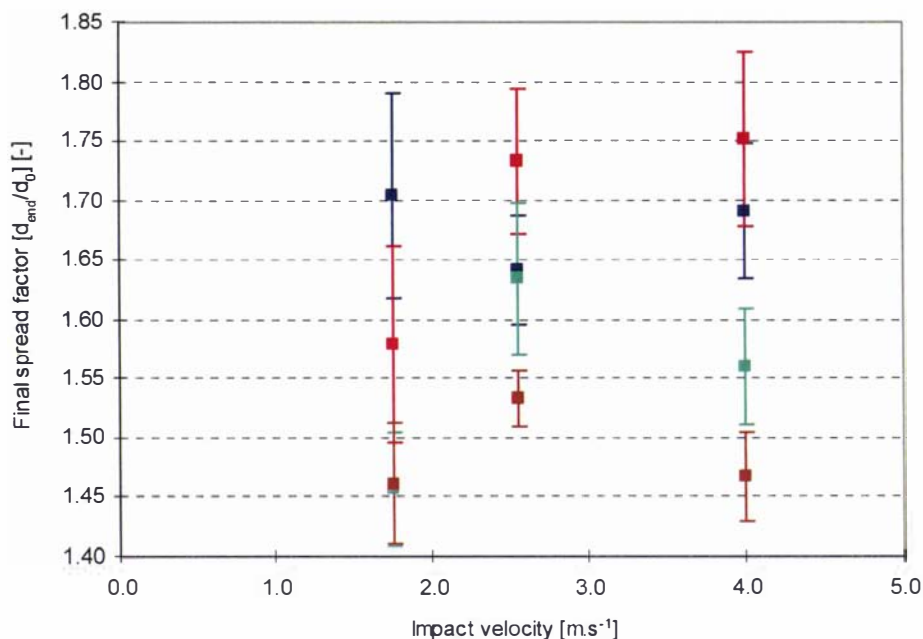


Figure 7.8: Concentration (viscosity) and inertia (velocity) effects on the final spread factor for water and maltodextrin DE5 droplets impacting on to AMF: ■ water; ■ 20% w/w maltodextrin DE5; ■ 30% w/w maltodextrin DE5; ■ 40% w/w maltodextrin DE5. Error bars represent 95% CI, $n = 8$ for all trials.

Whilst the 95% confidence interval (CI) error bars show significant scatter it is clear that higher viscosity droplets lead to slightly lower final spread diameters which becomes more pronounced at higher impact velocities. This is in agreement with Kleinbach and Riede (1995) who stated that low viscosity droplets enhance spreading. It should also be borne in mind that high dilution can lead to partial dissolution of the solid material, which is undesirable, as it will form part of the coating itself. The viscosity effect for glycerine–water mixtures on ξ_{end} presented by Scheller and Bousfield (1995) is difficult to understand as higher ξ_{end} values appear to favour more viscous solutions to a particular point at which ξ_{end} passes through a maximum. They do not give an explanation for this.

Figure 7.9 and Figure 7.10 show the dimensionless spread factor (for the first 50 ms and 500 ms respectively) as a function of concentration (viscosity) for droplets impacting at 2.6 m.s^{-1} . These droplets contained 0, 20, 30 and 40% w/w maltodextrin DE5. Pasandideh-Fard *et al.* (1996) normalised the time axis ($t^* = t.v_0/d_0$) to account for variations in droplet velocity and diameter. However, this did not alter the profiles significantly under the conditions investigated here and hence they are presented in real time, as it is more intuitive.

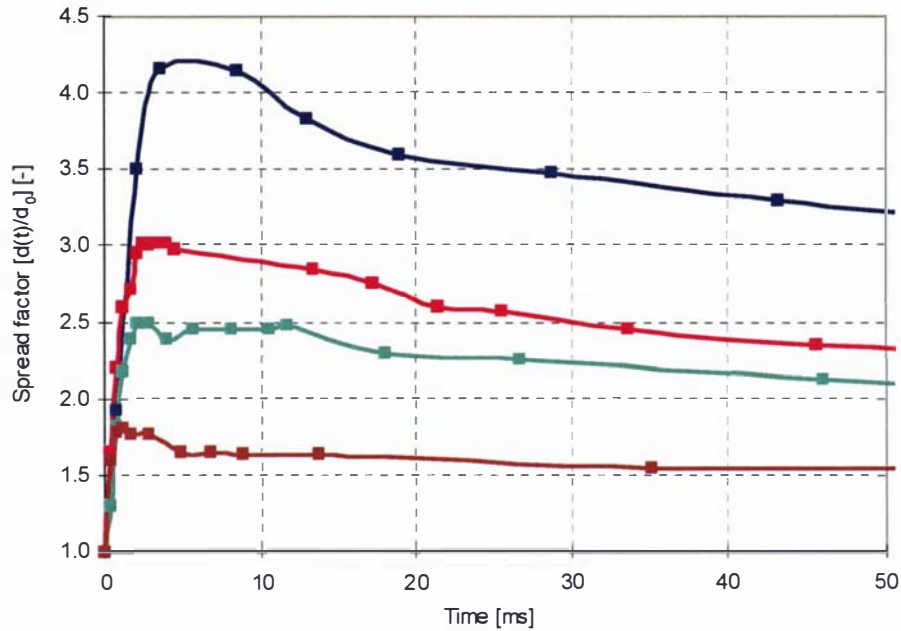


Figure 7.9: Evolution of the spread factor (up to 50 ms) as a function of concentration (viscosity) for droplets impacting at 2.6 m.s^{-1} on to AMF: ■ water; ■ 20% w/w maltodextrin DE5; ■ 30% w/w maltodextrin DE5; ■ 40% w/w maltodextrin DE5.

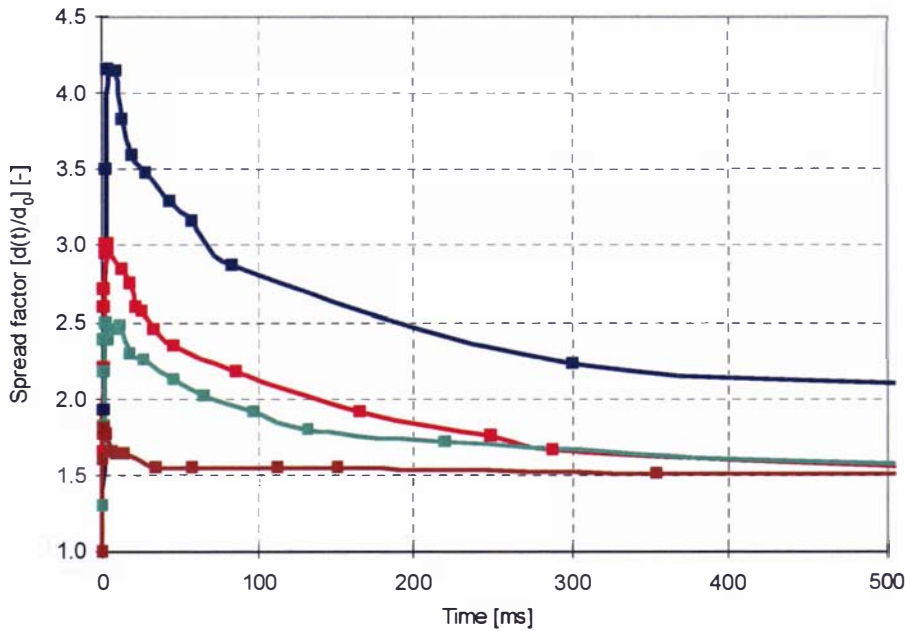


Figure 7.10: Evolution of the spread factor (up to 500 ms) as a function of concentration (viscosity) for droplets impacting at 2.6 m.s^{-1} on to AMF: ● water; ■ 20% w/w maltodextrin DE5; ● 30% w/w maltodextrin DE5; ■ 40% w/w maltodextrin DE5.

Inspection of the slope of Figure 7.9 reveals that spreading is fast initially, and decreases monotonically with time until ζ_{max} (slope zero) is reached. After this time, in agreement with the photographs in Figure 7.7, recoil occurs with the slope becoming negative until it plateaus towards its final ζ_{end} value (although not seen for some cases because of limited data). There is little difference in the initial rate of spreading over the first 2 ms for all droplet concentrations. This indicates that inertial forces dominate impact and then, as ζ_{max} is

approached, momentum is dissipated and the effect of viscosity is noticeable (peak broadening).

The rate of recoil shows an exponential-like decay, with the higher viscosity droplets reaching their final ξ_{end} value earlier as they do not spread as far in the first instance. This can be seen in the 40% w/w maltodextrin DE5 droplet, which forms only a very small doughnut shape (Figure 7.7(p-t)), suggesting that the majority of the inertial energy is consumed in viscous dissipation, so that the initial spreading distance and hence the time frame for recoil are very low. The dynamics are very fast and, on an industrial-scale, it is unlikely that the drying rate would be able to influence the recoil effect and retain ξ_{max} as ξ_{end} . In addition, the control of droplet drying would be problematic given the broad range of the diameters of the droplets likely to impinge on the substrate. This confirms the statement made earlier that it is d_{end} , and not d_{max} , that is of interest to air-suspension particle coating investigations. This contradicts Guignon *et al.* (2002), who suggested that, by using a similar ξ_{max} equation to that of Pasandideh-Fard *et al.* (1996), proposed by Fukai *et al.* (1996), one could predict ξ_{max} , assuming that it would be retained.

Although not shown here, it was also noted that smaller ξ_{max} and ξ_{end} values were achieved if the solutions were allowed to crystallise overnight, suggesting a small viscosity increase (possibly gellation). This could be responsible for slight differences seen in the results over a day's experiments.

The trials were repeated at impact velocities of 1.7 and 4.1 m.s⁻¹, and the ξ_{max} and ξ_{end} values are plotted in Figure 7.11. It should be noted that, because of the camera's limited frame capture storage and the time taken for ξ_{end} to be reached, the ξ_{end} value measured from a second test was plotted instead. At an impact velocity of 4.1 m.s⁻¹, the water droplet developed fingers at the periphery, which subsequently left behind satellite droplets upon retraction, leading to slightly lower ξ_{end} values as a result of lost droplet volume.

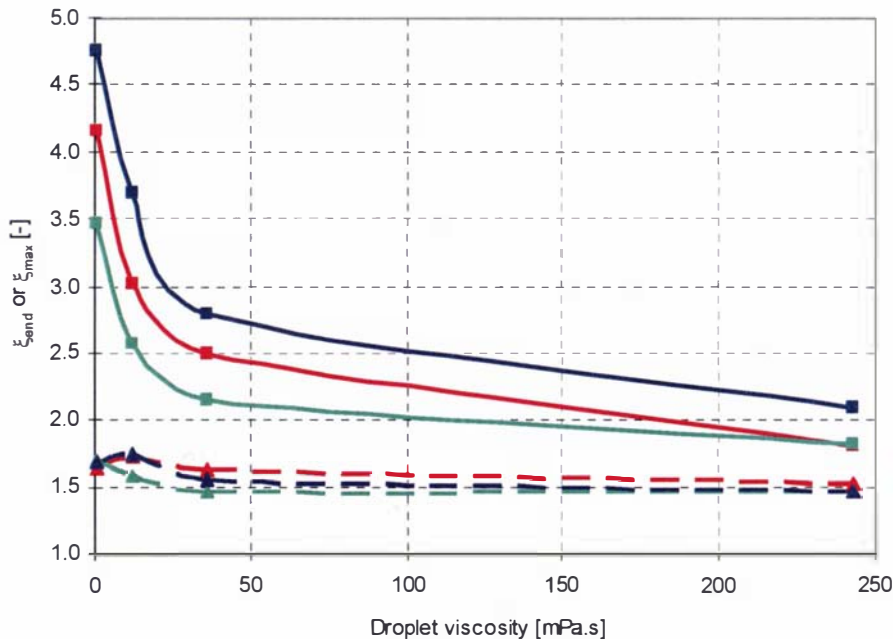


Figure 7.11: ξ_{max} and ξ_{end} as a function of viscosity and initial impact velocity for water droplets and droplets containing 20, 30 and 40% w/w maltodextrin DE5 impacting on to AMF: ● ξ_{max} 4.1 m.s⁻¹; ● ξ_{max} 2.6 m.s⁻¹; ● ξ_{max} 1.7 m.s⁻¹; ▲ ξ_{end} 4.1 m.s⁻¹; ▲ ξ_{end} 2.6 m.s⁻¹; ▲ ξ_{end} 1.7 m.s⁻¹.

The results confirm the observations of Scheller and Bousfield (1995), i.e. that ζ_{max} increases with increasing impact velocity but decreases with increasing viscosity. Both these observations are predicted from the Pasandideh-Fard *et al.* (1996) model. Using three-dimensional modelling, Toivakka (2003) suggested that high viscosities (up to 100 mPa.s) lead to reduced spreading (ζ_{max}). His study did not explore ζ_{end} . The same dependence on ζ_{max} was also found by Crooks *et al.* (2001); however, the ζ_{end} results were not given or were obscured by droplet rebound. The marginal decrease observed here in ζ_{end} with increasing droplet viscosity (in Figure 7.11) suggests that viscous dissipation during recoil does not greatly affect the final equilibrium diameter. It is clear that the surface tension forces were able to draw the droplet back after initial spreading, which does not support the notion proposed earlier that higher viscosity droplets may be able to dissipate the surface tension forces during recoil. Hence, viscosity is a key factor governing droplet impact, particularly ζ_{max} but not ζ_{end} in the absence of drying.

Scheller and Bousfield (1995) found that increasing the impact velocity increased ζ_{end} . Under the experimental conditions investigated in this work ($23 < Re < 12\,300$ and $140 < We < 741$), the effect of the impact velocity on ζ_{end} appears to be limited and obscured by scatter in the data. The 30 and 40% w/w maltodextrin DE5 droplets show an optimum ζ_{end} at 2.6 m.s^{-1} . It is not clear why this occurs, as it was expected that increasing the impact velocity would give rise to a higher ζ_{end} value for high viscosity solutions. The minimal effect of the impact velocity on ζ_{end} is in agreement with the statement of Zhang and Basaran (1997) that the final spreading diameter is only a weak function of the impact velocity for droplets that are free of surfactant or contain slowly transporting surfactant. It is not known whether the observed lack of effect occurs outside the range of Re numbers investigated here.

In summary, the work described in this section shows that increasing the impact velocity and lowering the droplet viscosity lead to greater ζ_{max} values. This is in agreement with the current literature, although much higher viscosities were used in this work than in previous investigations. The experiments show that higher impact velocities do not greatly enhance ζ_{end} , particularly for the higher viscosity droplets. This removes the need for the operator to optimise the impact velocity of the droplets, unless, of course, they lower the surface tension first (refer to Section 7.8.3). It was hypothesised that there would be a critical viscosity at which ζ_{max} was retained because the viscous dissipation during recoil is significant enough to resist the surface tension trying to pull the droplet back in. This was not the case, as recoil was still evident in the high viscosity (242.7 mPa.s) 40% w/w maltodextrin DE5 droplets. Even with drying, it is likely that the rate of retraction of such droplets occurs much faster than the time it takes for drying to arrest the droplet diameter at its ζ_{max} .

7.8.2 Surface tension effects

During the inertia and viscosity experiments, droplet recoil was significant and d_{end} was considerably less than d_{max} . This implies that the high surface energy created by the expanding droplet surface was able to overcome the viscosity and pinning forces at maximum spread diameter, resulting in recoil. Considering the surface energy (Equation (7.8)) at maximum droplet diameter, it is clear that, to minimise the recoil energy (and to try to retain ζ_{end} at ζ_{max}), a lower surface tension and a lower contact angle are required. Lowering the droplet surface tension can be accomplished by adding a surfactant to the droplet, which will also lower the contact angle. Additionally, the contact angle can be reduced by altering the chemical character of the surface, perhaps by using a pre-surface coating to render it more hydrophilic, like the droplet. This section explores the first method of reducing the surface energy at ζ_{max} , by adding a surfactant to the droplet.

Surfactants are used in many coating formulations on the premise that they will increase the final wetted surface area of the droplets upon impaction. In industry, surfactant incorporation is likely to have been based on a ‘black box’ approach and there is likely to be little understanding of the real benefits, especially from a quantitative perspective. Only recently have studies begun to address the role of surfactants in the dynamics of droplet spreading [Pasandideh-Fard *et al.* (1996); Zhang and Basaran (1997); Mourougou-Candoni *et al.* (1999); Crooks *et al.* (2001)]. Of particular interest is the role of dynamic surface tension (DST). DST values are usually measured by the maximum bubble pressure method [Mourougou-Candoni *et al.* (1999); Crooks *et al.* (2001)], which measures the surface tension as a function of bubble lifetime, resulting in a picture of the adsorption kinetics of the surfactant. Pasandideh-Fard *et al.* (1996) studied water droplets impacting a stainless steel surface with and without the surfactant sodium dodecyl sulphate (SDS). They found that adding SDS at up to 1000 ppm did not significantly increase the droplet spreading (i.e. essentially constant ξ_{max}). They attributed this observation to two major effects. The first effect can be seen by a simple order of magnitude analysis [refer to Chandra and Avedisian (1991)], which shows that, during the initial period of droplet spreading, inertial forces are much larger than surface tension and viscous forces (already observed in Figure 7.9). Hence, lowering the surface tension or the contact angle has little influence on fluid flow. The second effect is a mass transfer limitation in which the surfactant will reduce the surface tension only when it is available at the three-phase line. As a result, the experimental results were best modelled using the surface tension of pure water and not a DST value, which would lie between that of the surface tension of pure water and the equilibrium surface tension value. Although the focus of the study by Pasandideh-Fard *et al.* (1996) was on ξ_{max} , inspection of their figures reveals that addition of increasing concentrations of SDS to the water droplets significantly increased the ξ_{end} values. In fact, ξ_{end} remained at ξ_{max} for the addition of 1000 ppm SDS, suggesting little or no recoil. Surfactant addition appears to influence ξ_{end} by lowering the surface tension and, subsequently, the amount of recoil from ξ_{max} .

Zhang and Basaran (1997) were surprised that the Pasandideh-Fard *et al.* (1996) study did not find the DST to play a role in droplet impact, given recent work by other researchers in the field. Their study showed that the surfactant type and the impact conditions do affect ξ_{max} and can be explained by DST effects. In response to findings such as those of Mourougou-Candoni *et al.* (1997) and Zhang and Basaran (1997), Mourougou-Candoni *et al.* (1999) substituted γ_{lv} and θ_a with $\gamma_{lv,max}$ and $\theta_{a,dmax}$, i.e. the dynamic liquid–vapour surface tension and the advancing contact angle, both at maximum extension. This resulted in a modified form of the Pasandideh-Fard *et al.* (1996) equation, as shown in Equation (7.11).

$$\xi_{max} = \frac{d_{max}}{d_0} = \sqrt{\frac{We + 12}{3 \frac{\gamma_{lv,max}}{\gamma_{lv}} (1 - \cos \theta_{a,dmax}) + 4 \left(\frac{We}{\sqrt{Re}} \right)}} \quad (7.11)$$

The values of $\theta_{a,dmax}$ and $\gamma_{lv,max}$ were significantly different from those of their substituted counterparts, giving a better fit to their experimental data and confirming that the DST effects were significant. The consequences of DST are discussed in Section 7.8.3.

Surface tension also plays a vital role in the splashing of impacting droplets [Allen (1975)]. If the initial kinetic energy (inertial force) is much larger than the surface energy (surface tension force), the drop can ‘splash’ by ejecting a number of small ‘satellite’ droplets from its periphery [Zhang and Basaran (1997)]. In contrast, if the surface tension is strong enough, the restoring force it exerts will cause the contact line to retract rapidly from the maximum

droplet diameter and ejection of a satellite droplet from the centre of the recoiling droplet can result. Hence, a trade-off in surfactant addition must be met, as lower surface tensions will encourage periphery splashing upon initial spreading and will discourage droplet ejection from the droplet centre upon recoil.

The above information confirms the importance of investigating surface tension and surfactant type to maximise ξ_{end} . Five surfactants/wetting agents were selected for investigation for reasons outlined in Section 4.2.7. These were, sodium dodecyl sulphate (SDS), octylphenoxy polyethoxyethanol (Triton X-100 referred to TX), Performix E (PE), Ultralec P (UP) and Yelkin Gold (YG). A second concern was the concentration of the surfactant. The final spread factor increases with increasing surfactant concentration [Pasandideh-Fard *et al.* (1996); Zhang and Basaran (1997)]. Rather than investigate a range of surfactant concentrations, it was decided that the maximising ξ_{end} would be best achieved by lowering the surface tension as far as possible, i.e. to the critical micellar concentration (CMC). The decision not to match the physico-chemical characteristics of the solutions (see Section 7.5.2) is considered acceptable since many unknowns existed such as solid–surfactant interactions and the complicating hydrodynamics of droplet flow. At this stage observations were of primary interest.

The ξ_{end} values for droplets impacting at 2.6 m.s^{-1} on to the AMF surface are presented in Figure 7.12. It should be noted that these ξ_{end} values were measured 2–4 s after impact. It was found that secondary spreading occurs after this time frame and to large extents in some instances, particularly for the 20% w/w maltodextrin DE5 solution with 2% w/w PE, which spread to twice the initial ξ_{end} value. This was seen as a slow (up to 10 min) spreading of the droplet after its initial recoil to equilibrium after 2–4 s. Secondary spreading is probably a result of surfactant mass transfer to the droplet three-phase line to subsequently lower the liquid–vapour interfacial tension and increase the solid–vapour interfacial tension, allowing further spreading. Secondary spreading is not of interest to this study given the short drying time of a coating droplet in an industrial coater.

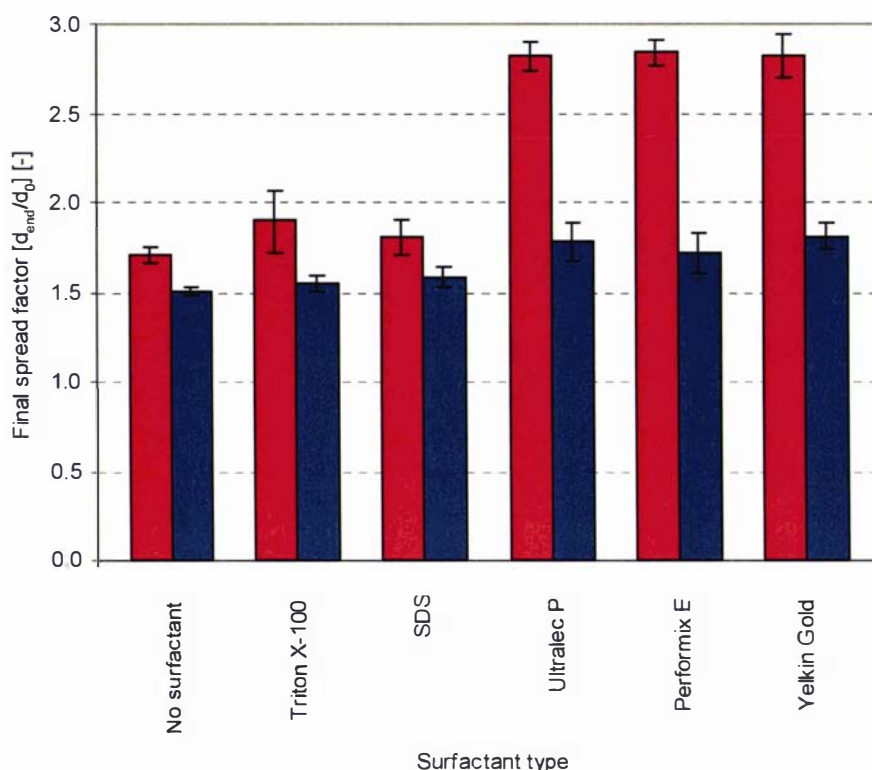


Figure 7.12: Effect of surfactant addition to a droplet formulation on the final spread factor for droplets impacting at 2.6 m.s^{-1} on to AMF: ■ 20% w/w maltodextrin DE5; ■ 40% w/w maltodextrin DE5. Error bars represent 95% CI, $n = 8$ for all trials.

Two statistically significant conclusions can be drawn from Figure 7.12. Firstly, addition of the three lecithins to the 20% w/w maltodextrin DE5 droplets, increased the final spread factor from 1.7 to 2.8. Secondly, there was also a slight positive effect on ξ_{end} with lecithin addition to the 40% w/w maltodextrin DE5 droplets from 1.5 to 1.7. This is in agreement with Toivakka (2003), who stated that viscosity provides more resistance to spreading than surface tension. However, there is no statistical difference in the type of lecithin used at either 20 or 40% w/w maltodextrin DE5. This is expected, given the similar molecular weight range of the lecithins, leading to similar diffusion rates to the free expanding surface. However, the activities of the lecithins are probably different because of their different HLB values (see Section 4.2.7), which are expected to promote differences in the rate of transfer to the three-phase line. In this case, the activity does not appear to play a part in the ξ_{end} value.

The 65% increase in ξ_{end} with the incorporation of a lecithin surfactant into the 20% w/w maltodextrin DE5 droplets clearly shows the importance of surfactant addition to a formulation to increase the final wetted area occupied by a droplet. This will lead to improved coating control through increased surface coverage and a thin coating thickness. Whilst the increase in ξ_{end} is not as large for the 40% w/w droplets with surfactant, it still shows a positive effect and maybe worth inclusion (pending a cost-benefit analysis) in an industrial formulation.

The incorporation of SDS and TX into the formulation did not show any statistical improvement to ξ_{end} in either the 20 or 40% w/w maltodextrin solutions. However, if a larger sample size was taken (i.e. $n > 8$), the 95% CI bounds may shrink to show a statistically significant difference. The limited spreading was surprising, given that the solutions containing SDS and TX had surface tension values of 53.6 and 42.8 mN.m^{-1} respectively.

Either the surface tension was not low enough to encourage a greater ζ_{end} value or the lecithins may exhibit a significant physico-chemical difference. Another trial was conducted under identical conditions but with a 20% w/w maltodextrin DE5 solution containing UP at a concentration of less than 0.1% w/w, giving the solution an equilibrium surface tension (EST) of 46.8 mN.m^{-1} . This gave an ζ_{end} value of 1.77 ± 0.09 (95% CI, $n = 8$). This was not significantly different from that for 20% w/w maltodextrin DE5 droplets containing TX or SDS, suggesting the possibility of a critical surface tension at which droplet recoil will be limited.

Despite the physico-chemical differences in the surfactants (predominantly molecular weight, ionic character and hydrophobicity), it is concluded that, based on this work, surfactant type is not a significant variable for formulation optimisation. This is confirmed in Figure 7.13 which shows that there is a strong relationship between the surface tension and the final spread factor, regardless of the surfactant type.

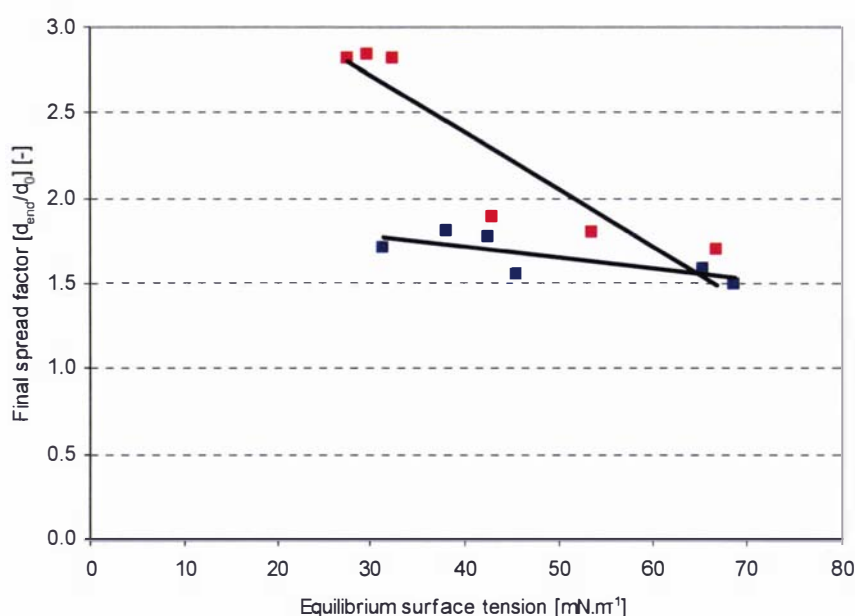


Figure 7.13: Final spread factor as a function of surface tension for droplets impacting at 2.6 m.s^{-1} on to AMF: ■ 20% w/w maltodextrin DE5; ■ 40% w/w maltodextrin DE5.

This is an important finding, since it is merely the surface tension lowering effect that accounts for the increase in ζ_{end} and not the type of surfactant. Further data, particularly data for lecithin-containing droplets having ESTs ranging between 30 and 40 mN.m^{-1} is required to confirm this. If confirmed, this finding should save the formulator valuable time that might have otherwise been spent investigating a broad range of surfactant types. From these tests it would appear that as long as the lowest possible EST can be achieved then surfactant type should be based solely on economic/labelling criteria and not on any fundamental physico-chemical aspect. However, this result may not hold true outside the experimental range investigated here, and the findings of Zhang and Basaran (1997) (discussed in Section 7.8.3) may become important.

High speed camera measurements of the droplets containing the wetting agents, particularly with lecithins at the 20% w/w maltodextrin DE5 concentration level, revealed limited recoil and larger ζ_{end} values than when surfactant was absent. Therefore, the surfactant must be playing a role during recoil. This is in agreement with the work of Pasandideh-Fard *et al.*

(1996) and the statement of Crooks *et al.* (2001) that the radial flow of fluid will result in the surfactant at the surface being swept to the droplet leading edge, where it will accumulate at the contact line in a greater local concentration resulting in a suppression in the recoil behaviour.

Figure 7.7(u–y), showing 20% w/w maltodextrin DE5 + 2% w/w UP, were typical of the solutions containing lecithins at the 20% w/w maltodextrin DE5 concentration, showing little if any droplet recoil. The spreading and recoil dynamics of 20% w/w maltodextrin DE5 droplets with the surfactants are depicted in Figure 7.14 and Figure 7.15.

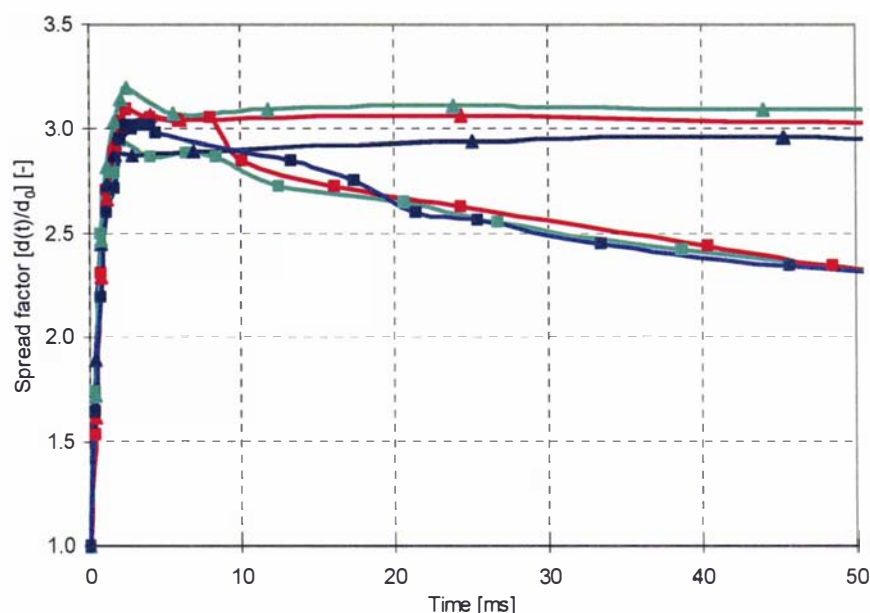


Figure 7.14: Evolution of the spread factor (up to 50 ms) for 20% w/w maltodextrin DE5 droplets containing surfactants impacting at 2.6 m.s^{-1} on to AMF: ■, 20% w/w only; ■, 20% w/w + TX; ■, 20% w/w + SDS; ▲, 20% w/w + UP; ▲, 20% w/w + PE; ▲, 20% w/w + YG.

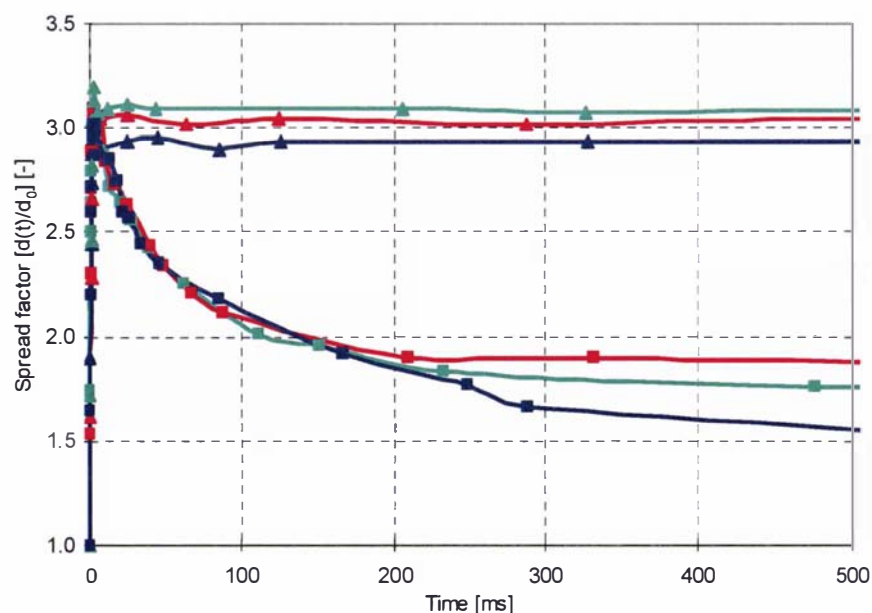


Figure 7.15: Evolution of the spread factor (up to 500 ms) for 20% w/w maltodextrin DE5 droplets containing surfactants impacting at 2.6 m.s^{-1} on to AMF: ●, 20% w/w only; ●, 20% w/w + TX; ■, 20% w/w + SDS; ▲, 20% w/w + UP; ▲, 20% w/w + PE; ▲, 20% w/w + YG.

Two important observations can be made from the above figures. Firstly, droplet recoil was inhibited in the droplets containing lecithins but not in the droplets containing TX or SDS. Secondly, despite the large physico-chemical differences between the surfactants, essentially the same ζ_{max} was achieved. These observations are best explained by considering the surfactant mass transfer mechanisms in a spreading droplet, depicted in Figure 7.16.

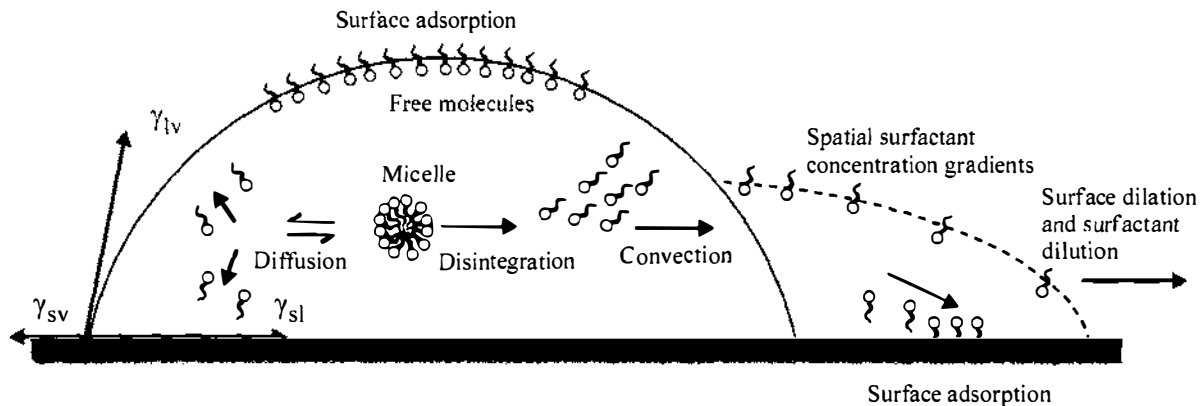


Figure 7.16: Surfactant mass transfer mechanisms during droplet expansion. Note: spreading in one direction only is shown here. ○ = surfactant polar head group; ~ = surfactant hydrophobic tail group.

Zhang and Basaran (1997) proposed three mechanisms influencing the distribution of surfactant along the three-phase line when a droplet impacts a surface: (a) surfactant dilution due to interfacial dilation or surface area creation; (b) surfactant convection towards the contact line, the intensity of which increases with the impact velocity; (c) surfactant repopulation of the interface from the bulk of the droplet.

With reference to surfactant mass transfer mechanism (a), the dilational rate can be calculated from the spread factor evolution figures and the following equation [taken from Zhang and Basaran (1997) and Mourougou-Candoni *et al.* (1999)]:

$$DR = \left(\frac{1}{A} \right) \left(\frac{dA}{dt} \right) = \left(\frac{\Delta A}{A_{max}} \right) \frac{1}{\Delta t} \quad (7.12)$$

where $\Delta A = A_{max} - A_{min}$ (where $A_{min} = \pi d_0^2$) and $\Delta t = t_{max} - t_0$. Take, for example, the 20% w/w maltodextrin DE5 + 2% w/w UP droplet at an impact velocity of 2.6 m.s^{-1} in Figure 7.14. The high dilation rate (60 s^{-1}) is responsible for the dilution of the surfactant at the droplet leading edge, which results in the DST value being higher than the EST value. Although not measured, the DST will lie between that of the 20% w/w maltodextrin DE5 droplet (66.9 mN.m^{-1}) and the surfactant-doped droplet EST of 32.4 mN.m^{-1} . As a result of this dilution effect, the ζ_{max} values for the 20% w/w maltodextrin DE5 droplets with and without surfactant are essentially the same, approximately 3.1. Crooks *et al.* (2001) found no difference in ζ_{max} value, and ζ_{end} value were only slightly increased with the incorporation of 2-butanol into glycerol solutions ($\mu = 6 \text{ mPa.s}$), which reduced the EST from 70 to a value as low as 44 mN.m^{-1} . This would suggest that, with the current initial kinetic energy, the rate of surfactant transfer to the surface is not fast enough to lower the surface tension at ζ_{max} and increase the maximum spread diameter.

With reference to surfactant mass transfer mechanism (b), although there may not be an appreciable amount of surfactant at the three-phase line at the instant of maximum spread, the

noticeable suppression of recoil behaviour immediately after results from the surfactant being convected to the periphery. This is likely to be further increased with the appearance of the rolling wave, as shown in Figure 7.7(v–w). The surface-tension-lowering effect (to around 30 mN.m^{-1}) of the lecithin surfactants lowers the surface energy such that it does not pull the droplet back into its equilibrium contact angle position and hence ξ_{end} is retained at ξ_{max} . The rolling wave is also present for the SDS and TX surfactants; however, their recoil was not suppressed to the same extent. Crooks *et al.* (2001) found that increasing the initial SDS concentration of the droplet from 600 to 800 ppm and thus reducing the surface tension from 58 to 52 mN.m^{-1} gave a noticeable suppression in recoil behaviour. The surface tension values of the droplets containing TX and SDS were 10 mN.m^{-1} higher than those containing lecithin, which possibly explains the limited recoil observed in this work.

With reference to surfactant mass transfer mechanism (c), this process can be divided into two sub-mechanisms. The first is surfactant diffusion. The diffusion of SDS in water is relatively slow, with an estimated diffusion coefficient of $8 \times 10^{-10} \text{ m}^2.\text{s}^{-1}$ [Chang and Franses (1992)]. Henderson and Micale (1993) determined the diffusion coefficient of SDS in water ($1.76 \times 10^{-10} \text{ m}^2.\text{s}^{-1}$) to be twice that of TX in water ($7.4 \times 10^{-11} \text{ m}^2.\text{s}^{-1}$). Given that TX has a similar molecular weight to the lecithins, the fastest rate of diffusion is likely to be in the droplets containing SDS. An order of magnitude estimate of the characteristic time for transport of SDS in the droplet by diffusion can be obtained using d^2/D_{SDS} . For the 20% maltodextrin DE5 + 0.5% w/w SDS droplets, the time taken for the surfactant to reach the surface at maximum extension based solely on diffusion ($\xi_{max} = 2.95$ for a droplet of initial diameter 2.63 mm, considering it travels from the initial droplet edge to the maximum spread diameter, i.e. a distance of 2.56 mm) is approximately 136 min. Hence, diffusion is clearly a negligible mechanism of surfactant supply to the free expanding surface under these conditions, which is why the droplets containing SDS and TX reached essentially the same ξ_{max} values. This also explains why no difference in ξ_{max} was noted with varying HLB value for the lecithins. These findings suggest that the droplet hydrodynamics control surfactant transfer to the expanding surface, which is in agreement with Crooks *et al.* (2001). Further evidence of the slow rate of surfactant mass transfer, particularly for the lecithin-containing droplets, is in the fact that the secondary spreading observed occurs for 5–10 min after initial impact.

The second sub-mechanism (of mechanism (c)) is demicellisation. The solutions employed in this work were above their CMCs and hence surfactant micelles will exist. Numerous studies [Mourougou-Candoni *et al.* (1997); Stoebe *et al.* (1997); Crooks *et al.* (2001)] have found that demicellisation plays a critical role in governing the supply of individual molecules to the interface of an impacting droplet. According to Crooks *et al.* (2001), below the CMC, the radial flow convects the surfactant already present at the interface to the droplet leading edge; thus hydrodynamics control surfactant mass transfer. However, when surfactant is present above the CMC, the surface is saturated with surfactant, and, in response to the non-equilibrium condition of surfactant being diluted at the liquid–vapour interface, the micelles will disintegrate to supply surfactant molecules over the new surface created by the droplet impact event. Both Dushkin and Iliev (1994) and Geeraerts and Joos (1994) [as cited in Crooks *et al.* (2001)] found the characteristic time of demicellisation of SDS and TX respectively to be shorter than that of the transport of free molecules to the surface. This implies that demicellisation responds immediately to droplet deformation to govern the supply of free molecules available for transport to the interface and swamps any contribution of hydrodynamics to the accumulation of any free molecules to the droplet leading edge by convection. However, this effect was not seen in the current series of experiments, although the solutions were at similar SDS and TX concentration levels to those employed by Dushkin

and Iliev (1994) and Geeraerts and Joos (1994). The CMCs of the lecithins were not measured. It is important to understand why this did not occur, because demicellisation could be a process worth exploiting to increase ζ_{max} and ζ_{end} .

According to Stoebe *et al.* (1997), there is also the issue of the rate of surfactant mass transfer to the solid–liquid interface and subsequent adsorption. However, this statement was with respect to unforced (spontaneous) or very slowly forced spreading cases (such as the contact angle measurements made in Section 4.9). According to Mourougou-Candoni *et al.* (1997), surfactants can adsorb on the surface only during the time elapsed between impact and the beginning of retraction (i.e. < 10 ms in this work) and, with the surface being hydrophobic, the surfactants adsorb by their hydrophobic tails via weak van der Waals' forces, which may not be resistant to the flow and interface friction during the retraction step. Hence, there is no need to select a wetting agent with a view to ensuring a high affinity for the substrate surface (as suggested by Shaw (1985) in Section 4.2.7) for impacting droplets.

Given the positive effect of surface tension on ζ_{end} , it is likely that impingement at higher droplet and air temperatures will further enhance spreading and adhesion, because of lower surface tensions at higher temperatures. However, increased temperature will lead to faster drying rates, and, in sprays, lower surface tension leads to smaller droplets which dry faster and can more easily drift off target. Hence, optimisation of droplet spreading needs to consider atomisation and droplet drying.

7.8.3 Surface tension and inertia effects

Given the positive effect of the impact velocity on ζ_{max} noted previously [Scheller and Bousfield (1995); Zhang and Basaran (1997); Crooks *et al.* (2001)] and the fact that ζ_{end} was retained at ζ_{max} for the 20% w/w maltodextrin DE5 droplets containing lecithins, it was thought that increasing the inertial force would promote greater ζ_{max} values and therefore a greater ζ_{end} value. Figure 7.17 and Figure 7.18 show the spreading results for 20% w/w maltodextrin DE5 droplets with and without 2% w/w UP impacting at 1.7, 2.6 and 4.1 m.s⁻¹.

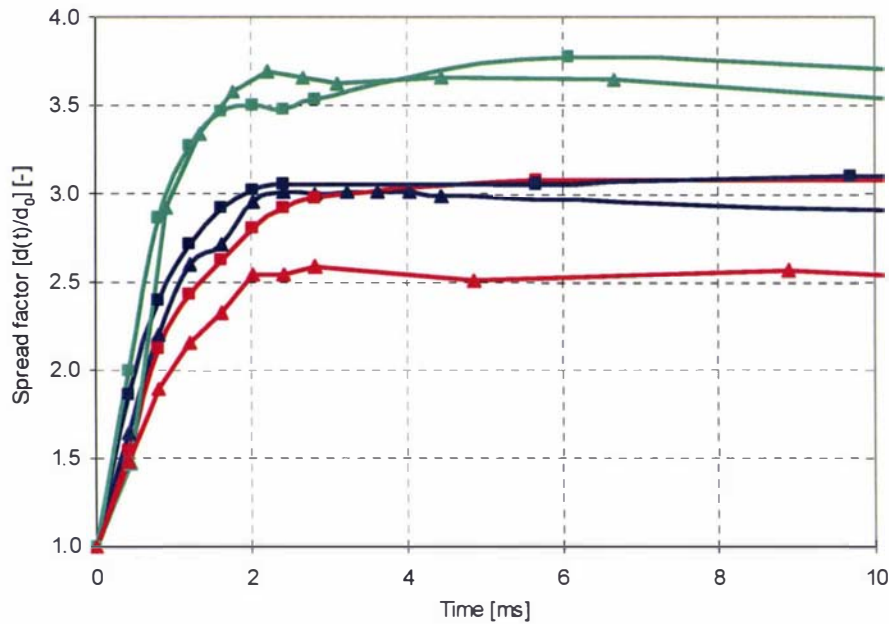


Figure 7.17: Effect of inertia (velocity) on the final spread factor (up to 10 ms) for 20% w/w maltodextrin DE5 droplets with and without 2% w/w UP impacting on to AMF: $\blacktriangle$ 20% w/w only at 1.7 m.s^{-1} ; $\blacktriangle$ 20% w/w only at 2.6 m.s^{-1} ; $\blacktriangle$ 20% w/w only at 4.1 m.s^{-1} ; $\blacksquare$ 20% w/w + UP at 1.7 m.s^{-1} ; $\blacksquare$ 20% w/w + UP at 2.6 m.s^{-1} ; $\blacksquare$ 20% w/w + UP at 4.1 m.s^{-1} .

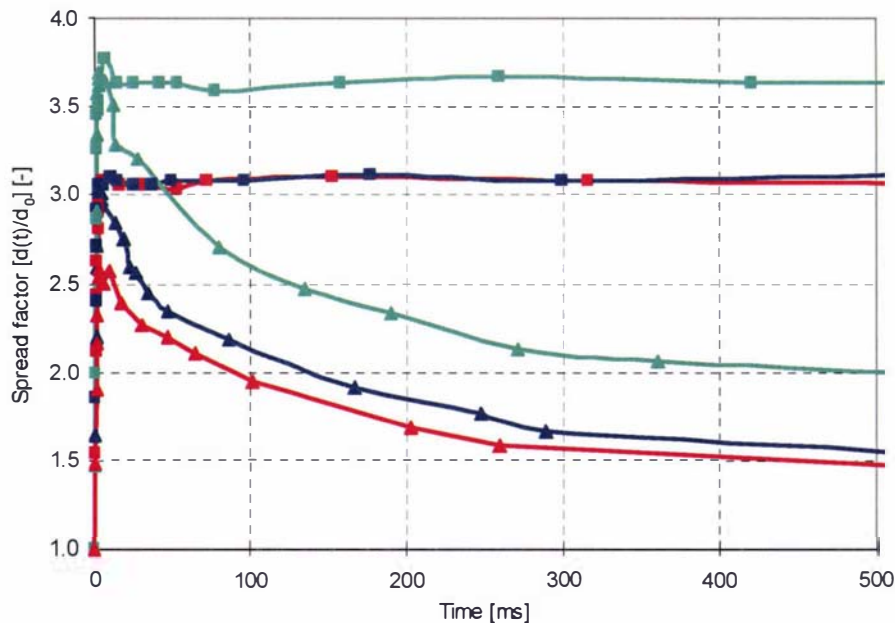


Figure 7.18: Effect of inertia (velocity) on the final spread factor (up to 500 ms) for water and 20% w/w maltodextrin DE5 droplets with and without 2% w/w UP impacting onto AMF: $\blacktriangle$ 20% w/w only at 1.7 m.s^{-1} ; $\blacktriangle$ 20% w/w only at 2.6 m.s^{-1} ; $\blacktriangle$ 20% w/w only at 4.1 m.s^{-1} ; $\blacksquare$ 20% w/w + UP at 1.7 m.s^{-1} ; $\blacksquare$ 20% w/w + UP at 2.6 m.s^{-1} ; $\blacksquare$ 20% w/w + UP at 4.1 m.s^{-1} .

The slightly lower rate of dilation found at the 1.7 m.s^{-1} droplet impact velocity resulted in a higher ζ_{max} value (3.0) for the surfactant-containing droplet as opposed to 2.6 for the droplet without surfactant. It can be hypothesised that the surfactant, in this case, was able to ‘keep up’ with the advancing droplet periphery to lower the DST and increase the maximum droplet spread diameter. This was not seen for the higher droplet impact velocities.

The results also support the earlier finding that greater ξ_{max} values occur with higher impact velocities up to 4.1 m.s^{-1} , and when surfactant UP is present, these are retained as the ξ_{end} value. Tests above this impact velocity were not possible because of the experimental constraints discussed earlier. It is reasonable to assume that, with a surfactant present, increasing the impact velocity increases ξ_{max} and consequently ξ_{end} as it is retained due to the reduction in the surface tension force acting over an increasingly large spread area trying to pull the droplet back in. However, based on an important finding by Zhang and Basaran (1997), there may be an upper bound on the positive effect of the impact velocity on ξ_{max} and therefore ξ_{end} . This is best explained with the aid of Figure 7.19 along with a discussion of the findings in Zhang and Basaran (1997).

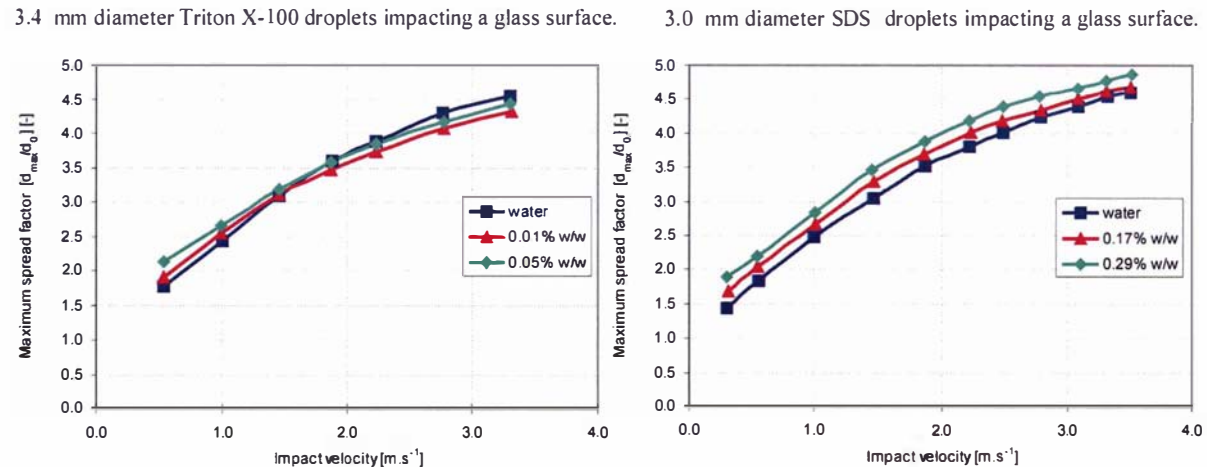
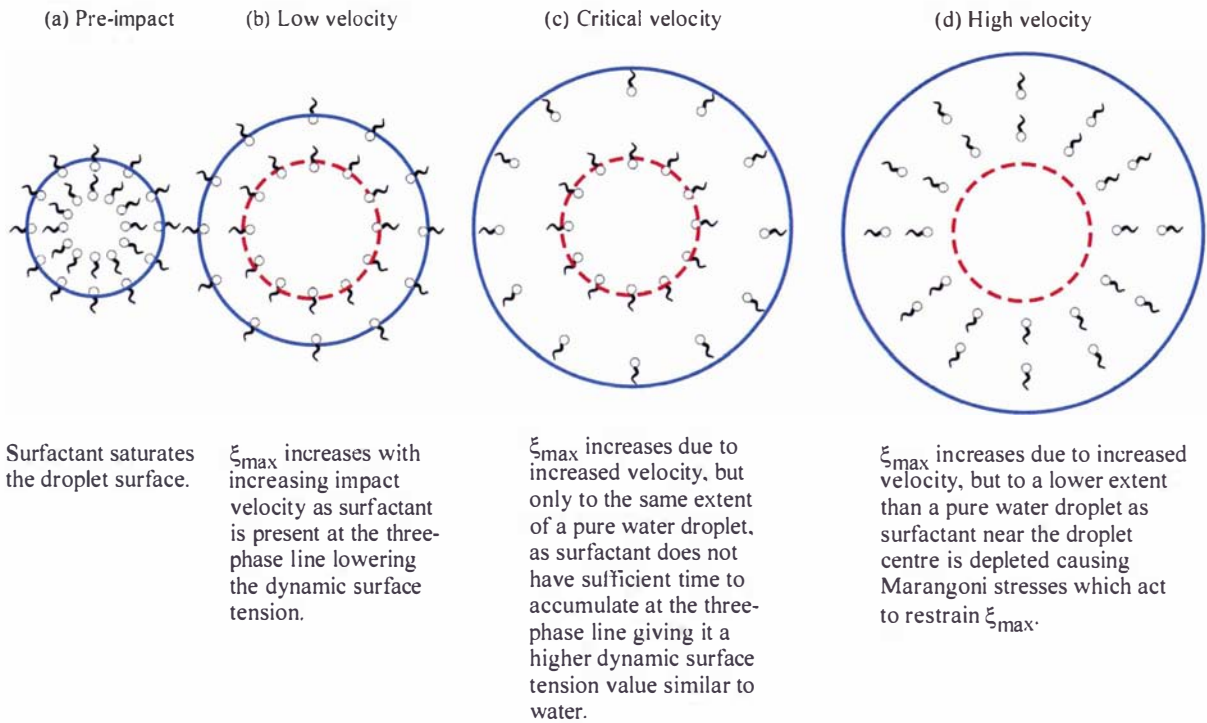


Figure 7.19: Hypothesised surfactant maldistribution on a droplet surface and the appearance of Marangoni stresses. Charts (a) and (b) were taken and modified from Zhang and Basaran (1997) to aid in the pictorial representation (developed here) of surfactant maldistribution on the droplet surface. ○ = surfactant polar head group; ~ = surfactant hydrophobic tail group.

Charts (a) and (b) are those of 3.4 mm diameter TX-containing droplets and 3.0 mm diameter SDS-containing droplets respectively impacting a glass surface. There is a critical velocity (approximately 1.5 and 2.0 m.s⁻¹ for 0.01% w/w and 0.05% w/w TX respectively) in chart (a) at which addition of surfactant limits the maximum spread diameter relative to that of pure water. According to Zhang and Basaran (1997), this arises because, as the impact velocity increases, interfacial velocities also increase (note the steeper slope for the impact velocity of 4.1 m.s⁻¹ in Figure 7.17) sweeping surfactant to the droplet periphery and resulting in a local rise in concentration at the periphery. The resulting surface tension gradient, low at the periphery and high at the centre, gives rise to Marangoni stresses that cause interfacial flow directed from the contact line to the droplet centre, which restrains the spreading of the droplet. This has important ramifications, suggesting that, if the impact velocity is too high, lower ξ_{max} values are achieved compared with droplet counterparts without surfactant. However, it must be borne in mind that, without surfactant present, droplet recoil will occur leading to lower ξ_{end} values.

Such an effect was not seen in chart (b) for the SDS-containing droplets, which Zhang and Basaran (1997) suggested was a result of the higher surfactant activity and diffusion coefficient of SDS, which can lessen or even eliminate the importance of the surface-tension-gradient-driven flows. Hence, DST can play apparently conflicting roles during droplet impact. If surfactant accumulates fast enough at the three-phase line, it can reduce the surface energy at maximum droplet extension, thereby enhancing spreading. However, this effect is small in relation to the effects of the impact velocity. It can also lead to a non-uniform distribution along the interface, giving rise to the Marangoni stresses that can inhibit droplet spreading.

Further research to investigate experimental impact conditions outside the ranges of this work is required. Marangoni stresses will become important at high impact velocities and low surfactant concentrations. In any event, as surfactant limits droplet recoil, it should be included in a coating formulation. It is also clear that smaller molecules of high activity and at concentrations above the CMC should be used.

The results and discussion above show that the hydrodynamics, surfactant transfer mechanisms, particularly the rate of micelle disintegration, and their effects on the DST are key processes that need to be understood to make quantitative predictions of both ξ_{max} and ξ_{end} values. Zhang and coworkers are now beginning to implement constitutive equations describing surfactant mass transfer mechanisms into existing three-dimensional numerical models [Zhang and Basaran (1997)].

7.8.4 Guar gum addition

The suppression of droplet rebound is of importance to many industrial applications, particularly pesticide application to plants as rebound represents lost product and reduced plant protection. By carefully constructing a series of tests solutions (constant shear viscosity and density) Crooks *et al.* (2001) studied the effect of polymer (polyethylene oxide, PEO) elasticity on spreading dynamics. The PEO is scattered throughout the solution in small discrete clumps that have no noticeable effect on solution properties. The stretching action that occurs during the droplet expansion and retraction unfolds and deforms the polymer. This deformation drains enough energy out of the droplet so that it can no longer escape the surface by rebound. Both increased molecular weight and polymer concentration were found to be responsible for increased suppression of rebound on hydrophobic surfaces. The high elongational viscosity dissipates the kinetic energy of the droplet during the strong

deformational flow, without increasing the shear viscosity that causes pumping and atomisation problems. The use of this polymer can be employed in cases that justify high impact velocities (i.e. atomiser constraints maybe). It should be noted that the high elongational viscosity creates larger drops upon atomisation as the neck of the atomising fluid jet is stabilised. PEO is a synthetic product, and to be effective needs extremely large molecules with molecular weights of 5000 kg per mole. However, a food grade analogue has been found in guar gum. The guar gum (NP 35 grade) was sourced from Danisco New Zealand Limited, Auckland. This polymer is extracted from the *Cyamopsis tetragonoloba* plant found in India and Pakistan, and is used widely as a food additive. This makes it excellent for spraying onto plants. Whilst the results of Crooks *et al.* (2001) showed greatly slowed recoil rates with increasing molecular weight of the PEO's employed they retracted essentially to the same ζ_{end} values. It was not known whether guar gum would also do the same or whether recoil could be slow enough for drying to arrest ζ_{end} close to ζ_{max} so a series of droplet impact tests was conducted. Two solutions (0.2 and 0.8% w/w) were prepared for initial trials before incorporation into the 20% w/w maltodextrin DE5 solution. The guar gum solutions were difficult to dissolve and significant gelling was evident at the 0.8% w/w concentration. Figure 7.20 shows the dynamics of droplet spreading for guar gum solutions impacting AMF at 2.6 m.s^{-1} .

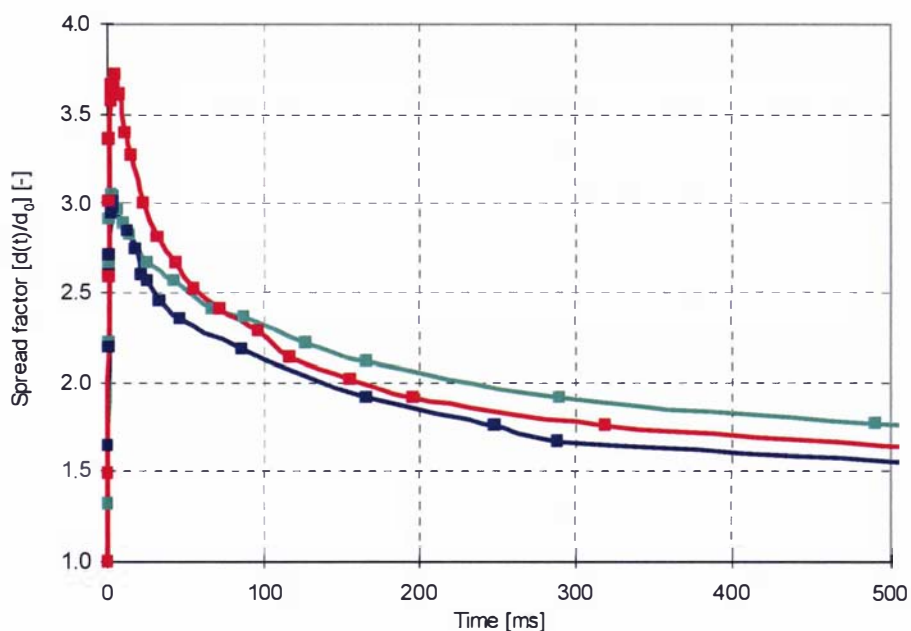


Figure 7.20: Evolution of the spread factor for droplets containing guar gum impacting at 2.6 m.s^{-1} on to AMF: ■ 20% w/w maltodextrin DE5 only; ■ 0.2% w/w guar gum; ■ 0.8% w/w guar gum.

Both guar gum solutions show similar recoil behaviour to that of maltodextrin DE5 at the 20% w/w concentration alone. Although guar gum also shows shear thinning behaviour, the higher ζ_{max} value for the 0.2% w/w addition is most likely to result from a diminished ability to dissipate the inertial energy as opposed to the 0.8% w/w guar gum case. The addition of guar gum as an additive to retain ζ_{end} and ζ_{max} of the 20% w/w maltodextrin DE5 droplets was not pursued any further.

7.8.5 Xanthan gum addition

Using a 3D model, Toivakka (2003) found that a shear thinning rheology improved spreading considerably (ζ_{max}). It was thought here that greater ζ_{max} values could be achieved with such a rheological property as the droplet viscosity is likely to decrease with the high shear experienced during spreading to its maximum diameter. As it reaches maximum spread, the droplet slows and the shear rate decreases, thus increasing viscosity again to hopefully impede its retraction, since it can dissipate more of the recoil energy to ultimately result in higher ζ_{end} values. Working along these lines an analogy to retaining ζ_{max} is that of chewing gum. Chewing gum is an example of a Bingham plastic. A coating material exhibiting a Bingham plastic, in which at high shear it deforms easily but then as it comes to rest (momentarily at ζ_{max}) it no longer flows due to a yield stress requirement, would represent an ideal coating material to achieve maximum spread diameter and limited recoil. The yield stress is imparted by significant polymer network formation. This property in addition to having a shear thinning rheology would represent an ideal coating candidate to spread further and then retain ζ_{max} . The main cause for concern was the speed at which the rheological network forms so that the yield stress prevents droplet recoil.

Xanthan gum exhibits both shear thinning and Bingham plastic properties and is used as a viscosity modifier at very low concentrations (0.1 to 1% w/w). The viscosity and yield value of xanthan gums does not change significantly with temperature up to 60 °C. Xanthan gum (Grinsted® 80) was sourced from Danisco New Zealand Limited, Auckland. Due to the shear thinning nature of xanthan gum it is difficult to match viscosities with the other polymers to enable comparisons. Given the low viscosity expected at the high shear rates as the droplet expands it was thought that it would only be of use in a lower viscosity 20% w/w maltodextrin DE5 droplet. Before incorporation as an additive it was decided to first compare xanthan gum as a function of concentration alone. The spread factor as a function of time for 0.2 and 0.8% w/w xanthan gum concentrations is shown in Figure 7.21.

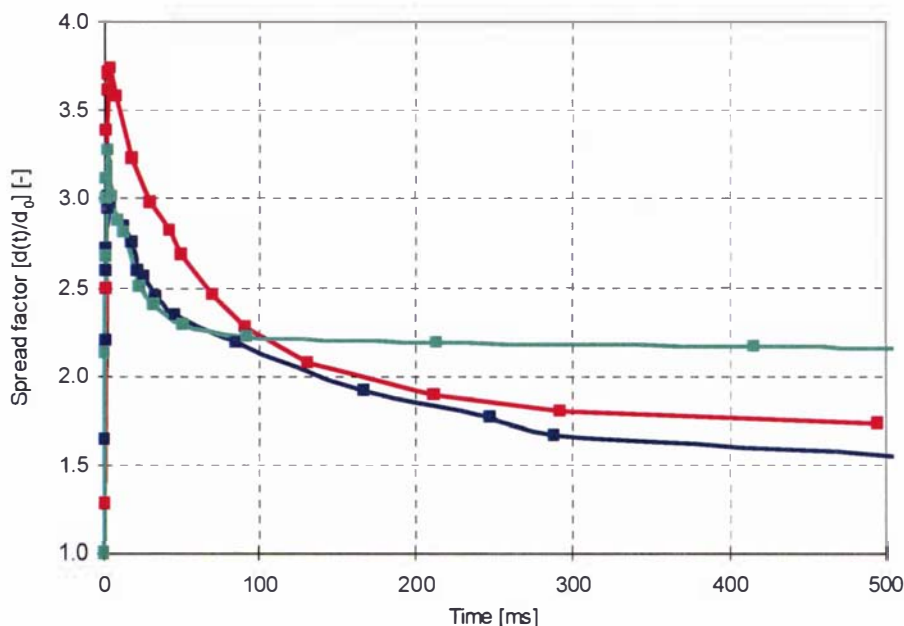


Figure 7.21: Evolution of the spread factor for droplets containing xanthan gum impacting at 2.6 m.s^{-1} on to AMF: ■ 20% w/w maltodextrin DE5 only; ■ 0.2% w/w xanthan gum; ■ 0.8% w/w xanthan gum.

The xanthan gum droplets recoil significantly in comparison to the droplets containing lecithins. Observation of droplet dynamics showed that the same doughnut shape appears suggesting the velocity at the edge of the droplet is not likely to be zero at ζ_{max} , hence, the time it remains at rest is not long enough for polymer networking to form to any significant extent. However, the 0.8% w/w xanthan gum concentration does show an ζ_{end} that is 46% higher than for the 20% w/w maltodextrin DE5 droplet alone. This could be further investigated but was not in the present work.

The search for other polymers showing rapid network formation at zero shear (at ζ_{max}) giving a high yield stress so to retain the droplet at ζ_{max} is worth further investigation. A similar line of thought is to have a surface pre-coat that once the droplet impinges, it retains its ζ_{max} through cross-linking of a polymer additive in the droplet. Future research should be aimed at creative rheological tailoring of the solutions.

7.9 SUBSTRATE EFFECTS

7.9.1 Pre-coating with surfactant

Pasandideh-Fard *et al.* (1996) found that droplet spreading on impact is so rapid that mass transfer limits surfactant accumulation at the droplet leading edge. This resulted in the limited increase in the maximum spread diameter observed in the above trials. In order to avoid this limit, the surface was pre-coated with surfactant to lower the surface energy at maximum droplet extension and consequently lower the solid–liquid contact angle. After this, surfactants were also added to the droplets to lower the liquid–vapour surface tension, γ_{lv} , to limit recoil and decrease the equilibrium contact angle with the view to obtaining greater ζ_{end} values than those achieved with surfactant incorporated into the droplet alone.

Scheller and Bousfield (1995) pointed out that the effect of contact angle on ζ_{max} is limited (less than 10%) for significant Re numbers (> 10). Asai *et al.* (1993) found that even for inkjet droplet impact, the ζ_{max} was independent of the surface for different grades of paper and plastic films. Using 3D model simulations Toivakka (2003) found a minimal effect of contact angle on ζ_{max} . Crooks *et al.* (2001) found that the same ζ_{max} was reached regardless of surface hydrophobicity, but ζ_{end} was significantly reduced on a more hydrophobic surface due to differences in droplet recoil behaviour. Based on the latter finding, chemical modification of the AMF surface corresponding to some form of pre-coating step on the dairy powder was seen as a potential method for increasing ζ_{end} .

Two methods of pre-coating were trialled, a spray-on solution, and a prepared surface. The spray-on solution is practical from an industrial viewpoint; atomised water droplets containing the surfactant of interest are deposited onto the surface. The water evaporates to leave a thin layer of surfactant on the surface. This was investigated by preparing 2% w/w solutions containing each lecithin which was poured, to give a thin film over the plates and allowed to evaporate. The plates were then re-chilled at 4 °C preventing surface crystallisation prior to use. Unfortunately, even with filtering (Buchner funnel with Whatman # 54 filter paper), the existence of small particulate matter (due to lecithins' low solubility in water) caused irregular shaped spread droplets due to contact pinning, preventing reproducible results. This was the smallest pore size available at the time. Much finer pore sizes exist that should remove the particulate matter and are worthy of future investigation. The second method was a prepared surface that incorporates the surfactant. Industrially this is somewhat similar to the existing lecithination process (with AMF/lecithin blends).

For industrial lecithination, depending on the phospholipid content of the lecithin (ranging from 60 to 90% w/w), the lecithin is blended with AMF at one- to two-thirds lecithin to AMF, to decrease its viscosity for spraying on to the powder. The addition rate is altered to give a final lecithinated whole milk powder that contains approximately 0.2% w/w phospholipid [D. L. Pearce, Fonterra Palmerston North, personal communication, 17 March, 2004]. In this work, the lecithin was incorporated by dissolving/dispersing the lecithins in molten AMF at the 2% w/w level during plate production. The higher concentration was chosen to ensure that there would be an excess of (although not measured directly) lecithin available at the plate surface to ensure spreading. From observation (by eye) the YG and PE largely dissolved, however, the powdered UP did not disperse well in the AMF, clumping together. Solid clumps were decanted out prior to pouring the plates as they could protrude above the surface. Lecithin addition to the surface is compared with lecithin addition to the impacting droplet in Figure 7.22. The final spread factor after impacting at 2.6 m.s^{-1} is used as the comparison measurement.

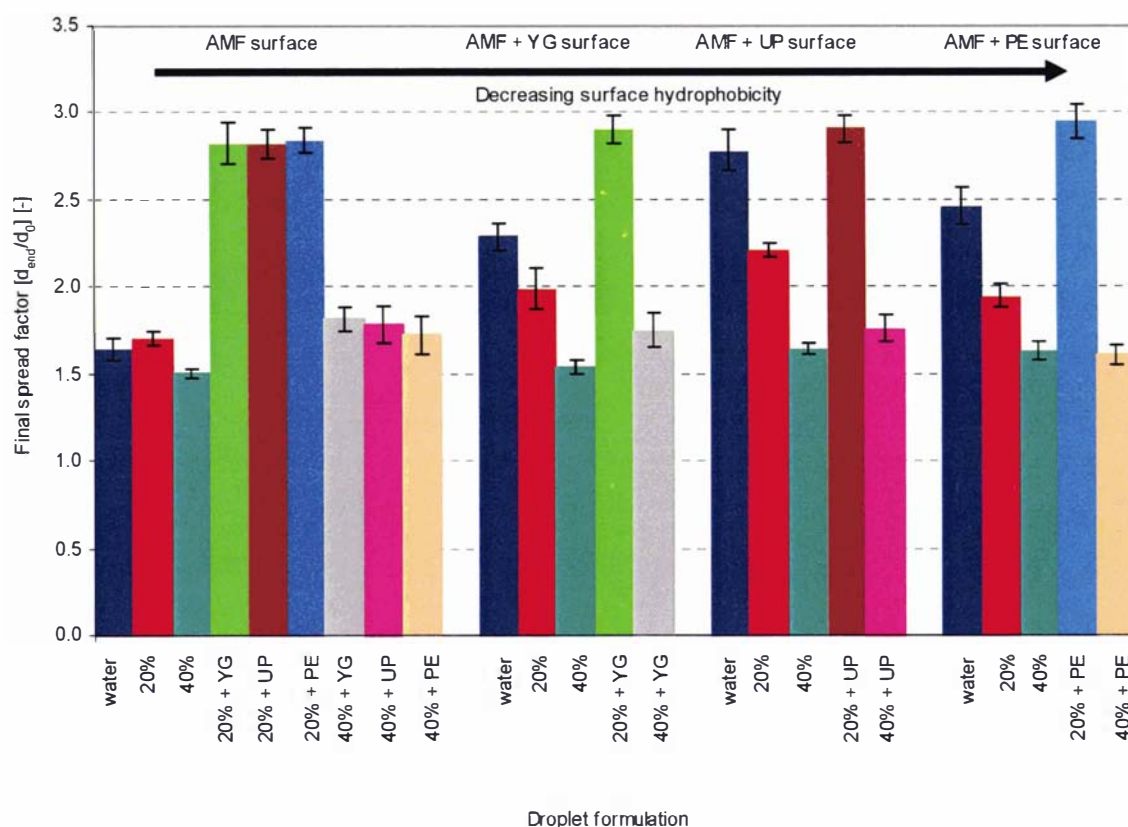


Figure 7.22: Comparison between lecithination of the AMF surface with lecithin incorporation into the droplet on the final spread factor for droplets impacting at 2.6 m.s^{-1} . 20 and 40% w/w represents maltodextrin DE5. UP, PE and YG represent the lecithin concentrations shown in Table 7.1. Error bars represent 95% CI, $n = 8$ for all trials.

Numerous statistically significant comparisons can be made. The main conclusions with respect to formulation optimisation for enhancing ξ_{end} are stated here.

The water droplets showed a marked increase in the spread factor when impacting the lecithinated surface (from 1.6 for the AMF surface to 2.8, 2.5 and 2.3 for the UP, PE and YG surfaces respectively). This suggests that the hydrophilic tails of the lecithins orient themselves at the solid–vapour interface to give a more hydrophilic surface character, encouraging droplet spreading. This has the effect of increasing the solid–vapour interfacial

tension, γ_{sv} and lowering the solid–liquid surface tension, γ_{sl} , both of which lead to a lower equilibrium contact angle and hence a larger spread factor (refer to Figure 6.1 and Equation (6.1)). This is in agreement with the finding of Crooks *et al.* (2001) that ξ_{end} was promoted for aqueous droplets on more hydrophilic surfaces. The measured equilibrium contact angles (sessile droplet and photographic technique, Section 4.9) on the AMF and lecithinated AMF plates were 67, 65, 56 and 36 ° for water on the AMF, YG (HLB = 4), UP (HLB = 7) and PE (HLB = 12) surfaces respectively. The lowering of the contact angle coincides with decreasing hydrophobicity of the lecithins (i.e. increasing HLB value). Based on the equilibrium contact angle values, it is not known why the AMF lecithinated with UP gave the highest ξ_{end} value.

Droplet spreading was also promoted by the expected reduction in the contact angle with plate lecithination for the 20% w/w maltodextrin DE5 droplets without surfactant (from 1.7 for the AMF surface to 2.2, 1.9 and 2.0 for the UP, PE and YG surfaces respectively). As for the water droplets, the neutral (HLB = 7) UP surface coating promoted the greatest ξ_{end} value for the 20% w/w maltodextrin DE5 droplet.

Incorporating the surfactant into the 20% w/w maltodextrin DE5 droplet had a far greater impact on ξ_{end} than incorporating the surfactant into the AMF surface. For example, for all lecithin types added to the droplets, a final spread factor of around 2.8 was achieved for impact on an AMF surface, whereas the surfaces lecithinated with UP, PE and YG gave final spread factors of 2.2, 1.9 and 2.0 respectively. This suggests that, for the 20% w/w maltodextrin DE5 droplets, the surface-tension-lowering effect far outweighs the effect of contact angle reduction on ξ_{end} .

For the 40% w/w maltodextrin DE5 droplets, incorporating the surfactant into the droplet impacting the AMF surface increased ξ_{end} . However, there was no additional benefit to spreading when the surfactant was incorporated into droplets impacting the lecithinated surfaces.

Finally, the combined lowering of the solid–vapour and solid–liquid surface energies by incorporating the surfactant both into the AMF and into the droplet did not promote spreading any further.

Figure 7.23 presents the spread factor evolution with time for water only and 20% w/w maltodextrin DE5 droplets containing lecithins impacting lecithinated AMF surfaces at 2.6 m.s^{-1} .

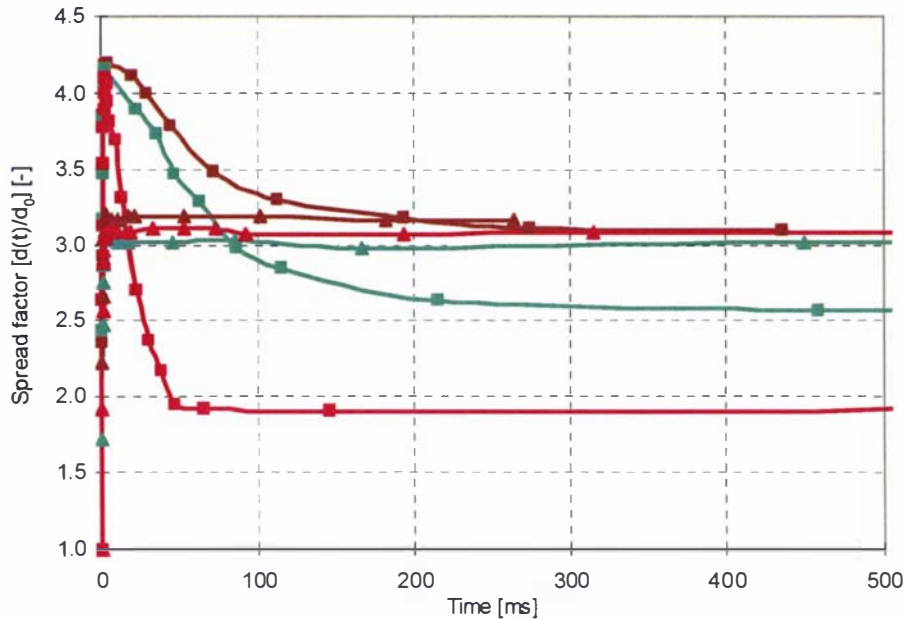


Figure 7.23: Evolution of the spread factor for 2.8 mm initial diameter water and 20% w/w maltodextrin DE5 droplets containing 2% w/w lecithins impacting at 2.6 m.s^{-1} on to lecithinated AMF: ■ water onto YG; ■ water onto PE; ■ water on to UP; ▲ 20% w/w maltodextrin DE5 + YG on to YG; ▲ 20% w/w maltodextrin DE5 + PE on to PE; ▲ 20% w/w maltodextrin DE5 + UP on to UP.

The results agree with observations made by Asai *et al.* (1993), Scheller and Bousfield (1995), Crooks *et al.* (2001) and Toivakka (2003), who all found that the chemical character of the surface had a minimal effect on ζ_{max} . The water droplets without lecithin spread to essentially the same ζ_{max} values regardless of the type of lecithin incorporated into the surface.

The 20% w/w maltodextrin DE5 droplets each incorporating a lecithin spread to a lower ζ_{max} compared to water (as expected because they are more viscous), but did not retract resulting in $\zeta_{end} \approx \zeta_{max}$. The presence of a lecithinated surface did not affect the ζ_{max} or ζ_{end} compared to impacting the lecithinated droplets onto a pure AMF surface.

This is the first known investigation of the combined effect of lowering both the solid–liquid surface tension and the solid–vapour interfacial tension and it is clear that there was an overriding effect of the lower solid–liquid surface tension, resulting in minimal effect on the final ζ_{end} value. It is not known why this occurred, given that water droplets did experience significantly reduced ζ_{end} values on more hydrophobic surfaces (YG > UP > PE). The recoil on the surface lecithinated with YG was also very rapid compared with that on the other lecithinated surfaces.

These are important findings, as pre-coating with surfactant and AMF (i.e. lecithination) would incur extra processing expense and not yield any significant benefit to the final droplet spread diameter, compared with adding the surfactant to the droplet.

7.9.2 Roughness and porosity effects

It is possible that a physical modification of the test surface will retard the recoil of the droplet after spreading to enhance the final spread diameter. Surface roughness can retard recoil by pinning the droplet at or near to its ζ_{max} . Both Link and Schlünder (1997) and Turton *et al.*

(1999) acknowledged increased wettability as penetration is improved. A series of qualitative trials was conducted to observe such phenomena.

Although several attempts were made, surface roughness was not successfully applied to the AMF plates: (1) tissue paper was passed over the surface, but the grooves left oblong-shaped droplets and led to little reproducibility; (2) a wire stamp placed divots into the surface, again leading to poor reproducibility. Instead, surface roughness was simulated on prefabricated plates. Two groups of plates, glass and stainless steel, were selected to mimic the range of contact angles likely to be encountered in an industrial coating operation. Glass (water equilibrium contact angle, $\theta = 34^\circ$) represents a hydrophilic (carbohydrate or protein) surface and stainless steel (water equilibrium contact angle, $\theta = 65^\circ$) represents a hydrophobic (milkfat) surface. Smooth (polished), lightly roughened (sand-blasted fine grit), rough (sand-blasted coarse grit), fine porous (sintered) and coarse porous (sintered) plates were included in both groups to investigate the effect of surface morphology in addition to the contact angle. Figure 7.24 shows photographs of the final spread diameters of 2.8 mm initial diameter, 20% w/w maltodextrin DE5 droplets impacting the surfaces at 2.6 m.s^{-1} .

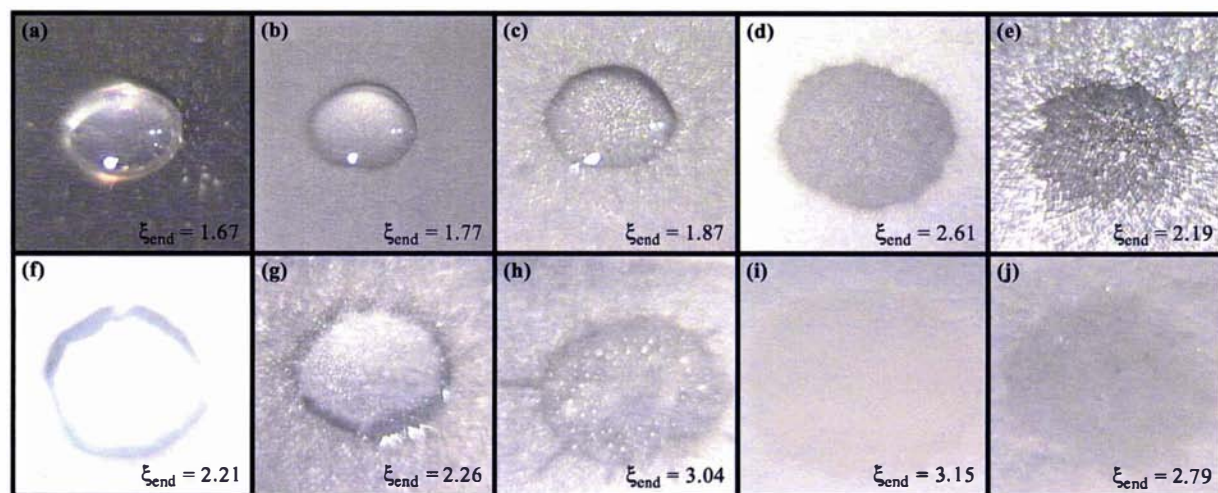


Figure 7.24: Effect of surface hydrophobicity, roughness and porosity on the final spread factor of 2.8 mm initial diameter 20% w/w maltodextrin DE5 droplets impacting at 2.6 m.s^{-1} : (a) smooth SS; (b) lightly roughened SS; (c) rough SS; (d) fine porous SS; (e) coarse porous SS; (f) smooth G; (g) lightly roughened G; (h) rough G; (i) fine porous G; (j) coarse porous G. SS = stainless steel; G = glass. Note: (i) and (j) are difficult to discern because of infiltration. The initial droplet diameter was approximately 2.8 mm.

Figure 7.24 shows the effect of substrate surface character on ξ_{end} . Although the surface preparations of the glass and stainless steel plates were not identical (particularly, roughness and porosity) and hence direct comparisons cannot be made, some important trends can be noted. Firstly, it can be seen that the final spread factor for a 20% w/w maltodextrin DE5 droplet on AMF (1.72) (refer to Figure 7.8) was a little greater than that on stainless steel (1.67) and lower than that on glass (2.21). The results were expected, given that the equilibrium contact angles on AMF and stainless steel were similar at 67° and 65° respectively, whereas the glass surface had an equilibrium contact angle of 34° . In all cases, as expected, the more hydrophilic glass surface promoted spreading extents that were greater than those achieved on the hydrophobic stainless steel surface. This is in line with the findings of Crooks *et al.* (2001).

The effect of surface roughness was pronounced. Within each class of material, the final spread factor increased with increasing surface roughness. This suggests that the spread

droplet remained pinned at an outer diameter greater than that expected based on its natural equilibrium contact angle on a smooth surface. However, there was obviously a limit to the positive effect of surface roughness, as fingering was evident in the rough (sandblasted coarse grit) glass plate. These fingers can break off from the main droplet to form small satellite droplets, which are seen as splashing [Scheller and Bousfield (1995)]. Many researchers [Stow and Hadfield (1981); Scheller and Bousfield (1995); Shakeri and Chandra (2002); Toivakka (2003)] have found that increasing surface roughness promotes peripheral splashing. According to Scheller and Bousfield (1995), splashing is also promoted by increasing droplet surface tension (liquid–vapour), droplet diameter and impact velocity. Stow and Hadfield (1981) studied the splashing of a droplet on dry, rough surfaces and proposed critical Re and We numbers for splashing to occur. The correlation was empirical in nature and related only to systems showing similar roughness scales. Pinning may occur naturally on the spray-dried powder surface. It might be increased by adding a flow agent, such as sipernat or diatomaceous earth at their permitted food additive levels, to act as the pinning points. Because of the large variability in the surface morphology (roughness and porosity) of spray-dried dairy powders [refer to Fäldt *et al.* (1993); Fäldt and Bergenståhl (1995); Fäldt and Bergenståhl (1996a); Fäldt and Bergenståhl (1996b); Chen (2001)], a quantitative exercise on splashing is not justified here.

Porosity can also have a positive influence on the final spread diameter. As with surface roughness, there is an upper limit to this positive effect. It can be seen that, in the coarse porous glass plate in Figure 7.24(j), the larger diameter pores led to a significantly higher infiltration rate during the spreading process, and, as a result, the droplet was unable to achieve a final spread diameter as large as on the surface with smaller pores. This is in agreement with the ‘ball park’ calculation in Section 3.9 and the findings of Holman *et al.* (2002), who found that increasing the mean pore size in a powder bed directly affected the maximum extension achieved by inkjet droplets impacting the bed.

Of important note was the lack of infiltration in the coarse porous stainless steel plate (Figure 7.24(e)). The hydrophobic nature of the surface impeded infiltration and resulted in a large amount of the droplet being retained above the surface. This is in agreement with the findings of Clarke *et al.* (2002), that pore filling is impeded with larger contact angles. This is important to note because infiltration may not enhance spreading to such great extents on a hydrophobic milkfat surface. The reason for the further spread on the coarse porous stainless steel plate (Figure 7.24(e)) compared with the rough stainless steel plate (Figure 7.24(c)) was likely to be a surface roughness issue. This was not seen in the same comparison with the glass plates (Figure 7.24(h) and Figure 7.24(j)). Hence, surface roughness and porosity are coupled.

For industrial coating of dairy powders infiltration will occur. The extent of its effect will be related to the relative rate of infiltration and spreading. There is little that can be done to reduce infiltration without an expensive pre-processing step, but maltodextrin DE5 is an inexpensive food grade material, so infiltration is accepted and excess coating material and time is required to account for the pore uptake.

7.10 CONCLUSIONS AND RECOMMENDATIONS

The work here represents the first attempt in the air-suspension particle coating field to focus on and identify key formulation and operating parameters relating to the key micro-level process of droplet impact and spreading. The droplet impact and spreading experiments have

provided the following useful guidelines for optimising formulation and operating conditions to achieve coating quality control, particularly the maximisation of ζ_{end} :

- Viscosity had a significant impact on the extent and the dynamics of spreading. Increasing the solution viscosity significantly decreased ζ_{max} . The effect of the impact velocity diminished with increasing viscosity. Higher viscosities also reduced the critical impact velocity at which splashing was observed and hence should reduce coating degradation.
- Lowering the surface tension did not increase the maximum spread diameter (under the conditions investigated in this work), as surfactant mass transfer to the contact line was not fast enough to accumulate an appreciable amount of surfactant. However, the surface tension did control the droplet recoil, because ζ_{end} was retained near ζ_{max} when a low surface tension ($< 40 \text{ mN.m}^{-1}$) was used, and preventing droplet ejection at the fullest extent of recoil.
- The experimental results in this work did not show a significant effect of the surfactant type on ζ_{max} . However, the findings of Zhang and Basaran (1997), under different conditions, suggest that smaller molecules with higher activities will enable larger ζ_{max} and ζ_{end} values. Although not investigated in this work, it has been shown that, at surfactant concentrations above the CMC, demicellisation can enhance the surfactant transfer rates.
- Lecithins (Performix E, Ultralec P and Yelkin Gold) representing a broad range of hydrophobicity had no effect on the extent or the dynamics of spreading when incorporated into a 20% w/w maltodextrin DE5 droplet, but produced greater spreading extents than droplets containing Triton X-100 or SDS. Thus, it is only the surface-tension-lowering effect that is important to the formulator and trialling different surfactants based on thermodynamic adsorption (to the droplet and substrate surface) is not likely to be fruitful.
- Rheological tailoring of the solutions to control droplet recoil was attempted. Guar gum was added as an elastic polymer able to dissipate inertial energy during spreading and recoil. However, the polymer alone did not significantly alter droplet recoil dynamics over 20% w/w maltodextrin DE5 alone. The addition of xanthan gum as a shear thinning polymer to increase ζ_{max} at the same time as retaining ζ_{max} due to the polymers ability to form a network with a yield stress was also unsuccessful.

It was also shown that certain physical modifications to the substrate surface can be made that are conducive to enhanced spreading. These include:

- Lecithination of the AMF surface reduces the droplet contact angle on the surface and promotes the spreading of water and 20% w/w maltodextrin DE5 droplets to larger ζ_{end} values. Addition of the lecithin to the droplet (as opposed to surface lecithination) has the same effect and is a much less expensive alternative to increasing the final spread diameter on an industrial-scale.
- Surface roughness serves to increase ζ_{end} as a result of contact angle pinning, but only to a certain extent because splashing will occur earlier than on a smooth surface.
- Porosity and subsequent coating infiltration serve to retain ζ_{end} at or close to ζ_{max} but at the expense of lost coating material when the porosity is high. When the rate of infiltration exceeds the rate of spreading, a lower final spreading extent results. Surface hydrophobicity is likely to limit infiltration and hence ζ_{end} for hydrophilic coating solutions.

- Despite the effects noted for surface roughness and porosity, control of these substrate properties at an industrial level has not been considered and is likely to be costly. A pre-processing step such as pre-coating or particle rounding would be needed to eliminate such effects.

It should be reiterated that these findings are limited to the experimental ranges ($23 < Re < 12\,300$ and $139 < We < 741$) investigated in this work. Future research should be aimed at modifying the experimental technique so that it operates within industrial-scale conditions, particularly the use of smaller droplets and higher impact velocities. These modifications to the method, along with a three-dimensional numerical model to predict the dynamics of droplets containing surfactants and their final spread diameter, will significantly aid future studies.

CHAPTER 8

KEY PERFORMANCE GUIDELINES, VALIDATION AND INDUSTRIAL PROCESSING

8.1 INTRODUCTION

This chapter condenses the findings of this thesis to the key performance guidelines for formulation selection, and the operation and design of dairy powder coaters. It then uses these guidelines in an attempt to validate them in a pilot-scale Glatt® Würster coater. The results of all studies are finally used to define the considerations, operating parameters and design innovations needed for dairy powder coating of the future.

8.2 SUMMARY OF IDEAL COATING CONDITIONS

Each micro-level process of dairy powder coating studied in this thesis highlights a few key performance guidelines that are essential in achieving control of both product quality and process performance. These performance guidelines are summarised below.

8.2.1 Droplet drying and droplet stickiness

Two key problems can occur as a result of stickiness development during drying: over-drying of the spray droplet before impingement on the substrate, resulting in non-adherence; unwanted inter-particle agglomeration of particles with sticky surfaces.

Droplets that do not successfully adhere upon impingement onto the substrate particles represent a coating process inefficiency, as coating material is lost. The material either is carried away to dilute the final bagged product or needs to be recaptured and reprocessed, and the required coating time must be extended to make up for the adhesion inefficiency. Numerous researchers have observed this problem [Yang *et al.* (1992); Aronson and Tsaur (1993); Fukumori (1994); Link and Schlünder (1997)]. The moisture content of the droplet surface, in particular the degree of stickiness associated with the surface, is a key parameter governing this micro-level process.

Unwanted inter-particle agglomeration is the most serious problem that is encountered in the spray coating process [Fukumori *et al.* 1987, 1988, 1991a, 1991b, 1992; Maa *et al.* (1996)]. Agglomeration can cause rapid defluidisation, resulting in process shut-down and product loss. Again, the moisture contents of the droplet and the coating surface layer and the associated stickiness have a direct influence on the degree to which this micro-level process occurs.

Although dealt with separately in this work, drying and stickiness are closely related through skin formation and the increase in surface tack during the drying of high molecular weight materials. The investigations described in Chapter 6 showed that skin formation resulted in droplets showing increasing stickiness during drying up until a maximum was reached. After this point, the stickiness fell away until the surface was completely non-sticky. The maximum and minimum points of stickiness represent the ideal states for ensuring successful droplet–substrate impact and adherence and for preventing unwanted inter-particle agglomeration respectively. The key stickiness findings for maltodextrin DE5 are shown in Figure 8.1.

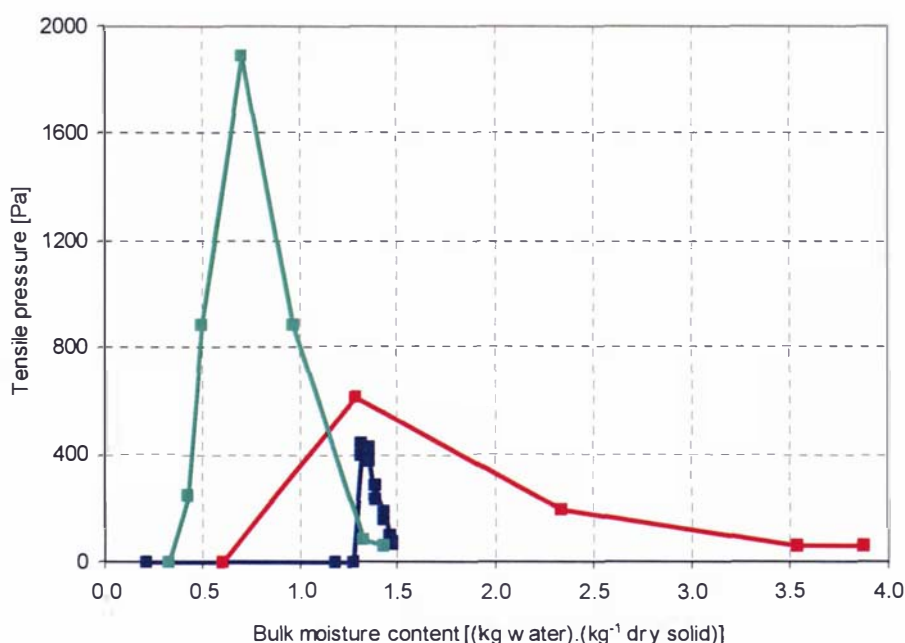


Figure 8.1: Summary of key findings for control of droplet stickiness: ■ 40% w/w maltodextrin DE5 drying at 40 °C; ■ 20% w/w maltodextrin DE5 drying at 78 °C; ■ 40% w/w (3:1) maltodextrin DE5:glycerol drying at 78 °C.

For successful droplet–substrate impact and adherence, a broad stickiness profile, such as that for 20% w/w maltodextrin DE5, is required. However, for minimum inter-particle agglomeration, a narrow stickiness profile, such as that for 40% w/w maltodextrin DE5, is required, so that a rapid transition to the glass state occurs at the surface. In addition, the surface morphology is influenced by the formulation and the drying conditions. A smooth coating with minimal cracks is required to give good barrier resistance, and can be made with the addition of plasticisers (e.g. 40% w/w initial solids concentration (3:1) maltodextrin DE5:glycerol). Addition of plasticisers significantly broaden the stickiness profile.

8.2.2 Droplet impact and spreading

Maximising the droplet coating coverage will give control over the coating barrier performance and the amount of material required to coat the substrate particles. To optimise the droplet impact and spreading micro-level process, the formulation and the operating conditions to maximise the final spread diameter were investigated in Chapter 7. Figure 8.2 summarises the key droplet impact and spreading findings.

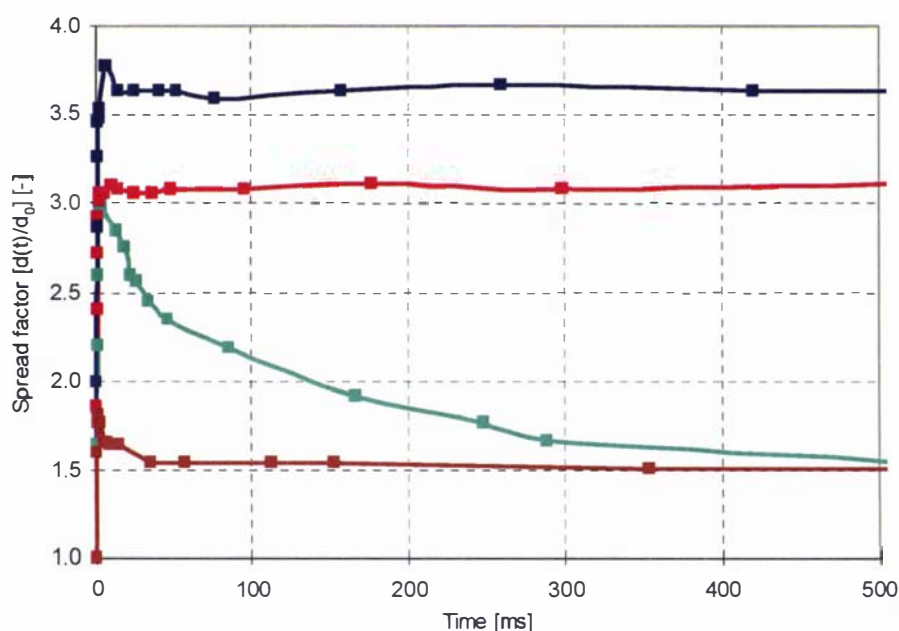


Figure 8.2: Summary of key findings for control of droplet impact and spreading: ■ 20% w/w maltodextrin + 2% w/w UP at 4.1 m.s⁻¹; ■ 20% w/w maltodextrin + 2% w/w UP at 2.6 m.s⁻¹; ■ 20% w/w maltodextrin only at 2.6 m.s⁻¹; ■ 40% w/w maltodextrin only at 1.7 m.s⁻¹.

The final spread diameter was controlled by the droplet surface tension. For example, the 20 and 40% w/w maltodextrin DE5 droplets had the same surface tension and achieved the same final spread factor, despite the viscosity difference (11.9 compared to 242.7 mPa.s) and the fact that the 20% w/w droplet initially spread twice as far as the 40% w/w droplet. However, addition of the lecithin surfactant Ultralec P at 2% w/w retained the final spread factor at the maximum spread factor and therefore reintroduced the importance of viscosity. This was validated, because increasing the impact velocity from 2.6 to 4.1 m.s⁻¹ with the Ultralec P present increased the final spread factor by 21%. Addition of a surfactant to the coating formulation should drastically enhance control of the coating quality.

The ideal coating formulation will be of low viscosity at high solids contents, show enhanced spreading ability (wetting agent addition), will form coherent films with minimal defects (plasticiser addition) and show significant stickiness prior to spray droplet impact on to the powder substrate particles followed by rapid drying to a non-sticky state before the particles exit the dilute pneumatic transport region of the Würster insert and into the fluidised bed region of a Würster-style coater.

8.3 PILOT-SCALE COATING TRIALS

8.3.1 Scope

It was the intention to conduct pilot-scale coating trials at the boundary between successful coating and the first sign of agglomeration. The droplet stickiness and droplet impact and spreading guidelines could then be used to explain observations of the micro-level processes and drive the process to a successful outcome in terms of the coating objectives mentioned in Section 2.4. However, the limited flexibility of the Würster coater meant that the response variables, particularly the degree of agglomeration, were too insensitive to the control variables leading to ‘all-or-nothing’ agglomeration. This along with the limited remaining

time available led to a constrained study. The pilot-scale coating trials were limited to a spray droplet adhesion efficiency (spray drying) study and to qualitative observations on coating morphology.

8.3.2 Experimental set-up

Trials were conducted on a Glatt® (UniGlatt D7852, Glatt® Process Technology GmbH, Binzen, Germany) Würster coater housed in the pilot plant at Fonterra, Palmerston North. Figure 8.3 is a photograph of the Glatt® coater and auxiliary equipment.

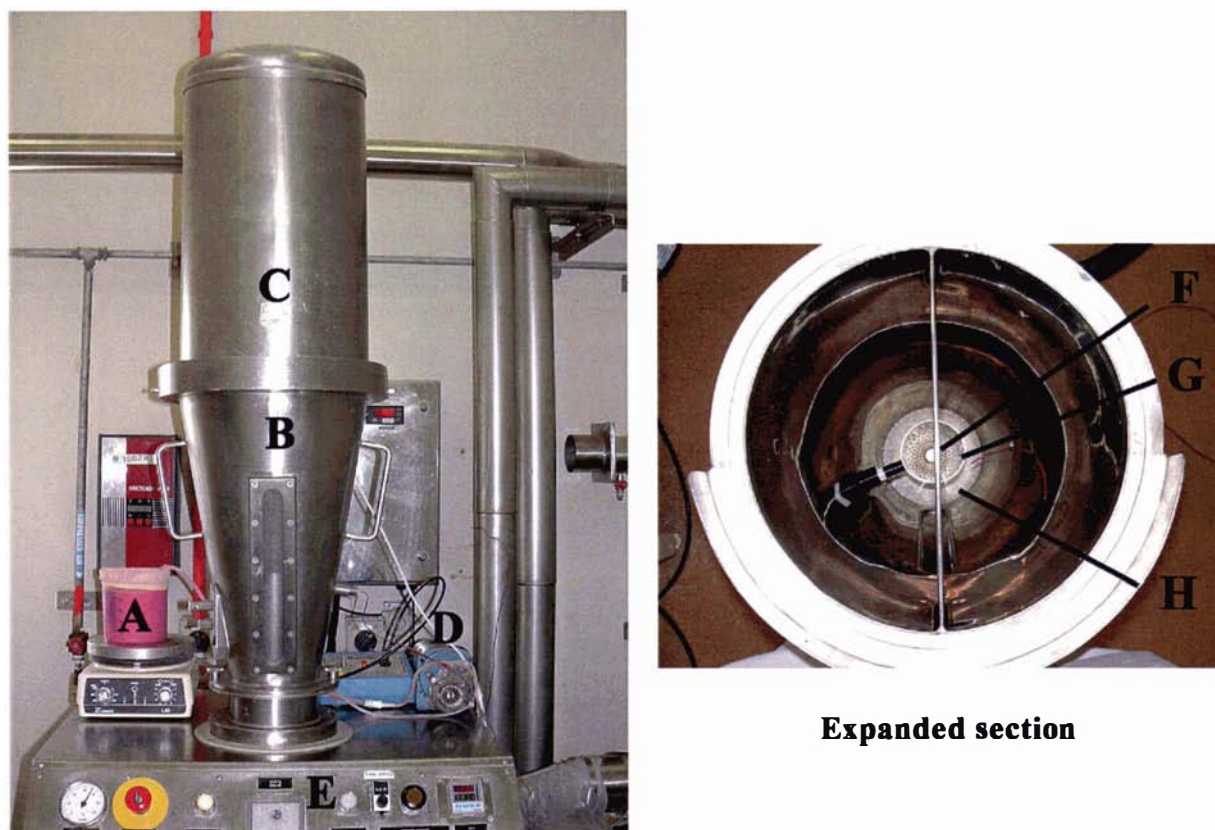


Figure 8.3: Photograph of the Glatt® Würster coater and auxiliary equipment used for the pilot-scale coating trials. The expanded section shows a 'bird's-eye' view of the inside of the coating chamber. A = coating solution vessel; B = coating/drying chamber; C = head unit (containing filter sock); D = peristaltic pump; E = base unit; F = nozzle; G = air distribution plate; H = Würster insert. Printed with permission from J. Hill, Fonterra, Palmerston North.

The coater consisted of a conical drying chamber and a cylindrical Würster insert. A suction blower and an outlet throttling valve maintained a constant airflow through the chamber. The air was heated in two stages with electric element heaters and entered the bottom of the coater via an air distribution plate, with larger holes in the plate centre to concentrate the airflow through the Würster insert. Coating solution was fed to a two-fluid air atomising nozzle via a peristaltic pump (Masterflex, 100 rpm, head model 7013 00, Cole-Parmer Instrument Co., Vernon Hills, IL, USA). The atomising air pressure was maintained by a regulating dial on the Glatt®. In all trials, the air pressure was set to 2 bar to give the smallest possible droplet diameter. T-type thermocouples (Omega Engineering Inc., Stamford, CT, USA) were used to monitor the air temperature in the chamber at the positions shown in Figure 8.4. No significant difference in temperature between the positions was noted because of the high air flowrate through the system. A relative humidity probe (thermistor type, HIH-3602-A, Honeywell International Inc., Morgantown, NJ, USA) measured the relative humidity at the

top of the chamber near the air outlet. The air temperature and relative humidity measurements were datalogged with a PicoLog datalogger (TC-08, Pico Technology Ltd, Cambridgeshire, UK) connected to a PC (Compac Presario). The atomising air pressure, fluidising air velocity (dial setting) and coating solution flowrate were recorded manually. Figure 8.4 shows a schematic of the pilot-scale Glatt® Würster coater and measurement devices.

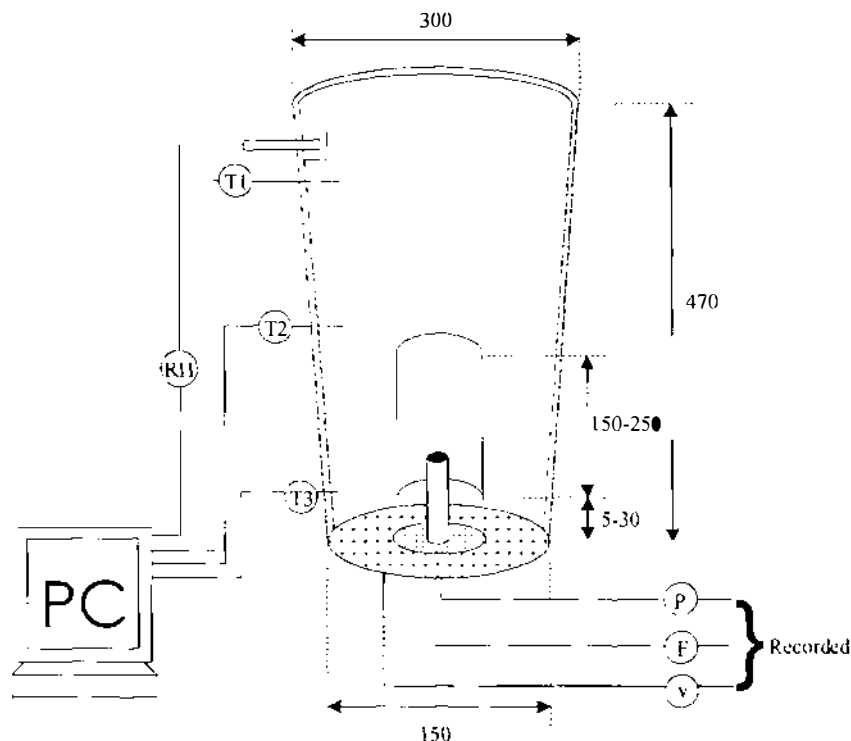


Figure 8.4: Schematic of the Glatt® Würster coater drying chamber showing the Würster insert and the position of various sensors: T1, T2, T3 = T-type thermocouples measuring air temperatures; RH = relative humidity sensor; P = pressure gauge; F = coating solution flowrate; v = air velocity (dial setting); PC = personal computer for datalogging.

Solutions were made as outlined in Section 7.5.2, but, in addition, red food dye (Hansells, New Zealand) was added at 10 ml per 4 litres to facilitate observation of the coating (see Figure 8.6) and to ensure that all the coating was dissolved from the substrate during the coating mass tests (Section 4.11). The general procedure for conducting coating trials was as follows: the fluidising airflow and atomising airflow were turned on and the chamber was allowed to preheat to the desired set-point temperature; the chamber was then taken off the base unit, the substrate particles were added (approximately 215 g) and the chamber was immediately placed back on to the base unit and allowed to heat back up to the set-point temperature; once the air temperature was stable, the coating solution pump was turned on to indicate the start of the coating trial. A typical temperature and relative humidity history for a coating trial are shown in Figure 8.5.

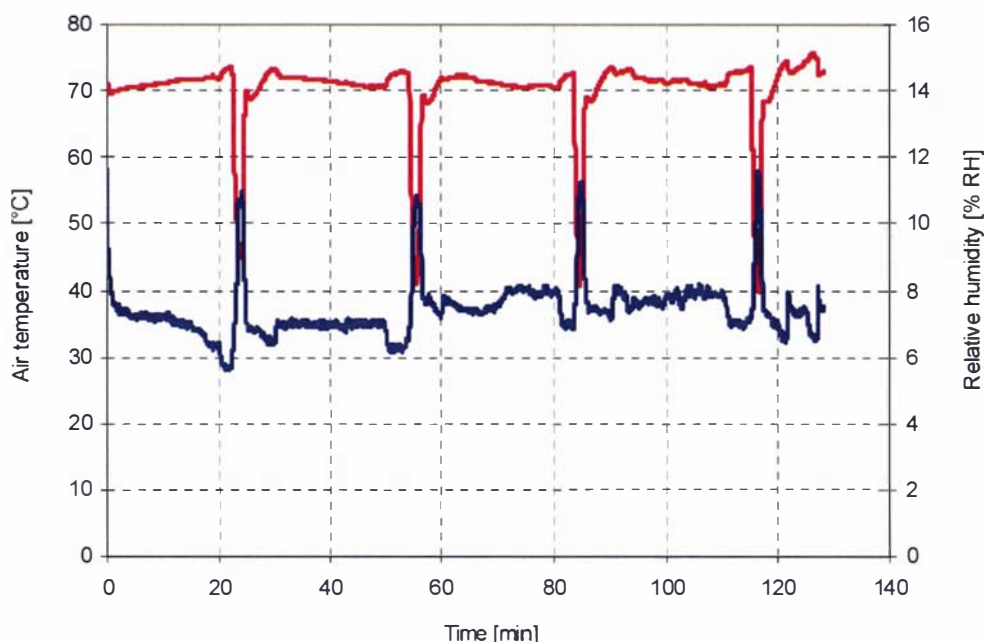


Figure 8.5: Typical temperature and relative humidity histories for a coating trial. Set-point air temperature = 90 °C; air velocity (dial setting) = 300; coating solution flowrate = 3.5 g.min⁻¹ (20% w/w maltodextrin DE5). — air temperature; — relative humidity.

From time 0 to 20 min, the system was at steady-state, with an air temperature of 70 °C at the top of the Würster insert (heat losses accounted for the deviation from the set-point of 90 °C) and a relative humidity of 7.5%. After 20 min coating time, the solution flowrate was turned off and the particles were allowed to dry for 5 min before a sample was taken. As there was no sampling port, the process was stopped momentarily and a sample was collected from the bottom of the chamber. The sampling process took approximately 60 s, including time to clear the nozzle of blockages. This appeared as the large drop in the temperature profile at 25 min and the corresponding spike in relative humidity. The coater took close to 5 min to heat back up to the process temperature and then the coating solution pump was turned back on (time 30 min). The air temperature fell slightly, accounting for the latent heat of vaporisation to evaporate the water in the spray and coating droplets. The process was repeated five times to give a total coating time of 100 min. The mass of coating material on the particles was measured for the five coated samples and the initial uncoated sample.

8.3.3 Coating equipment limitations

The Würster coater used in this study was designed for easily spoutable particles, i.e. Geldart D particles that are of higher density and have larger particle diameters than dairy powders. This limited the range of operating variables and levels that could be used in these coating trials. These limitations highlight possible challenges with the current state of the coating equipment for application to dairy powders. The major limitations and suggested improvements are discussed below.

The spray nozzle imposed the major constraint on the system because, at the 2 bar operating air pressure, the majority of the dairy powder charge ended up in the filter sock. Reducing the atomising air pressure to 1 bar did not alleviate this problem and also resulted in broader spray droplet distributions. Because of this, a constant recirculating flow of dairy powder particles was not maintained, which led to non-uniform coating and significant amounts of droplet spray drying.

The powder was susceptible to rising in plugs without the constant mechanical dislodging of powder build-ups on the coater wall and in the annular fluidised bed region. The chamber height needs to be lengthened significantly to address this. Of equal importance is the need for a straight cylindrical drying chamber (not tapered). This will prevent the build-up of the cohesive dairy powder on the walls, as its own weight will slough it off and back down to the fluidised bed region. A tapered expansion zone at the top of the cylindrical section is required for particle deceleration, so that the majority of the particles are not retained in the filter sock but fall back to the annular fluidised bed region. Despite these limitations, when the atomising air was turned off, whole milk powder, the natural cheddar cheese flavoured powder and the natural butter flavoured powder (both described in Section 4.3) could be relatively well circulated below an air temperature of 50 °C. Above 50 °C surface fat melting was prominent and excessive agglomeration occurred. However, there is still work to be done on the fluidisation/circulation side of the coating process to improve the ease of particle circulation.

For the glass ballotini® trials, temperatures below 55 °C resulted in excessive agglomeration. This occurred because a small portion of the spray impinged on the inside of the Würster insert and the low drying temperature meant there was not enough drying capacity to prevent further build-up of sticky agglomerates assembling there. According to Christensen and Bertelsen (1997), the lower part of the inside of the Würster insert is the Achilles heel for the Würster coating process because agglomeration commonly occurs here. This was attributed to sticky particles contacting the inside surface of the Würster insert, which consequently built up a substantial caked particle layer. It was exacerbated by the spray angle, which was slightly too large, resulting in a small fraction of the spray impinging directly on to the inside surface of the Würster insert. Frequently, large agglomerates would disengage back into circulation and these were not representative of the actual degree of inter-particle agglomeration taking place in the system. Consequently, an accurate indication of the relative importance of the formulation binding forces compared with the inertial forces present in the coater could not be gained. To remedy some of these problems, a larger Würster insert diameter is required to account for the current spray angle. There also needs to be a method of clearing the nozzle of blockages during processing. This might be achieved with a periodic pneumatic burst of air to the coating solution fluid-line. An additional design aspect here is that the unit should have provision for independent control of the inner and annular airflows to optimise the particle circulation patterns and the drying and wetting conditions.

8.3.4 Spray droplet adhesion efficiency trials

Because of the above-mentioned limitations with respect to dairy powders, glass ballotini® (Potters spec C, minimum roundness 75%, US sieve 40–60, Potters Industries Inc., Valley Forge, PA, USA) were selected as the substrate for the spray droplet adhesion efficiency (spray drying) trials. The objective of this set of trials was to observe the effect of the formulation and the operating conditions on the amount of over-drying occurring in the process as a measure of spray droplet adhesion efficiency. It was not possible to carry out an accurate mass balance on the system to determine the amount of spray-dried material because of the continual loss of material through the filter sock. Because of these same losses, it was not possible to calculate a mass-average-based result on any spray-dried material remaining in the system using particle size data. Hence, the spray drying losses were inferred by measuring the amount of dry coating material collected on each sample and comparing this with the amount of dry coating solids supplied to the system.

The ballotini® were easy to manage, being spherical, insoluble and relatively non-porous, and their large size and density (Sauter mean diameter of 300 μm , $\rho_p = 2550 \text{ kg.m}^{-3}$) made particle circulation relatively easy. The large size also enabled a large particle–droplet diameter ratio, leading to reduced potential for inter-particle agglomeration [Maa *et al.* (1996)].

The two key engineering approaches to increasing coating efficiency while minimising inter-particle agglomeration are to keep freshly wetted particles apart for as long as possible and to provide a constant [Cheng and Turton (2000a); Jono *et al.* (2000)] dilute flow of particles to the coating zone. The bed load was always 215 g to provide dilute conditions that minimised inter-particle contact probability and thus reduced the potential for agglomeration. The coating solution flowrate to the system was also kept low (3.5 g.min^{-1}) to ensure rapid drying of the coating, thus minimising the potential for agglomeration. Although the particle–air volume ratio and the coating solution flowrate seemed to be low, they were in line with other work [Wan and Lai (1992b); Jono *et al.* (2000)]. Because of the dilute (low particle–air volume ratio) conditions, a fluidised bed region was not observed in the coater. The Würster gap height was set to 30 mm.

Three air temperatures were investigated: 55, 70 and 85 °C at the top of the Würster insert. There was no means of controlling the relative humidity in the coater because air was taken directly from the pilot plant compressed air line. The relative humidities in the coater under these conditions were approximately 9.1, 7.1 and 5.3% respectively.

The air velocity was set to a dial value of 300, which gave a stable particle circulation rate. Actual air velocities could not be determined because there was no means of introducing the anemometer into the chamber.

Figure 8.6 shows the progression of the coating layering micro-level process with coating time.

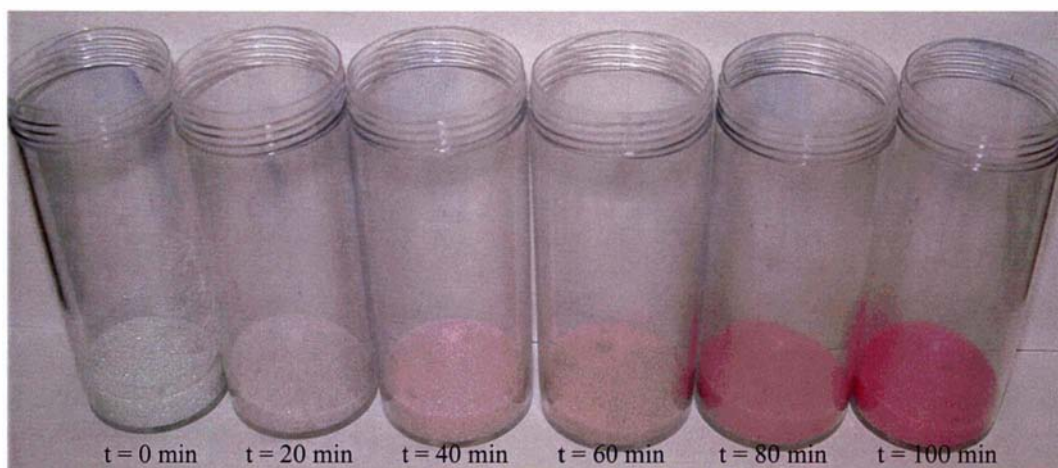


Figure 8.6: Evidence of coating layer growth (increasing colour intensity) with increasing coating time.

The photographs progress from green (uncoated ballotini®) through to dark pink. The increasing colour intensity of the coated ballotini® indicates increasing mass deposition of the spray droplets with increasing coating time. The dye did not alter the surface tension of any of the solutions from the standard values recorded in Table 7.1. The following figures present the mass of coating material measured on the particles as a function of the amount delivered

to the system. The mass of solids delivered was chosen as the abscissa to account for slight differences in the amount of coating solution delivered by the peristaltic pump (on average $3.5 \text{ g} \cdot \text{min}^{-1}$). The data for 20 and 40% w/w maltodextrin DE5 at 70°C were the average of five trials, to give an estimate of the standard error in the trials. It was assumed that the same degree of accuracy applied for the other experimental combinations. All other trial data presented were the average of two replicate trials. It is also of interest that the value of the coating mass per particle corresponded to the thickness of the coating material. Hence, a coating mass of 35 kg dry coating per 100 kg uncoated substrate had a coating thickness of approximately $35 \mu\text{m}$.

Figure 8.7 shows the mass gain of ballotini® as a function of the amount of coating solids sprayed into the system for 20 and 40% w/w maltodextrin DE5 coating solutions at different drying air temperatures.

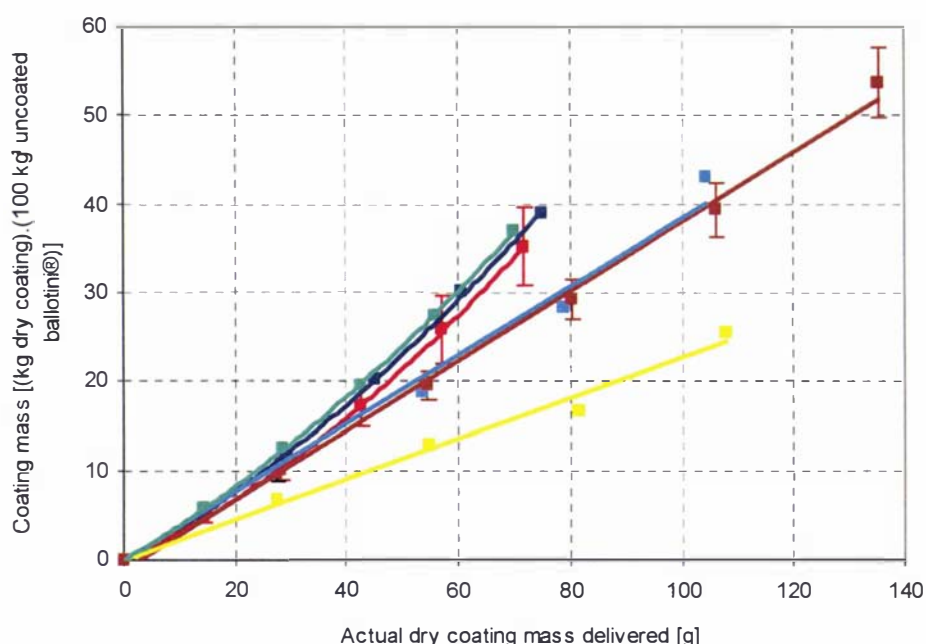


Figure 8.7: Coating mass gain of ballotini® as a function of the mass of dry solids sprayed into the system for 20% w/w and 40% w/w maltodextrin DE5 solutions at air temperatures of 55, 70 and 85°C : ■ 20% w/w maltodextrin DE5 at 55°C ; ■ 20% w/w maltodextrin DE5 at 70°C ; ■ 20% w/w maltodextrin DE5 at 85°C ; ■ 40% w/w maltodextrin DE5 at 55°C ; ■ 40% w/w maltodextrin DE5 at 70°C ; ■ 40% w/w maltodextrin DE5 at 85°C .

The slope of the charts is an indicator of the efficiency of coating droplet adhesion. Given that both the 20% w/w and 40% w/w maltodextrin DE5 trials used the same coating solution flowrate, the dry solids application rate of the 40% w/w initial solids concentration formulation was twice that of the 20% w/w initial solids concentration formulation. Despite this, the rate of mass change for the 40% w/w formulations was lower in all cases. This demonstrates excessive amounts of spray droplet over-drying for higher initial solids concentration formulations. This is in agreement with Figure 8.1, which shows a much narrower stickiness profile and hence a lower window of opportunity for successful droplet adherence during impingement on to the substrate.

Given the inherent scatter in the data, it is difficult to draw statistically significant conclusions about the effect of air temperature on the efficiency of coating. For the 20% w/w maltodextrin DE5 coating solution formulation, the trends did not show a statistically

significant effect. However, for the 40% w/w maltodextrin DE5 coating solution formulation, a marked decrease in coating efficiency occurred at an air temperature of 85 °C. This was a result of the faster drying of the spray droplets to a lower surface moisture content, decreasing the likelihood of successful droplet adherence during impingement on to the substrate.

For the 40% w/w coating solution formulation trials, there was a near linear relationship (except maybe for a short time at the beginning, when coating was a little slower) between the particle mass gain and the coating time, because the initial substrate particle diameter was large compared with the thickness of the coating layer that grew by uniform coating. Therefore, the projection area of the particle, which is a determinant in the impingement efficiency of the droplets, was practically constant for all the experiments and during the experimental time. This is in agreement with Link and Schlünder (1997). However, the 20% w/w coating solution formulation trials were best represented with a quadratic correlation. This was unexpected and suggested a super-proportional increase with increasing coating time and substrate diameter for lower initial solids concentration formulations. The 40% w/w maltodextrin DE5 with glycerol trial also showed a quadratic-type growth rate. The reason for this is unclear.

Figure 8.8 shows the mass gain of substrate particles with the amount of coating solids sprayed into the system for different formulations at both 20 and 40% w/w initial solids concentration drying at an air temperature of 70 °C.

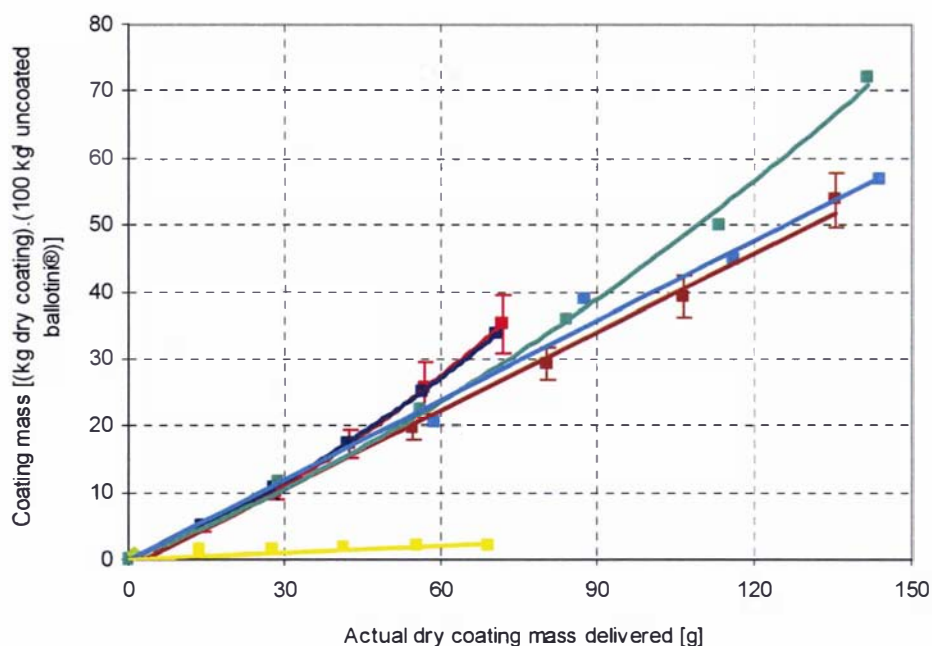


Figure 8.8: Mass gain of ballotini® for various formulations for 20% w/w and 40% w/w initial solids concentration formulations drying at 70 °C: ■ 20% w/w maltodextrin DE5; ■ 20% w/w (3:1) maltodextrin DE5:glycerol; ■ 40% w/w (3:1) maltodextrin DE5:glycerol; ■ 40% w/w maltodextrin DE5; ■ 40% w/w (3:1) maltodextrin DE5:maltodextrin DE18; ■ 20% w/w maltodextrin DE5 + 2% w/w PE.

Glycerol did not affect the rate of coating build-up that occurred for the 20% w/w maltodextrin DE5 coating solution formulation. These results can be considered alongside the single droplet drying kinetics in Figure 5.25. Although the stickiness curves for these formulations were not measured, it is a reasonable finding because they have very similar rates of evaporation with a long constant rate period. There was also no significant difference

in the efficiency of coating when maltodextrin DE18 was added as a plasticiser of maltodextrin DE5 in the 40% w/w coating solution formulation. This result was unexpected because the addition of maltodextrin DE18 was expected to broaden the stickiness curve for this formulation (Figure 6.17). A possible explanation is that, with a large nozzle distance, the droplets dried before impinging on to the particles regardless of the formulation. However, this does not explain why the addition of glycerol as a plasticiser of the 40% w/w maltodextrin DE5 coating solution formulation increased the efficiency of droplet adhesion, despite having an almost identical surface stickiness profile to the 40% w/w maltodextrin DE5 coating solution formulation that was plasticised with maltodextrin DE18.

Almost no coating was obtained for the 20% w/w maltodextrin DE5 + 2% PE trial at 70 °C, with only 2 (kg dry coating).(kg⁻¹ uncoated substrate). Inspection by eye showed little or no coating over the entire trial; the coating mass measured was probably spray-dried droplets being measured in the sample. The same results were obtained at 55 °C and even 35 °C for this formulation. This was an unexpected result, given that surfactants generally slow the drying rate by lowering the surface vapour pressure. However, surfactants are also expected to reduce the droplet size during atomisation, but this was not the case, as the spray droplet size for the 20% w/w maltodextrin DE5 + 2% w/w PE surfactant formulation had an MPD of 13.7 µm compared with 14.2 µm for the 20% w/w maltodextrin DE5 alone formulation. Surface hydrophobicity also cannot explain the result. The earlier droplet impact and spreading work showed an insignificant effect of surface hydrophobicity on the maximum droplet spread diameter. When a surfactant is employed, the final spread diameter is essentially the same for a hydrophilic substrate surface and a hydrophobic substrate surface. A possible explanation is that, because of the high activity of the surfactant molecules, they could have rapidly formed a skin at the droplet surface (similar to the observed in Section 5.9.4 but not for PE) before the maltodextrin DE5 was able to and produced a non-sticky surface. This phenomenon was not expected and cannot be explained at this time; further mechanisms need to be explored. This, again, points to the need to be able to adjust the nozzle position (height) relative to the particle flow through the Würster insert. In an industrial coater, this flexibility is crucial to controlling the droplet drying time and to ensuring successful droplet adherence if a surfactant is incorporated into the formulation for increased spreading.

8.3.5 Coating morphology

The droplet impact and spreading and coating layering micro-level processes can be seen in the scanning electron micrographs in Figure 8.9.



Figure 8.9: Scanning electron micrographs depicting the droplet impact and spreading and coating layering micro-level processes for a 20% w/w maltodextrin DE5 formulation drying at 70 °C: (a) prior to coating (uncoated ballotini®); (b) 10 min coating time; (c) 30 min coating time; (d) 50 min coating time; (e) 70 min coating time. Note: the uncoated ballotini® sample in (a) has a Sauter mean diameter of 300 µm. All micrographs taken at 200 times magnification.

The images show the formation of successive coating layers as the thickness increases with coating time. Figure 8.9(e) shows evidence of droplet impact and spreading, with the formation of a large platelet on the surface (centre of the image). This was probably not the result of a single droplet, given the size of the platelet compared with the size of the ballotini®. It was the intention to determine the effect of surfactant addition on droplet impact and spreading, with the postulate that more uniform coatings would result. However, the surfactant-containing formulation could not be compared because no coating occurred.

Other morphological features can be distinguished from the spray droplet adhesion efficiency trials. Figure 8.10 is a magnification series of scanning electron micrographs showing the coating morphology of various coating formulations dried at an air temperature of 70 °C.

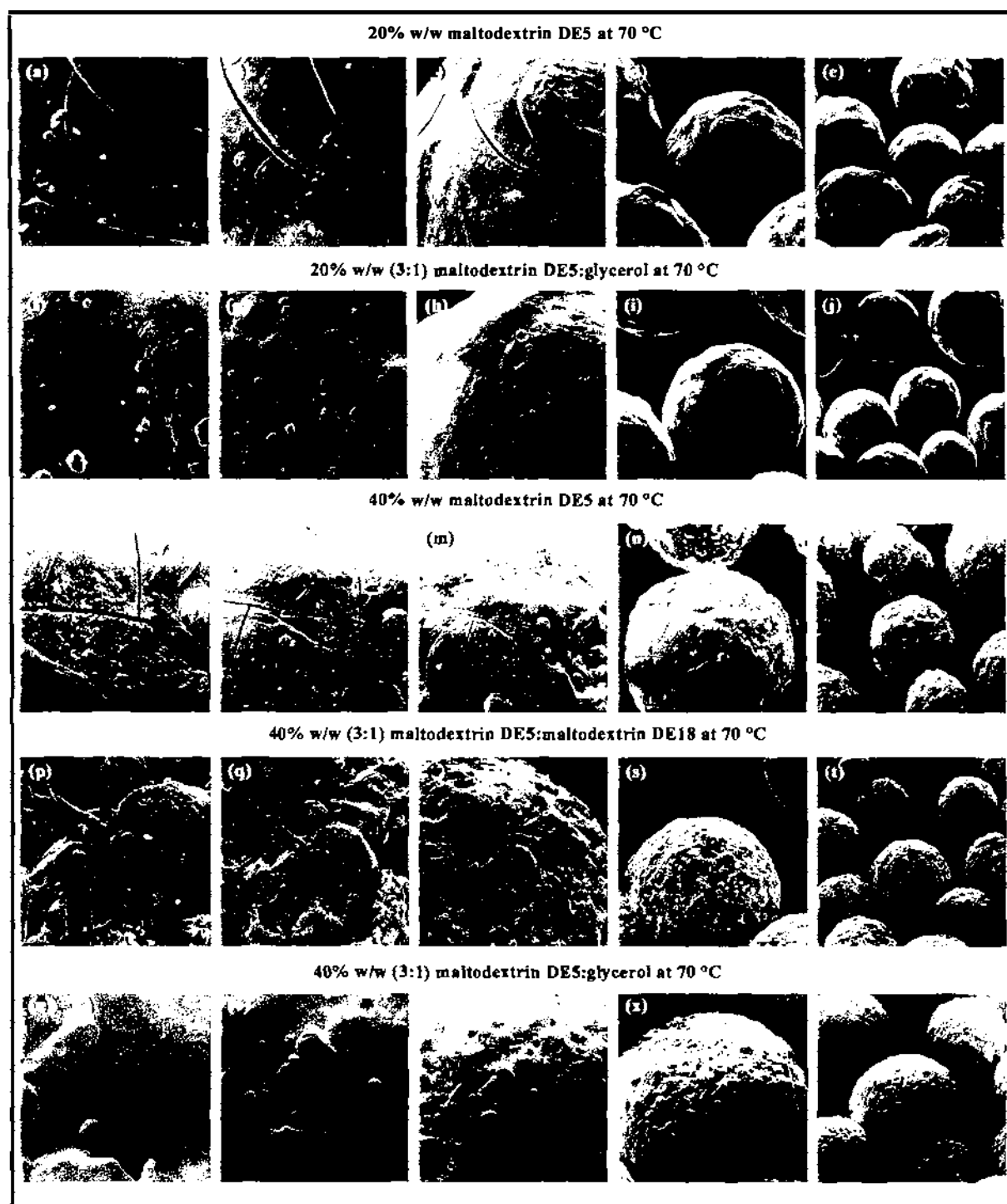


Figure 8.10: Scanning electron micrograph magnification series of coating morphological features for various coating formulations drying at 70 °C. From left to right, the magnification series proceeds as 2000, 1000, 500, 200 and 100 times the original image size. Taking the centre ballotini® in (e) to have a Sauter mean diameter of 300 μm , gives a fracture width in (a) of approximately 3.5 μm .

Figure 8.10(a–c) clearly show evidence of droplet impact and spreading in the form of platelets. Also clear are the large cracks in the coating. There are cracks in the majority of the images of the non-plasticised formulations (Figure 8.10(a–e) and Figure 8.10(k–o)), which was expected from the work to date with maltodextrin DE5. The 20% w/w maltodextrin DE5 formulation may have given a slightly smoother surface than the 40% w/w formulation, as

there was a little more time for droplet coalescence to occur. There was no significant difference in coating morphology over the air temperatures investigated in the non-plasticised 20 and 40% w/w maltodextrin DE5 formulation trials, with all showing signs of coating imperfections. This was probably the result of the very high particle inertia in the system causing damage during inter-particle collisions. The damage is not likely to be as significant in a system with dairy powders, as these have a particle density half that of the ballotini® and a diameter one-third that of the ballotini®.

The addition of maltodextrin DE18 to the 40% w/w maltodextrin DE5 initial solids concentration formulation produced a more rough and porous morphology (Figure 8.10(p–t)) compared with the 40% w/w maltodextrin DE5 formulation (Figure 8.10(k–o)). However, the cracks were not as prevalent in these coatings. It is not clear why this occurred. The absence of cracks and the appearance of much smoother coatings were seen for the formulations that were plasticised with glycerol (Figure 8.10(f–j) and Figure 8.10(u–y)). This was expected, given the observations in the single droplet drying tests and the liquid nature of glycerol allowing more time for droplet coalescence to occur.

Although the evidence is only qualitative in nature, plasticisation of the coating formulation was seen to produce coatings with fewer imperfections than for the non-plasticised coatings.

8.3.6 Conclusions

The limited flexibility of the Würster coater made validation of the micro-level process guidelines difficult. Many unexplained and conflicting observations remain. Further work on a custom-built, pilot-scale coater, constructed to have greater flexibility and specifically developed for dairy powder coating, is required. This represents step 4 of the ‘micro-level process approach’ (see Section 3.14).

8.4 RECOMMENDATIONS FOR INDUSTRIAL-SCALE COATING

This section briefly discusses how the knowledge developed in this thesis should be used in future development work, in particular the knowledge transfer necessary for the development of an industrial-scale dairy powder coating process.

8.4.1 Product development

The following is a general set of questions that should be answered at the beginning of the product development process for an air-suspension-coated dairy powder.

1. What are the objectives of the coating operation, i.e. coating barrier to protect the substrate, mask the flavour, impart controlled-release properties?
2. How will the coatings release the substrate, e.g. pressure rupture, melting, dissolution, sustained or instant release?
3. What are the product specifications: acceptable level of inter-particle agglomeration, coating weight percent of the product and coating coverage, desired production rate and acceptable coating material losses?
4. What materials will meet the above requirements? Are additives (surfactants, plasticisers) required and do these additives cause labelling concerns?
5. What is a rough estimate of the product and process cost given the specifications in step 3 and the coating materials?
6. If the cost is acceptable, then process development can commence.

8.4.2 Process development

Pilot-scale coating trials can now be conducted. The coating solution formulation (polymer type, polymer concentration, plasticisers, wetting agents) should be optimised to achieve the greatest extent of droplet spreading. After this, the droplet drying model can be used to establish the base operating conditions such as nozzle distance, atomiser pressure, drying air temperature, relative humidity and air velocity.

The starting point for pilot-scale trials is to ensure minimal inter-particle agglomeration. Therefore, it is acceptable to conduct the initial trials under uneconomical coating conditions, i.e. the use of both dilute coating solutions at low spray rates and dilute particle to air volume ratios. This will ensure minimal inter-particle agglomeration. Low relative humidities and low air temperatures should also be employed to minimise agglomeration. Low temperatures are also important if the substrate contains a surface layer of fat. The air velocity and turbulence in the coater should be high enough to minimise the success of particle coalescence during impact but not so high as to cause significant particle attrition.

After this, the formulation and operating guidelines should be used to advance the formulation and the operating parameters towards their optima. If successful, a decision can then be made as to whether to proceed with industrial-scale trials.

8.4.3 Industrial processing scenarios

Some ideas on an appropriate industrial-scale coating process, specifically for dairy powder coating, are presented although not investigated in this thesis. Batch mode is generally preferred because of its higher degree of control and coating efficiency [Christensen and Bertelsen (1997)]. The batch process also minimises losses after process problems, such as contamination or formulation errors. A typical batch coating process consists of three phases: start-up, coating and the drying/cooling. The start-up phase consists of (optional) preheating of the equipment and heating of the substrate. Preheating the equipment is advantageous when the substrate is fragile and the heating period should be as short as possible. The batch process should be selected for high value products with low throughput volumes. This would include controlled-release products such as the encapsulation of high value enzymes, which is a possible future application [D. L. Pearce, Fonterra, Palmerston North, personal communication, 1 November 2004]. The product price margin would justify the use of a single high capital cost unit operation dedicated to coating under the inefficient conditions required to produce high quality coated products. Labour costs are high; according to Teunou and Poncelet (2002), there is almost no batch fluid bed coater running automatically and, thus, constant operator supervision is required. A standard 'off-the-shelf' batch Würster coating unit from a major fluid bed manufacturer (Glatt Air Technologies Inc., Ramsey, NJ, USA or Niro Inc., Columbia, MD, USA) would probably not be suitable (without significant modifications) for such dairy applications because of the limitations mentioned earlier. However, these companies are now beginning to address the food industry requirements for fine particle coating applications on a continuous process scale.

To reduce manufacturing costs, the continuous process is an attractive alternative for food powder coating [Teunou and Poncelet (2002)]. This option would suit low to medium value products requiring high throughput rates. Teunou and Poncelet described the various continuous (single bed, horizontal, multicellular, multicellular quasi-continuous) fluid bed coating arrangements. They cite the multicellular quasi-continuous fluid bed arrangement developed by Leuenberger (2000) in conjunction with a manufacturer which they claim

combines the advantages of batch and continuous processes in the pharmaceutical industry. It is described as a train of mini batches passing like parcels of compartments of dry mixing, granulation and drying [Teunou and Poncelet (2002)]. However, there is no information about coating with this system and it is likely to be an expensive installation [Teunou and Poncelet (2002)].

It is possible that a multicell arrangement could be built in-house by linking a series of pipes, each containing a bottom-spray nozzle arrangement with a Würster insert. Figure 8.11 is a drawing of an envisaged apparatus.

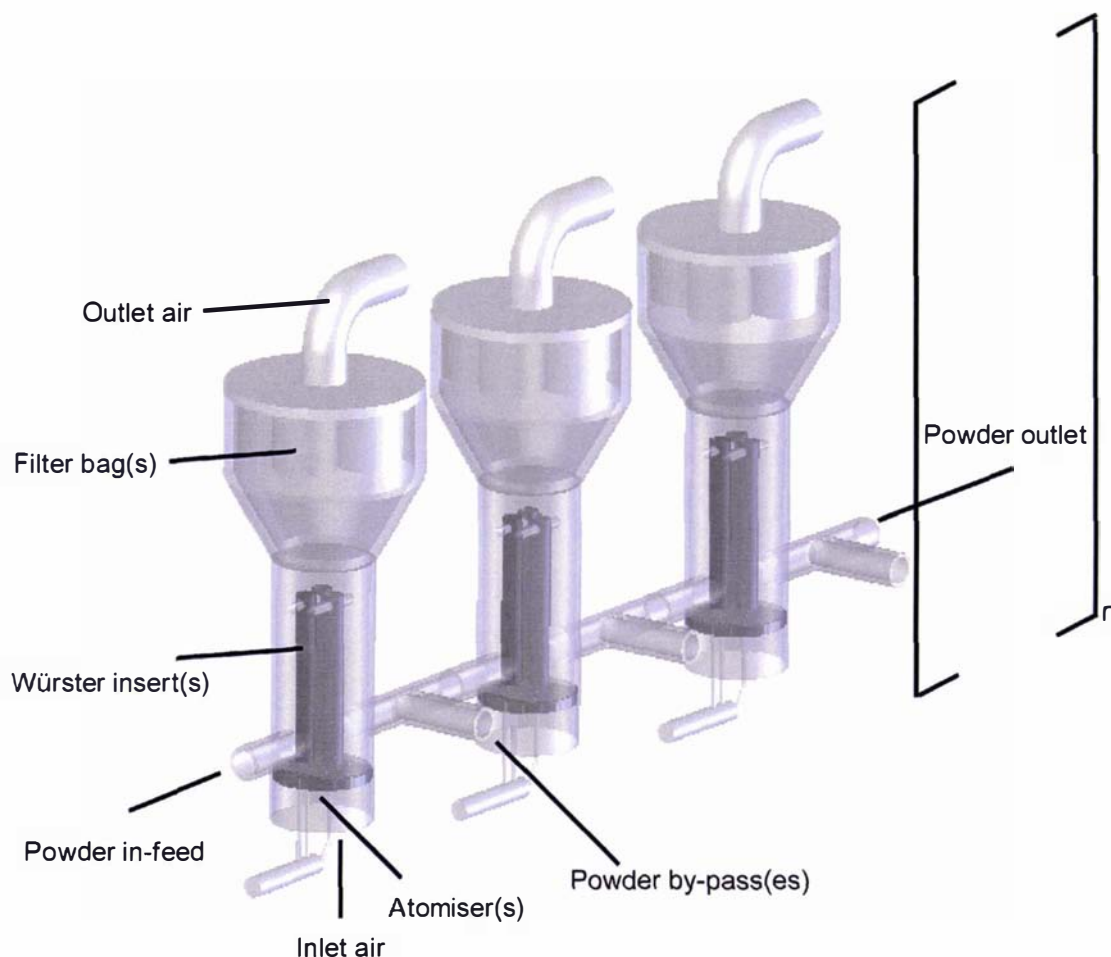


Figure 8.11: Envisaged custom-built multicell continuous powder coater for dairy industry applications.

The apparatus should permit greater operational flexibility and can be operated in continuous or batch mode. Any number of units can be connected together with multiple Würster inserts and nozzles in each unit. It can also apply different coating formulations along the length of the process and can employ different coating solution flowrates and drying conditions in each section. It essentially acts as a recirculating batch fluid bed but on a continuous production line.

The majority of spray droplets delivered to the system must 'see' the substrate particles. Minimising the 'sheltering effect' described by Cheng and Turton (2000b) is crucial to achieving high coating coverage and uniformity. Although not covered in this work (see

Section 2.8.1), the optimisation of the flux of spray droplets impinging a powder curtain warrants careful design thought.

From an industrial coating perspective, it would be of economic benefit to separate the coating and drying operations to avoid a bottleneck in a high throughput process. The bottleneck arises for two key reasons. Firstly, dilute particle–air volume conditions are required to minimise inter-particle agglomeration and increase the droplet–particle hit rate. Secondly, the drying time can be significant in the diffusion-controlled drying process, which means that, once the desired coating level has been achieved, the coater will be tied up for drying and not coating. Hence, coating and drying should be done separately. The most obvious scenario would be to coat in a specified coating apparatus and then, once the particle population has completed its set number of passes to attain the desired coating thickness, the population can be sent off to an existing vibro-bed operating at high particle–air volumes where the drying is ‘finished off’ prior to bagging. The only drying required in the coater will be to ensure that the surface moisture content of the coating layer is low enough such that the coated particle is not sticky when it passes out the top of the Würster insert. This surface moisture content will set the Würster insert height and the drying air conditions (relative humidity, temperature, air velocity). The amount of drying required in the vibro-bed will be the difference between that already achieved in the Würster coater and that required for the bagged product, typically 3–4% w/w moisture.

8.5 CONCLUSIONS AND RECOMMENDATIONS

The science of air-suspension particle coating was advanced through the study of key micro-level processes in isolation. However, the limited flexibility of the Würster coater made validation of the micro-level process guidelines difficult. Further work on a custom-built, pilot-scale coater, constructed to have greater flexibility and specifically developed for dairy powder coating, is required. The next step is to put the formulation and operating guidelines and process knowledge into practice and craft the engineering of a continuous coating apparatus for dairy powder applications.

CHAPTER 9

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

9.1 CONCLUSIONS

Traditionally air-suspension particle coating research has taken a statistical ‘black box’ approach. As a result, little understanding of the fundamentals is known, which has led to formulation and apparatus specific results, long and costly product development cycles and low scalability success.

This thesis proposes a new approach to air-suspension particle coating research. The basis of this ‘micro-level process approach’, is to deconvolute the complex coating process into smaller manageable parts based on classical physical phenomena for which descriptions already exist. The central thesis of this work is that deconvolution enables a better understanding of the key formulation and operating variables governing coating quality and process performance and therefore will reduce the need for large experimental studies and statistical differentiation of results.

Four key micro-level processes were selected for further study: drying, droplet impact and spreading, and stickiness which encompasses the two key micro-level processes of droplet impact and adherence and inter-particle agglomeration. Models were identified in the literature to elucidate key variables for experimental study. Three simple experimental set-ups (a single droplet drying rig, a probe tack test and a droplet impact and spreading rig) were used to investigate the effect of these key variables independently of each other and of the other key micro-level processes. Formulation and operating guidelines were established for each micro-level process with a view to achieving the ultimate coating objective, that is to produce individually coated particles, each with a well defined, even coating.

Chemical formulation was shown to significantly influence the key micro-level processes. Chemical formulation defines the initial solids concentration and the incorporation of additives such as plasticisers and wetting agents. The ideal coating formulation will be of low viscosity at high solids contents, show enhanced spreading ability (wetting agent addition), will form coherent films with minimal defects (plasticiser addition) and show significant stickiness prior to spray droplet impact on to the powder substrate particles followed by rapid drying to a non-sticky state before the particles exit the dilute pneumatic transport region of the Würster insert and into the fluidised bed region of a Würster-style coater.

Kinetic data were collected for the drying droplets containing maltodextrins, whey protein isolate and gum arabic. A predictive model describing single droplet drying kinetics and surface glass transition temperature was developed. The model is the first to discretise both droplet moisture content and droplet temperature based on the ‘ideal shrinkage’ assumption.

The model accurately predicted the kinetics until significant morphological changes occurred in the droplet. To better predict the kinetics late in the drying process, the droplet radius was set to be constant at a time based on the surface proximity to the surface glass transition temperature (critical X concept). This was done to arrest droplet shrinkage in line with experimental observations and more accurately depict the drying of high molecular weight, amorphous glass forming polymers than assuming 'ideal shrinkage'. After this point, a new flexible calculation scheme was used to better predict the variation in internal droplet structure being able to predict a dense, 'collapsed shell' structure or a 'dense skin-porous crumb' structure. Droplet drying could be further advanced by studying both surface and internal droplet structure (porosity and mechanical integrity) development during drying, particularly the conditions leading to the arresting of the droplet radius and the subsequent rate of skin thickness progression.

The critical X concept was used to make industrial-scale predictions of the optimum drying conditions to ensure maximum droplet impact and adherence efficiency and minimum inter-particle agglomeration in a Würster-style coating operation. This enabled the prediction of the key design parameters of the nozzle distance from the powder impact point and the Würster insert height. The span in design parameters showed that there is significant opportunity for design optimisation based on the critical X concept

A probe tack test was used to map the level of stickiness of droplets of different coating materials as they dried. As skin formation progressed, the stickiness passed through a maximum, in most cases to arrive at a point at which the droplet was no longer sticky at all (non-adhesive state). The maximum point of stickiness represents the ideal state to ensure successful droplet-substrate impact and adherence. The minimum point of stickiness represents the ideal state to prevent unwanted inter-particle agglomeration. The time interval between the onset of stickiness and the non-adhesive state was particularly dependent on the addition of plasticisers, but also on the formulation and the drying air conditions.

The impact and spreading of droplets containing maltodextrin DE5 on to solid anhydrous milkfat was studied using a high speed video camera. It was found that the final droplet spread diameter was able to be fixed close to the maximum spread diameter by using surfactants, thus avoiding significant recoil.

The formulation and operating guidelines were used in a series of population based coating experiments in a pilot-scale Würster coater. This study highlighted the limited flexibility of the standard 'off-the-shelf' Würster coating apparatus for the coating of fine sized dairy powders. Because of this, the validation of the guidelines was inconclusive and optimisation could not be carried out. Further validation work is required on a custom-built apparatus for dairy powders. This represents step 4 of the 'micro-level process approach' proposed in this study.

The results here use scientific principles to advance product development in air-suspension particle coating away from the traditional statistical 'black box' approach. The results here are phenomenological, meaning they are not material or apparatus specific and are directly scalable. With this knowledge, it is now possible to undertake product development trials on a pilot-scale at considerably reduced time and cost.

9.2 SUGGESTED FUTURE WORK

There are many fundamental and engineering challenges remaining. In the short term, the next step is to put the guidelines into practice and craft the engineering of a continuous coating apparatus for dairy powder applications; that is to produce coated dairy powders on a continuous system at throughputs of 1–5 tonnes per hour. This will necessitate some significant engineering challenges. In particular, the droplet–particle sheltering effect may require a significant redesign of the spray zone and addressing the control and automation of a continuous coating process. The difficulty of particle fluidisation, particularly for particle diameters smaller than 100 μm also represents a significant challenge for current equipment design.

Given that the coating field originated out of the granulation field, its research and development has been based upon equipment originally designed to encourage particle–particle interaction. It is no wonder that these current challenges exist and the solution to these may best be addressed by starting afresh. The results from this work are not limited to current air-suspension coating equipment. They can be used to design from scratch a piece of coating equipment that can meet the demanding specifications for a coated product.

In the longer term, there remains a significant lack of understanding of the key micro-level processes, particularly with respect to being able to model them. Droplet drying could be further advanced by studying both surface and internal droplet structure (porosity and mechanical integrity) development during drying, particularly the conditions leading to the arresting of the droplet radius and the subsequent rate of skin thickness progression. To advance the knowledge of stickiness development in coating formulations, a possible relationship between the surface glass transition temperature and the probe tack test stickiness measurements should be sought. Finally, droplet impact and spreading could be advanced by 3D mathematical modelling of the process including surfactant mass transfer mechanisms. Once these are better understood, then attempts can be made to integrate these micro-level process models describing the particle quality attributes such as coating mass uniformity and coating morphology with existing macro-level models describing process-wide effects such as substrate and droplet population dynamics, hydrodynamics, droplet–substrate collisional and coalescence outcomes and efficiencies.

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APPENDIX A1

NOMENCLATURE

Latin symbols

a	fitting coefficient in binary moisture diffusion correlation and water activity correlation	—
a	particle radius	m
A	Antoine equation constant	5.11564
A_c	area of conductive heat transfer and diffusive mass transfer at the inside surface of the shell	m ²
A_d	droplet surface area	m ²
a_w	water activity coefficient	—
b	fitting coefficient in binary moisture diffusion correlation and water activity correlation	—
B	Antoine equation constant	1687.537
Bi_h	Biot number for heat transfer	—
Bi_m	Biot number for mass transfer	—
c	constant in bridge rupture energy equation	1.8
c	fitting coefficient in binary moisture diffusion correlation and water activity correlation	—
C	Antoine equation constant	230.17
C	total molar concentration of gas (water-vapour and air)	(moles of gas).(m ⁻³ of gas)
C_0	initial droplet average moisture content	(kg water).(kg ⁻¹ dry solid)
C_1	first integration constant	moles.s ⁻¹
Ca	Capillary number	—
C_D	droplet–air drag coefficient	—
C_e	average droplet moisture content at equilibrium	(kg water).(kg ⁻¹ dry solid)
c_{pd}	specific heat capacity of the droplet	J.kg ⁻¹ .°C ⁻¹
$c_{pd\ s}$	specific heat capacity of the droplet surface shell	J.kg ⁻¹ .°C ⁻¹
c_{pp}	specific heat capacity of the polymer	J.kg ⁻¹ .°C ⁻¹
c_{pw}	specific heat capacity of water	J.kg ⁻¹ .°C ⁻¹
c_{pww}	specific heat capacity of water-vapour	J.kg ⁻¹ .°C ⁻¹
C_s	droplet solids (solute) concentration	(kg dry solid).(m ⁻³ droplet)
$C_s(r,t)$	droplet solids (solute) concentration as a function of radial position and time	(kg dry solid).(m ⁻³ droplet)
C_{ss}	solids (solute) concentration at the droplet surface	(kg dry solid).(m ⁻³

C_t	average droplet moisture content at time, t	droplet) (kg water).(kg ⁻¹ dry solid)
C_w	droplet moisture content	(kg water).(m ⁻³ droplet)
$C_{w,av}$	average droplet moisture content	(kg water).(m ⁻³ droplet)
$C_{w,c}$	droplet moisture content at the centre node	(kg water).(m ⁻³ droplet)
$C_{w,l}$	droplet moisture content at the node	(kg water).(m ⁻³ droplet)
$C_{w,s}$	droplet moisture content at the surface	(kg water).(m ⁻³ droplet)
d	fitting coefficient in binary moisture diffusion correlation and water activity correlation	–
$D(3,2)$	Sauter mean diameter	μm
$d(t)$	droplet spread diameter as function of time	m
d_0	initial droplet diameter	m
$D_{0,ref}$	moisture diffusivity in dilute solution at the reference temperature (in this case 303 K)	m ² .s ⁻¹
d_d	droplet diameter	m
D_{eff}	effective moisture diffusion coefficient	m ² .s ⁻¹
d_{end}	final droplet spread diameter	M
d_f	glass filament diameter	m
d_i	droplet diameter at atomiser nozzle outlet	m
d_{max}	maximum droplet spread diameter	m
D_{min}	binary moisture diffusion coefficient minimum value	m ² .s ⁻¹
D_{probe}	diameter of stickiness test probe	3 mm
D_{SDS}	diffusions coefficient of SDS	m ² .s ⁻¹
D_v	diffusivity of water-vapour in air	m ² .s ⁻¹
D_w	binary moisture diffusion coefficient	m ² .s ⁻¹
$D_w(u, T_d)$	binary moisture diffusion coefficient as a function of droplet moisture content and droplet temperature	m ² .s ⁻¹
$D_{w,porous}$	effective moisture diffusivity for a droplet developing an internal porous structure	m ² .s ⁻¹
$D_{w,ref}$	binary moisture diffusion coefficient in dilute solution at a reference temperature (in this case 303 K)	m ² .s ⁻¹
$D_{ws,i}$	binary moisture diffusion coefficient at the inside surface of the shell	m ² .s ⁻¹
$D_{ws}(u_s, T_s)$	binary moisture diffusion coefficient at the droplet surface as a function of surface moisture content and surface temperature	m ² .s ⁻¹
e	fitting coefficient in binary moisture diffusion correlation and water activity correlation	–
e	particle coefficient of restitution	–
$e(t)$	thickness of flattened middle droplet zone	m
E_D	activation energy for binary moisture diffusion coefficient	kJ.mole ⁻¹
f	fitting coefficient in binary moisture diffusion correlation and water activity correlation	–

F_{12}	droplet–environment view factor	–
F_{ar}	flux of air through the air–water–vapour system	moles.m ⁻² .s ⁻¹
Fo	Fourier number	–
F_{wv} or F_{wvr}	water–vapour flux	moles.m ⁻² .s ⁻¹
F_{wvR}	water–vapour flux at the droplet surface, R	moles.m ⁻² .s ⁻¹ and kg.m ⁻² .s ⁻¹
g	acceleration due to gravity	9.81 m.s ⁻²
h	length of fluid penetration	m
$h(t)$	spread film height	m
h_a	characteristic length scale of surface asperities	μm
h_c	thickness of the coating/binder layer	μm
h_g	gas side heat transfer coefficient	W.m ⁻² .°C ⁻¹
h_g^*	corrected gas side heat transfer coefficient	W.m ⁻² .°C ⁻¹
h_w	length of Würster insert	m
j	general node	–
J	surface node	–
$j \pm 1/2$	node interface	–
K	dimensionless proportionality constant	–
k_1	coefficient in Nu correlation	0.6
k_2	coefficient in Sh correlation	0.6
KE_1	initial droplet kinetic energy	J
k_g	gas side mass transfer coefficient	m.s ⁻¹
k_g^*	corrected gas side mass transfer coefficient	m.s ⁻¹
L_c	characteristic length of the body	m
Le	Lewis number	–
m	mass	kg
m	m^{th} root of the series represented by Equation (A2.97)	–
M_a	molecular mass of air	28.97 g.mole ⁻¹
m_d	droplet mass	kg
$m_{d\ i}$	initial droplet mass	kg
$m_{d\ s}$	mass of droplet in the droplet surface shell	kg
$m_{d\ s}$	mass of dry solid in the droplet surface shell	kg
m_f	final mass of powder	(kg water + dry powder)
m_i	initial mass of the powder	(kg water + dry powder)
M_i	molecular weight of component i (water–vapour)	g.mole ⁻¹
M_j	molecular weight of component j (air)	g.mole ⁻¹
m_p	particle mass	kg
M_p	molecular weight of polymer	g.mole ⁻¹
m_s	mass of dry solid in a shell	kg
$m_{s\ d}$	mass of dry solid/solute in the droplet	kg
M_w	molecular mass of water	18 g.mole ⁻¹
$m_{w\ s}$	mass of water in droplet shell surface	kg
n	Number of measurements in a sample	–
Nu	Nusselt number	–
Pr	Prandtl number	–
P_T	total system pressure	101 325 Pa
P_v	water–vapour partial pressure at the dry bulb air temperature	Pa

P_{vs}	saturated water-vapour pressure	Pa
$\dot{Q}_{filament}$	conductive heat transfer rate from glass filament	W
$\dot{Q}_{radiation}$	radiative heat transfer rate from environment	W
$\dot{Q}_{thermocouple}$	conductive heat transfer rate from thermcouple	W
r	droplet radial position (within the droplet or at the droplet surface)	m
R	droplet radius	m
R	R index	—
R_1	radial integration bound	m
r_b	radial position at droplet–air boundary surface layer	m
R_c	average pore-throat radius	m
Re	Reynolds number	—
Re_r	relative droplet Reynolds number	—
r_g	radius of gas bubble at droplet centre	m
R_g	universal gas constant	8.314 J.mole ⁻¹ .K ⁻¹
r_r	radial position at inner surface of the droplet surface shell	m
r_s	radial position at droplet surface	m
R_{wv}	rate of water-vapour transfer	moles.s ⁻¹
s	thickness of the solidified layer	m
s^*	dimensionless thickness of the solidified layer	—
Sc	Schmidt number	—
SE_1	pre-impact droplet surface energy	J
SE_2	droplet surface energy	J
Sh	Sherwood number	—
$S_{L.S}$	spreading coefficient	N.m ⁻¹
St_v	viscous Stokes number for coalescence	—
St_v^*	critical viscous Stokes number for coalescence	—
t	time	s
T	process temperature	°C
t^*	normalised spreading time	—
t_1	first time-step	s
T_a	air temperature	°C
t_{anal}	predicted time value in the droplet radius simplified analytical solution check	s
T_d	droplet temperature	°C
T_{di}	initial droplet temperature	°C
T_f	film temperature	°C
T_g	glass transition temperature	°C
T_{gp}	dry polymer glass transition temperature	°C
T_{gw}	water glass transition temperature	°C
t_{num}	numerically predicted time	s
T_r	droplet temperature at radial position r	°C
T_{ref}	sample reference temperature (in this case 303 K)	K
T_s	droplet surface temperature	°C
T_{si}	droplet temperature at the inside surface of the shell	°C
T_{wall}	drying chamber wall temperature	K
T_z	temperature at position z along the droplet radius	°C
u	droplet moisture content on a dry solids basis	(kg water).(kg ⁻¹ dry solid) or

U_{at}	air volumetric flowrate	$\text{kg} \cdot \text{kg}^{-1}$ $\text{m}^3 \cdot \text{s}^{-1}$
u_c	moisture content at droplet centre	$(\text{kg water}) \cdot (\text{kg}^{-1}$ dry solid)
u_i	initial droplet moisture content	$(\text{kg water}) \cdot (\text{kg}^{-1}$ dry solid)
u_i	initial powder moisture content on a dry solids basis	$(\text{kg water}) \cdot (\text{kg}^{-1}$ dry powder)
u_s	moisture content at the droplet surface	$(\text{kg water}) \cdot (\text{kg}^{-1}$ dry solid)
U_{sol}	fluid volumetric flowrate	$\text{m}^3 \cdot \text{s}^{-1}$
V_b^*	the dimensionless bridge volume	—
W	work done in deforming the droplet against viscosity	J
W^*	dimensionless rupture energy	—
W_a	work of adhesion	$\text{N} \cdot \text{m}^{-1}$
We	Weber number	—
x	spatial coordinate	m
X	Difference between the droplet surface temperature and the glass transition temperature	$^{\circ}\text{C}$
x_1	power value for Re in Nu calculation	0.5
x_2	power value for Re in Sh calculation	0.5
x_i	mole fraction of component i (water-vapour)	—
x_i	mole fraction of component i (air)	—
x_p	mass fraction of polymer (solute)	—
X_p	powder moisture content on a dry solids basis	$(\text{kg water}) \cdot (\text{kg}^{-1}$ dry powder)
x_w	mass fraction of water	—
x_{wab}	mole fraction of water-vapour at droplet–air boundary surface layer	$(\text{moles water-vapour}) \cdot (\text{total}^{-1}$ moles of gas)
x_{wvr}	mole fraction of water-vapour at radial distance, r	$(\text{moles water-vapour}) \cdot (\text{total}^{-1}$ moles of gas)
x_{wvs}	mole fraction of water-vapour at droplet surface	$(\text{moles water-vapour}) \cdot (\text{total}^{-1}$ moles of gas)
y_1	power value for Pr in Nu calculation	0.33
y_2	power value for Sc in Sh calculation	0.33
y_i	distance of nozzle from droplet–particle point of impingement	m
z	spatial coordinate on a solute fixed coordinate system (i.e. distance in terms of mass)	kg
Z	radius of the droplet on a solute-fixed coordinate system (i.e. distance in terms of mass)	kg

Greek symbols

ΔC	driving force for evaporation	$\text{kg} \cdot \text{m}^{-3}$
Δr	small increment in droplet radial position	m
Δt	small increment in time	s
Δz	constant dry solid mass distance increment	kg

v_{dh}	droplet velocity at atomiser nozzle outlet	m.s^{-1}
$v_r(t)$	droplet radial spreading velocity	m.s^{-1}
α_T	thermal diffusivity	$\text{m}^2.\text{s}^{-1}$
β	gas side heat transfer coefficient correction factor	—
β_m	the value of the m^{th} root of Equation (A2.97)	—
γ_{lv}	surface tension (liquid–vapour)	N.m^{-1}
γ_{sl}	solid–liquid interfacial tension	N.m^{-1}
γ_{sv}	liquid–vapour interfacial tension	N.m^{-1}
δ/τ_2	constrictivity/tortuosity constant	—
ΔH_v	latent heat of water vaporisation	J.kg^{-1}
ΔKE	change in kinetic energy due to solidification	J
ΔP	pressure drop between the meniscus and the bulk liquid	Pa
Δr	small increment in distance along the radial dimension to the boundary layer	m
ΔT	difference between the droplet surface temperature and air temperature	$^{\circ}\text{C}$
ΔT_d	difference between the droplet centre temperature and droplet surface temperature	$^{\circ}\text{C}$
ε_a	voidage of air in bulk powder sample	$(\text{m}^3 \text{ of air}).(\text{m}^{-3} \text{ total volume of powder})$
ε_i	volume fraction of the i^{th} component	$(\text{m}^3 \text{ of component } i).(\text{m}^{-3} \text{ total volume})$
θ	angle between the fluid meniscus and pore wall	$^{\circ}$
θ_a	droplet advancing liquid–solid contact angle	$^{\circ}$
θ_e	droplet equilibrium contact angle	$^{\circ}$
λ_a	air thermal conductivity	$\text{W.m}^{-1}.^{\circ}\text{C}^{-1}$
λ_d	droplet thermal conductivity	$\text{W.m}^{-1}.^{\circ}\text{C}^{-1}$
$\lambda_{d,s}$	thermal conductivity at the droplet surface	$\text{W.m}^{-1}.^{\circ}\text{C}^{-1}$
$\lambda_{d,si}$	thermal conductivity at the inside surface of the shell	$\text{W.m}^{-1}.^{\circ}\text{C}^{-1}$
$\lambda_{\text{effective}}$	effective thermal conductivity	$\text{W.m}^{-1}.^{\circ}\text{C}^{-1}$
λ_{EMT}	Effective medium theory thermal conductivity model	$\text{W.m}^{-1}.^{\circ}\text{C}^{-1}$
λ_f	thermal conductivity of the glass filament	$1.14 \text{ W.m}^{-1}.^{\circ}\text{C}^{-1}$
λ_i	thermal conductivity of the i^{th} component	$\text{W.m}^{-1}.^{\circ}\text{C}^{-1}$
λ_{Kr}	Krischer thermal conductivity model	$\text{W.m}^{-1}.^{\circ}\text{C}^{-1}$
λ_p	polymer thermal conductivity	$\text{W.m}^{-1}.^{\circ}\text{C}^{-1}$
λ_{pa}	parallel thermal conductivity model	$\text{W.m}^{-1}.^{\circ}\text{C}^{-1}$
λ_{se}	series thermal conductivity model	$\text{W.m}^{-1}.^{\circ}\text{C}^{-1}$
λ_w	water thermal conductivity	$\text{W.m}^{-1}.^{\circ}\text{C}^{-1}$
μ	solution/coating layer/liquid bridge viscosity	Pa.s
μ_d	droplet viscosity	Pa.s
μ_{mix}	air–water–vapour mixture viscosity	Pa.s
μ_w	water viscosity	mPa.s
$\mu_{w,\text{ref}}$	viscosity of water at the reference temperature (in this case 303 K)	Pa.s
v_0	initial droplet impact velocity	m.s^{-1}
v_a	air velocity	m.s^{-1}
v_d	droplet velocity	m.s^{-1}
v_i	infiltration velocity	m.s^{-1}

v_{r0}	initial relative particle collisional velocity	m.s^{-1}
v_{rel}	relative outlet air velocity	m.s^{-1}
$\zeta(t)$	spread factor as function of time	—
ζ_{end}	final factor as function of time	—
ζ_{max}	maximum factor as function of time	—
ρ_a	air density	kg.m^{-3}
ρ_{bulk}	bulk polymer/powder density	kg.m^{-3}
ρ_d	droplet density	kg.m^{-3}
ρ_p	polymer/particle density	kg.m^{-3}
ρ_w	water density	kg.m^{-3}
ϕ_{ij}	dimensionless function for gaseous mixture	—
α	gas side mass transfer correction factor	—
$\delta(t)$	droplet boundary layer thickness	m
ε_{enviro}	environmental emissivity	—
$\theta_{a,dmax}(t)$	advancing contact angle at d_{max}	°
$\theta_e(t)$	equilibrium (receding) contact angle after recoil	°
σ_{sb}	Stefan-Boltzmann constant	$5.669 \times 10^{-8} \text{ W.m}^{-2}.\text{K}^{-4}$

Abbreviations

ADM	Archer–Daniels–Midland Company
AMF	Anhydrous milkfat
ASDA	Axisymmetric drop shape analysis
AVI	Audio video interleaved
CCD	Charge coupled device
CCS	Constant shear stress
CI	Confidence interval
CMC	Critical micelle concentration or carboxymethylcellulose
codec	Compression/decompression
COV	Coefficient of variation
DE	Dextrose equivalent
DE10	Dextrose equivalent value 10
DE18	Dextrose equivalent value 18
DE5	Dextrose equivalent value 5
DMA	Dynamic mechanical analysis
DMTA	Dynamic mechanical thermal analysis
DP	Degree of polymerisation
DSC	Differential scanning calorimetry
DST	Dynamic surface tension
EMT	Effective medium theory
ESCA	Electron spectroscopy for chemical analysis
ESR	Electron spin resonance
EST	Equilibrium surface tension
FD	Finite difference
FDA	Food and Drug Administration
GA	Gum arabic
HPMC	Hydroxypropylmethylcellulose
LHS	Left hand side
MPD	Mean particle diameter

NMR	Nuclear magnetic resonance
NZMP	formally New Zealand Milk Products
ODE	Ordinary differential equation
PC	Personal computer
PDE	Partial differential equation
PE	Performix E
PEO	Polyethylene oxide
PSA	Particle size analysis
PSD	Particle size distribution
PVP	Polyvinylpyrrolidone
RESS	Rapid expansion of supercritical solutions
RH	Relative humidity
RHS	Right hand side
RO	Reverse osmosis
RSM	Response surface methodology
SDS	Sodium dodecyl sulphate
SEM	Scanning electron microscopy/micrographs
TMA	Thermomechanical analysis
TX	Triton X-100
UP	Ultralec P
UQ	The University of Queensland
WLF	Williams-Landel-Ferry
WMP	Whole milk powder
WPC	Whey protein concentrate
WPI	Whey protein isolate
YG	Yelkin Gold

APPENDIX A2

SINGLE DROPLET DRYING – MATHEMATICAL MODEL DEVELOPMENT, SOLUTION AND INITIAL VALIDATION

A2.1 INTRODUCTION

A mathematical model was required to predict the drying kinetics of single droplets of aqueous polymer solutions and their surface glass transition temperature as an indicator of stickiness development during drying. The model can be used as a predictive tool to aid formulation development and operating conditions optimisation for a Würster coating process. The objective of this appended chapter is to formulate, implement and analytically check the mathematical model based on the effective diffusion conceptual model (discussed in Chapter 5).

A2.2 CONCEPTUAL MODEL DEVELOPMENT

A2.2.1 Conceptual model

In particular, the model addresses the surface moisture content and temperature because they are not able to be directly measured but are important in defining the state of the surface. For instance, these two parameters can be used to define whether or not the surface is sticky which affects adherence during droplet–particle impingement and subsequent inter-particle agglomeration. The physical situation to be modelled is illustrated in Figure A2.1.

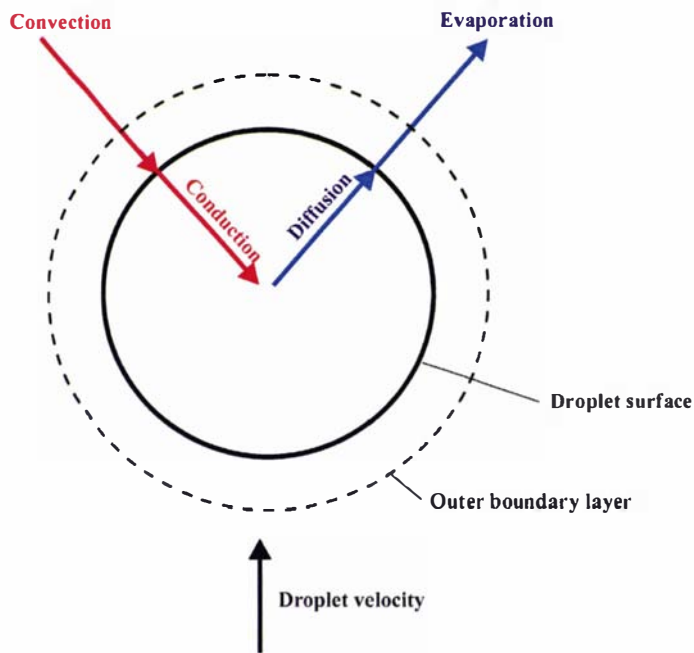


Figure A2.1: Physical phenomena for modelling during droplet drying.

Two parts of the system are considered, the internal part (droplet) and the external part (the surrounding environment) since no assumptions are made on the controlling mechanism. To verify the model simulations against experimental data, the model is developed for the case incorporating the effects of the experimental set-up, namely, the incorporation of a wire thermocouple to measure the temperature change and a glass filament (connected to a digital mass balance) to suspend the droplet in the air stream. Figure A2.2 is a schematic of the conceptual droplet drying model incorporating the experimental set-up equipment.

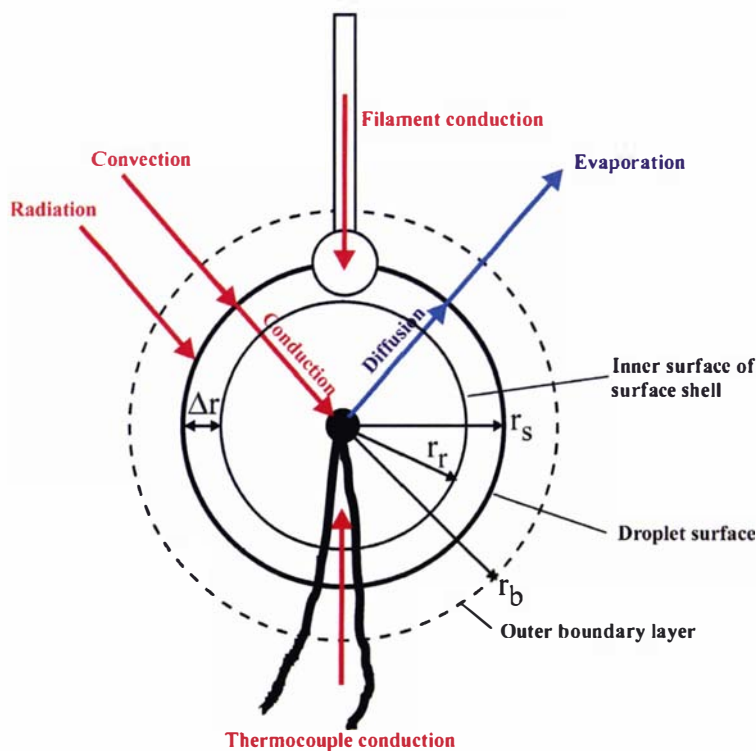


Figure A2.2: Schematic of conceptual droplet drying model including experimental set-up equipment. r_b , r_s and r_r are the radii [m] at the droplet–air boundary layer, the droplet surface and the inner surface of the droplet surface shell respectively.

It should be noted that, although the thermocouple was positioned at the droplet centre, its contribution to heat transfer was taken to be from the surface of the droplet as a first approximation.

A2.2.2 Assumptions

The following assumptions were used in the model development:

1. A single droplet is representative of the entire population in a dilute spray system.
2. Non-turbulent air flow conditions exist, i.e. constant relative velocity between air and the droplet after deceleration to terminal velocity.
3. The droplets are solid (non-hollow), and remain, perfectly spherical [Ferrari *et al.* (1989)], and the change in volume of the droplet corresponds to the amount of water evaporated ('ideal shrinkage') [Ferrari *et al.* (1989); Räderer (2001)].
4. The product is compact, non-porous and homogenous without cracks or air bubbles [Räderer (2001)] allowing the mode of internal moisture transfer to be represented by an effective diffusion coefficient.
5. No internal convection, component segregation or droplet oscillations.
6. The gas phase is an infinite medium.
7. Ranz and Marshall (1952a) correlations for gas side heat and mass transfer coefficients hold true.
8. No chemical reactions and negligible heat of crystallisation [Ranz and Marshall (1952a)].
9. The droplet surface moisture content is in equilibrium with the water-vapour pressure at the surface. Thus, the moisture partial pressure driving force can be determined from the moisture sorption isotherm.

The validity of the assumptions is discussed separately below.

A2.2.3 Validity of the assumptions

1. *A single droplet is representative of the entire population in a dilute spray system.*

There are many different opinions in the literature as to whether such a simplification is justified. van der Lijn (1976) provided a detailed discussion on this and concluded that the droplet interactions in a spray must be taken into account to make accurate calculations on drying. The use of a single droplet to represent that of the spray in an air-suspension particle coating operation is justified here for four reasons. (1) The focus of this work is on accurately predicting temperature and moisture profiles within a single droplet, not a population of droplets. (2) The use of ultrasonic atomisers is advocated for tight droplet size distributions to accurately control coating mass uniformity; hence, it is assumed that the Sauter mean diameter of the spray population is indicative of the whole population. (3) It is expected that the droplets will undergo most of their drying in the first few millimetres of the spray zone and hence there should not be much variation in environmental conditions over such a short distance. (4) Operating conditions will be dilute (low coating spray rates and low particle–air volume ratios) so the effects of droplet–droplet interactions should be less than that in typical high throughput spray driers.

With further advances in computational power, spray droplet interaction effects can be incorporated and coupled to air flow pattern modelling (from computational fluid dynamics) to give a more accurate description of the droplet drying process in a spray system.

2. *Non-turbulent air flow conditions exist, i.e. constant relative velocity between air and droplet after deceleration to terminal velocity.*

As the droplet leaves the atomiser it will experience a very short period of deceleration to its terminal velocity. Any subsequent complex aerodynamics affecting droplet motion are not considered as they will be a strong function of the flow patterns in the particular coating apparatus. The droplet is assumed to move in the vertical direction only and behaves like a rigid sphere and employs steady-flow drag coefficients [Meerdink (1993)].

Steady-flow drag coefficients can be applied to accelerating or decelerating droplets. In reality, the drag coefficients (C_D) for acceleration can be 20–60% higher than values at constant velocity [Masters (1991)]. Hughes and Gilliland (1952) [as cited in van der Lijn (1976)] also stated that drag coefficients are higher during an acceleration period than those for steady-flow at the same Reynolds number. However, Ingebo (1956) [as cited in van der Lijn (1976)] gave data for evaporating and accelerating droplets which did not deviate too much from those for rigid spheres in steady motion. It is this latter finding that supports the use here of steady-flow drag correlations.

3. *The droplets are, and remain, perfectly spherical [Ferrari et al. (1989)], and the change in volume of the droplet corresponds to the amount of water evaporated ('ideal shrinkage') [Ferrari et al. (1989); Räderer (2001)].*

The use of the one-dimensional moisture diffusion equation assumes that 'ideal shrinkage' occurs, resulting in asymmetric concentration profiles. Many spray-dried powders show a clearly spherical form [van der Lijn (1976)], hence this form of equation was adopted. Yamamoto (1999) observed unidirectional shrinkage during the drying of gelatin and sugar (sucrose and maltodextrin) slabs and films. However, the majority of researchers have noted otherwise. Ferrari *et al.* (1989) found that initial 10 mm spheres of skim milk solutions gelled with agar did not remain perfectly spherical during drying. These geometric changes are very difficult to account for mathematically and the error introduced from this simplifying assumption is accepted at this stage.

4. *The product is compact, non-porous and homogenous without cracks or air bubbles [Räderer (2001)] allowing the mode of internal moisture transfer to be represented by an effective diffusion coefficient.*

Internal mass transfer can be described as a combination of several mechanisms. Luikov (1980) [as cited in Bronlund (1997)] specifies ten separate mechanisms for moisture movement that can contribute to a diffusion coefficient as measured from drying curves. Some of these include, molecular diffusion, mixing, recirculation, closed pores, dispersion, pore diffusion and surface diffusion. Due to the complexities of experimentally identifying and then mathematically describing each of the contributing mechanisms for a system, most studies refer to an effective diffusion coefficient, D_{eff} [$\text{m}^2 \cdot \text{s}^{-1}$]. Although crucial information on the effect of matrix parameters such as porosity/tortuosity and of fluid properties such as viscosity are lost [Achanta and Okos (1995)], it is a commonly accepted practice employed with reasonable success by most researchers in light of the experimental and mathematical difficulties. It is implicit that this work is concerned with the effective moisture diffusivity in a non-porous, solid medium and is represented by D_w [$\text{m}^2 \cdot \text{s}^{-1}$].

5. *No internal convection, component segregation or droplet oscillations.*

Internal heat transfer is assumed to occur by conduction only, i.e. no internal fluid convection. Heat and mass transfer inside droplets can be enhanced by internal convection and droplet oscillations. Internal convection in a droplet effectively reduces the thickness of the film boundary layer, reducing droplet drag and increasing the values of the overall Nusselt and Sherwood numbers [Downing (1966); van der Lijn (1976)]. Fuchs (1959) [as cited in van der Lijn (1976)] stated that, the gas side heat and mass transfer coefficients may nearly double with internal circulation. 2–5 fold increases in the rate of transfer have been reported by Kronig and Brink (1950) for fully developed streamline circulation [as cited in van der Lijn (1976)] and up to 14 fold increases for oscillations [Marsh and Heideger (1965) as cited in van der Lijn (1976)]. Immediately after atomisation droplets are oscillating. Stable oscillations occur only at very high Reynolds numbers and therefore the oscillation effect may be neglected for most of the drying period [van der Lijn (1976)]. Farid (2003) considered it reasonable to assume negligible fluid internal circulation due to the small size of droplets used in single droplet drying studies. Internal convection seriously complicates such models, although [Räderer (2001)] provides a relatively simple way to incorporate it based on a critical viscosity empirical correction. Alternatively, if internal convection is important, it can be incorporated by a correction to the binary moisture diffusion coefficient. Internal convection was not incorporated in this model.

More complex mechanisms than simple molecular diffusion result when fibrous materials, or dispersed material of larger size, or materials which do not remain in solution (e.g. salts and proteins) are present [van der Lijn (1976)]. Segregation is not considered in this model because only a single solute is used as a coating material in the current work. Meerdink (1993) successfully modelled the drying kinetics of a segregating sucrose–caseinate system with the generalised Maxwell–Stefan equations. Adhikari (2002) ignored solute segregation in his multicomponent systems (mixtures of maltodextrin DE5 with low molecular weight solutes such as sucrose, fructose and citric acid) and successfully modelled drying kinetics using a weighted binary moisture diffusion coefficient.

6. *The gas phase is an infinite medium.*

Droplets in a spray do not evaporate in an infinite medium. The presence of surrounding droplets creates an equipotential plane around each droplet, through which no transfer takes place [van der Lijn (1976)]. This causes a rise in the water-vapour concentration in the local plane and means the diffusion equation cannot be integrated from the surface to infinity. In general, the deviation caused by the integration distance is limited when the plane is located at a distance of more than 10 times the radius of the droplet.

According to Colburn and Pigford (1950), under conditions of large temperature and concentration driving forces, corrections for sensible heat carried by the water-vapour molecules and diffusion due to thermal gradients must be taken into account [as cited in Ranz and Marshall (1952a)]. Such large gradients are not likely in industrial coating and so the above corrections were not incorporated.

In a coating situation, especially in a high humidity spray zone and during constant rate evaporation, the boundary layer may be saturated and hence the thermal properties of this transfer path were taken as those of the air–water-vapour mixture at the arithmetic average film temperature [e.g. Ranz and Marshall (1952a)].

7. Use of Ranz and Marshall (1952a) correlations for gas side heat and mass transfer coefficients hold true.

The Ranz and Marshall (1952a) correlations are largely empirical and include many unknowns. van der Lijn (1976) quantifies some of the potential deviations from the Nusselt and Sherwood numbers. These include the effects of net mass flow, the Soret effect, deviations from continuum theory, effect of unsteady-state, local variation in transfer coefficients, free convection, non-infinite medium, effect of radiation, effect of mass flux on heat flux, internal circulation and oscillations, effect of turbulence. However, most of these effects can be dismissed with simple calculations, but for engineering purposes such minor corrections are often not warranted if the general trends provide sufficient understanding of the process involved [van der Lijn (1976)].

8. No chemical reactions and negligible heat of crystallisation [Ranz and Marshall (1952a)].

A negligible heat of reaction is assumed for maltodextrin DE5 as it solidifies out of solution.

9. The moisture content at the liquid–vapour interface is in equilibrium with the water-vapour pressure in the air boundary layer.

This is a simplifying assumption to enable the moisture partial pressure driving force to be determined from the moisture sorption isotherm. The error from this approximation is likely to be small.

A2.3 MATHEMATICAL FORMULATION

A2.3.1 Moisture history

Mass transfer occurs in the opposite direction to heat transfer, from the droplet centre towards the surface, by a number of mechanisms. Internal moisture transfer is assumed to be solely by diffusion and can be described by Fick's first law for transient mass transfer across an interface. However, since it is concentration, not mass, that is of interest, the equation for the changes in concentration under non-stationary conditions is described by Fick's second law and represented by the partial differential equation (PDE) in Equation (A2.1) for spherical coordinates [taken from Rädlerer (2001)].

$$\frac{\partial C_w}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_w(C_w, T_r) \frac{\partial C_w}{\partial r} \right) \quad \text{for } 0 < r < R \text{ and } t > 0 \quad (\text{A2.1})$$

where C_w , t , r , D_w and T_r the moisture content [(kg water).(m⁻³ droplet)], the time [s], the droplet radial position through which water is transported [m], the binary moisture diffusion coefficient [m².s⁻¹] and the temperature [°C] at radial position r , respectively. The term 'm⁻³ droplet' accounts for the amount of solute (dissolved or solid) and water present.

Equation (A2.2) and Equation (A2.3) describe the moisture content on a water-free basis and the relationship between the spatial and solids-fixed coordinate systems respectively.

$$u = \frac{C_w}{C_s} \quad (\text{A2.2})$$

$$\frac{dz}{dr} = C_s r^2 \quad (\text{A2.3})$$

where u is the moisture content on a dry solids basis [(kg water).(kg⁻¹ dry solid)], C_s is the solids concentration [(kg solids).(m⁻³ droplet)] and z is the spatial variable in solid-fixed coordinates [kg dry solid]. Equation (A2.2) and Equation (A2.3) are used to transform Equation (A2.1) from a spatial to a solute-fixed coordinate system, yielding Equation (A2.4) which provides a simpler numerical solution procedure as discussed in Section 5.2.

$$\frac{\partial u}{\partial t} = \frac{\partial}{\partial z} \left(C_s^2(r, t) r^4 D_w(u, T_z) \frac{\partial u}{\partial z} \right) \quad \text{for } 0 < z < Z \text{ and } t > 0 \quad (\text{A2.4})$$

where T_z [°C] is the temperature at position z [kg solid] along the droplet radius, Z [kg] is the droplet radius in solute-fixed coordinates and $4\pi Z$ [kg] is the total mass of dry solid in the droplet given by the relationship in Equation (A2.58).

Equation (A2.4) is now of the form of the PDE commonly given in the literature [e.g. Lijn *et al.* (1972); Wijlhuizen *et al.* (1979); Ferrari *et al.* (1989); Meerdink (1993); Yamamoto and Sano (1995); Hecht and King (2000b); Räderer (2001); Adhikari (2002)]. Both Lijn (1976) and Räderer (2001) mathematically compared the calculation of water flux in various reference frames to the water-free solids reference frame (coordinate system) confirming the mathematical rigor of the transformation. Equation (A2.4) was solved numerically using finite difference equations as discussed in Section A2.4.6.

A2.3.2 Temperature history

During air drying of droplets, transport of heat occurs from the bulk air to the droplet surface, primarily by convection and within the droplet by conduction and convection. Internal convection is assumed to be negligible, hence the PDE representing transient heat conduction in a sphere is given by Fourier's second law [taken from Farid (2003)]:

$$\frac{\partial T_r}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \alpha_T (C_w, T_r) \frac{\partial T_r}{\partial r} \right) \quad \text{for } 0 < r < R \text{ and } t > 0 \quad (\text{A2.5})$$

where α_T is the droplet thermal diffusivity [m².s⁻¹] which is itself defined as $\lambda_d/(\rho_d.c_{pd})$ where λ_d is the droplet thermal conductivity [W.m⁻¹.°C⁻¹], ρ_d is the droplet density [kg.m⁻³] and c_{pd} is the droplet specific heat capacity [J.kg⁻¹.°C⁻¹]. Note that the variables making up the thermal diffusivity are not constant, but are all a function of both temperature and composition (water and polymer) and cannot be moved outside the bracket to simplify the equation. Equation (A2.5) was solved numerically using finite difference equations as discussed in Section A2.4.6.

Note that the PDE for moisture content is on a solids-fixed coordinate system whereas the PDE for temperature is on a spatial (radial position) coordinate system. A transformation of the temperature PDE into solids-fixed coordinates was not sought because the spatial distance at each solid-fixed coordinate could easily be calculated using the radius and solids content relationship in Equation (A2.60).

A2.3.3 Droplet velocity

The droplet velocity was calculated by considering a momentum balance over a falling droplet, subject to the constraints that the droplet moves in the vertical direction only and behaves like a rigid, non-rotating sphere as given in Meerdink (1993) in Equation (A2.6).

$$\frac{dv_d}{dt} = \left(\frac{\rho_d - \rho_a}{\rho_d} \right) g - \frac{3}{8} \frac{C_D \rho_a (v_d - v_a)^2}{\rho_d R} \quad \text{for } t > 0 \quad (\text{A2.6})$$

where v_d , ρ_d , ρ_a , g , C_D , R , v_a and t are the droplet velocity [m.s^{-1}], the droplet density [kg.m^{-3}], air density [kg.m^{-3}], the acceleration due to gravity [9.81 m.s^{-2}], the droplet–air drag coefficient [–], the droplet radius [m], the air velocity [m.s^{-1}] and time [s] respectively. The steady-state drag coefficient correlations used here are taken from Bird *et al.* (1960):

$$C_D = \frac{24}{Re_r} \quad \text{for } Re_r \leq 2 \quad (\text{A2.7})$$

$$C_D = \frac{18.5}{Re_r^{0.6}} \quad \text{for } 2 < Re_r < 500 \quad (\text{A2.8})$$

$$C_D = 0.44 \quad \text{for } 500 \leq Re_r \leq 3 \times 10^5 \quad (\text{A2.9})$$

where Re_r [–] is the relative droplet Reynolds number and is given by:

$$Re_r = \frac{2R\rho_a |v_d - v_a|}{\mu_a} \quad (\text{A2.10})$$

Equation (A2.6) is an ordinary differential equation (ODE) that requires the velocity result to enable calculation of the relative Reynolds number and drag coefficient. Consequently, it is incorporated into the model as an ODE.

A2.3.4 Thermophysical properties of air

The physical properties of air are required to predict the external heat and mass transfer rates in the drying model. Many and varied correlations are available in the literature. A critical review was not undertaken; the formulae used in the model and detailed below are taken from sources the author deems reputable. Many of the relationships were verified independently by checking against the original references or with other sources of data.

A2.3.4.1 Constants and simplifications

The molecular mass of air, M_a , was taken to be $28.97 \text{ g.mole}^{-1}$ [Bird *et al.* (1960)]. The universal gas constant, R_g , was taken to be $8.314 \text{ J.mole}^{-1}.\text{K}^{-1}$. The total system pressure, P_T , was taken to be that at atmospheric conditions, i.e. $101\,325 \text{ [Pa]}$. The properties of the air were calculated at the boundary film temperature, T_f [$^{\circ}\text{C}$] taken to be the arithmetic average of the bulk air and the droplet surface temperature. This is a commonly accepted approach [Incropera and DeWitt (1981b); Coumans (1987); Perry and Green (1997)] for cases of moderate temperature differences [Incropera and DeWitt (1981b)].

$$T_f = \frac{T_a + T_s}{2} \quad (\text{A2.11})$$

in [°C]. Unless stated otherwise all the temperatures used in the model are calculated in °C.

A2.3.4.2 Thermal conductivity of air

$$\lambda_a = 1.97 \times 10^{-4} (T_f + 273.15)^{0.858} \quad (\text{A2.12})$$

in [W.m⁻¹.°C⁻¹], taken from Adhikari (2002) over the range 0–205 °C.

A2.3.4.3 Specific heat capacity of air

$$c_{pa} = 4 \times 10^{-4} T_f^2 + 2.38 \times 10^{-2} T_f + 1004.5 \quad (\text{A2.13})$$

in [J.kg⁻¹.°C⁻¹], taken from Adhikari (2002) over the range 0–205 °C.

A2.3.4.4 Density of air

The density of air, ρ_a [kg.m⁻³] was calculated using the ideal gas law:

$$\rho_a = \frac{P_f M_a}{R_g (T_f + 273.15)} \quad (\text{A2.14})$$

A2.3.4.5 Diffusivity of water-vapour in air

Ranz and Marshall (1952a) and Poling *et al.* (2001) acknowledged the large variation in literature data for prediction of diffusion coefficients of binary gas systems at low pressures. Poling *et al.* (2001) recommended the procedure of Fuller *et al.* (1969) as yielding the smallest average error (approximately 4%, Poling *et al.* (2001)). Using the constants specified by Fuller *et al.* (1969), the equation was simplified to give:

$$D_v = 1.1923 \times 10^{-9} (T_f + 273.15)^{1.75} \quad (\text{A2.15})$$

in [m².s⁻¹].

A2.3.4.6 Viscosity of air

Sano and Keey (1982) proposed Equation (A2.16) to predict the variation of viscosity [Pa.s] of dry air with temperature.

$$\mu_a = 1.097 \times 10^{-6} \frac{(T_f + 273.15)^{0.5}}{1.453 - 0.0243(T_f + 273.15)^{0.5}} \quad (\text{A2.16})$$

A2.3.4.7 Saturated water-vapour pressure at droplet surface

There are numerous relationships for the saturated water-vapour pressure each yielding slightly different results dependent on the coefficients used in the calculation. In this study, the saturated water-vapour pressure was calculated using the Antoine equation. The

coefficients [$A = 5.11564$, $B = 1687.537$, $C = 230.17$] for the Antoine equation were taken from Poling *et al.* (2001).

$$P_{vs} = 10^{\left(5.11564 - \frac{1687.537}{T_s + 230.17}\right)} \quad (\text{A2.17})$$

in [$\times 10^{-5}$ Pa] for the range 0.05–200.05 °C. Poling *et al.* (2001) stated that extrapolation of the Antoine equation outside the stated temperature range may lead to absurd results.

A2.3.4.8 Partial water-vapour pressure of bulk air

$$P_v = \frac{RH}{100} \times P_{vs} \quad (\text{A2.18})$$

where P_{vs} [Pa] is calculated with Equation (A2.17) at the dry bulb air temperature.

A2.3.5 Thermophysical properties of water

Physical properties of water are required to predict both the internal and external heat and mass transfer rates in the drying model. Again many and varied correlations are available in the literature. The formulae used in the model are taken from sources the author deems reputable. Many of these have been verified independently by checking against the original references or with other sources of data. Most of these correlations were established by the least squares technique based on data taken from Rahman (1995) over a 0–100 °C temperature range. Due to the fitting method, large errors can occur if too few decimal places are carried, hence, the large number of significant figures in some of these equations.

A2.3.5.1 Density of water

$$\rho_w = -0.0038T_d^2 - 0.0477T_d + 1000 \quad (\text{A2.19})$$

in [kg.m^{-3}].

A2.3.5.2 Latent heat of vaporisation of water

$$\Delta H_v = -0.0013T_d^2 - 2.29618T_d + 2500 \quad (\text{A2.20})$$

in [kJ.kg^{-1}].

A2.3.5.3 Specific heat capacity of water

$$c_{pw} = 0.00876T_d^2 - 0.6042T_d + 4190 \quad (\text{A2.21})$$

in [$\text{J.kg}^{-1}.\text{°C}^{-1}$].

A2.3.5.4 Thermal conductivity of water

$$\lambda_w = 1.2109 \times 10^{-5}T_d^2 + 2.5149 \times 10^{-3}T_d + 0.5516 \quad (\text{A2.22})$$

in [$\text{W.m}^{-1}.\text{°C}^{-1}$].

A2.3.5.5 Viscosity of water

$$\mu_w = -2.58 \times 10^{-6} T_d^3 + 0.00058 T_d^2 - 0.0472 T_d + 1.7584 \quad (\text{A2.23})$$

in [mPa.s].

A2.3.5.6 Thermophysical properties of water-vapour–air mixtures

Since the gas phase contains both air and water-vapour, the effect of the water-vapour on the thermophysical properties of the air (particularly the droplet–air boundary interface) should be accounted for. In an industrial-scale coating situation, this could be significant, especially if the coater is operating under moist air conditions, which is typical in the spray nozzle location. For example, since the thermal conductivity of water at 20 °C is approximately 25 times greater than that of air [Ranz and Marshall (1952a)] the conductivity of the water-vapour–air mixture should be used to ensure accurate calculation of the heat transfer in the boundary layer.

For most purposes, the semi-empirical formula of Wilke (1950) [as cited in Bird *et al.* (1960)] is adequate to compute both the viscosity and thermal conductivity of low density, non-polar gases and gas mixtures. For polar gases such as water-vapour, the angle dependent modification of Monchick and Mason (1961) is required [Bird *et al.* (1960)]. However, Reid (1987) stated that Wilke's approximation has proved reliable even for polar–polar gas mixtures of aliphatic alcohols. Wilke's approximation is used in the work here.

$$\mu_{mix} = \frac{\sum_{i=1}^n \frac{x_i \mu_i}{\sum_{j=1}^n x_j \phi_{ij}}}{\sum_{j=1}^n x_j \phi_{ij}} \quad (\text{A2.24})$$

where x_i and x_j are the mole fractions [–] of the respective components (i and j), in this case water and air. μ_{mix} is the air–water-vapour mixture viscosity [Pa.s], and ϕ_{ij} is a dimensionless function given by Equation (A2.25).

$$\phi_{ij} = \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j} \right)^{1/2} \left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{1/2} \left(\frac{M_j}{M_i} \right)^{1/4} \right]^2 \quad (\text{A2.25})$$

where M_i and M_j are the corresponding molecular weights [g.mole^{–1}] of components i and j . μ can be substituted for λ to calculate the thermal conductivity of the air–water-vapour mixture, λ_{mix} [Bird *et al.* (1960)].

The specific heat capacity of water-vapour, $c_{p_{wv}}$ [J.kg^{–1}.°C^{–1}] was calculated with Equation (A2.26) constructed from data taken from Rogers and Mayhew (1980).

$$c_{p_{wv}} = 0.0167 T_f^2 - 0.0261 T_f + 1866.4 \quad (\text{A2.26})$$

A2.3.6 Thermophysical and chemical properties of polymers

The mathematical predictions were made for maltodextrin DE5 only. The majority of the properties were taken from Adhikari (2002) which were properties for maltodextrin DE6.

They should not be significantly different to that of maltodextrin DE5 used here. Future work should look to collect actual data on the substance used as these can vary markedly depending on suppliers.

A2.3.6.1 Polymer density

Adhikari (2002) measured the particle density of maltodextrin DE6 to be to be 1400 kg.m^{-3} . The density of maltodextrin DE20–22 used by Meerdink (1993) was taken to be 1600 kg.m^{-3} . The maltodextrin DE5 density, ρ_p , for the work here was taken to be 1500 kg.m^{-3} .

A2.3.6.2 Polymer specific heat capacity

The polymer specific heat capacity for maltodextrin DE5, $c_{pp} [\text{J.kg}^{-1}.\text{°C}^{-1}]$ was taken to be that measured by Adhikari (2002) for maltodextrin DE6. It is represented as a function of temperature for the range 30–80 °C.

$$c_{pp} = 3.5242T_d + 1319.7 \quad (\text{A2.27})$$

This is close to the value used by Meerdink (1993) for maltodextrin DE20–22 being $1500 \text{ J.kg}^{-1}.\text{°C}^{-1}$.

A2.3.6.3 Polymer thermal conductivity

The thermal conductivity of maltodextrin DE5, $\lambda_p [\text{W.m}^{-1}.\text{°C}^{-1}]$ was taken to be the thermal conductivity of maltodextrin DE6 measured by Adhikari (2002). Although thermal conductivity will be temperature dependent a single value of $0.094 \text{ W.m}^{-1}.\text{°C}^{-1}$ was found to be adequate in Adhikari's model predictions. However, this value was for a bulk powder sample, hence it is an effective thermal conductivity, $\lambda_{effective}$, and requires correction for the thermal resistance of entrained air by Equation (A2.28) taken from Bronlund (1997).

$$\lambda_{effective} = (1 - \epsilon_a)\lambda_p + \epsilon_a\lambda_a \quad (\text{A2.28})$$

The voidage of the air in the powder, $\epsilon_a [-]$, is given by Equation (A2.29).

$$\epsilon_a = 1 - (\rho_{bulk} / \rho_p) \quad (\text{A2.29})$$

The bulk powder density, $\rho_{bulk} [\text{kg.m}^{-3}]$ was measured for maltodextrin DE5 and found to be 760 kg.m^{-3} to give a polymer thermal conductivity, λ_p , of $0.16 \text{ W.m}^{-1}.\text{°C}^{-1}$. This is similar to the thermal conductivity of skim milk powder which was $0.1 \text{ W.m}^{-1}.\text{°C}^{-1}$ [Bylund (1995), as cited in Farid (2003)]. It is likely that the change in solid conductivity with temperature over the drying temperatures of interest (less than 100 °C) is minimal and insignificant in the models results. The thermal conductivity of the droplet (polymer + water) was calculated via effective medium theory (EMT) as discussed in Section A2.3.7.

A2.3.6.4 Binary moisture diffusion coefficient

Moisture diffusivity is the most crucial property in drying calculations [Zogzas and Maroulis (1996)] and knowledge of such concentration dependent diffusivities is very important in designing drying processes [Yamamoto (1999)]. Unfortunately, very little experimental data are available on the concentration-dependent diffusivities for liquid foods [Zogzas and Maroulis (1996); Yamamoto (1999)] and their variation is enormous [Chirife (1983) as cited

in Räderer (2001)]. Furthermore, experimental and calculation methods for determining the diffusivity are not properly understood [Yamamoto (1999)] making its prediction or estimation very difficult.

In foodstuffs the water diffusion coefficient is greatly affected by both water concentration and to a significant, but lesser extent, temperature [Räderer (2001)]. Numerous semi-empirical relationships exist for the binary moisture diffusion coefficient [refer to Räderer (2001)]. Moisture diffusivity and related equations can be found in the works of Sano and Keey (1982), Furuta *et al.* (1984), Singh *et al.* (1984), Ferrari *et al.* (1989), Nesic and Vodnik (1991), Zogzas and Maroulis (1996) and Yamamoto (1999). The correlation for the binary moisture diffusion coefficient as a function of moisture content and temperature proposed by Luyben *et al.* (1982) was used here. The correlation was used by Adhikari (2002) to successfully model maltodextrin DE6 drying kinetics.

$$D_w(u, T_d) = D_{w,ref} \exp \left[-\frac{E_D}{R_g} \left(\frac{1}{T_d} - \frac{1}{T_{ref}} \right) \right] \quad (A2.30)$$

Equation (A2.30) is composed of a number of constituent relationships. $D_{w,ref} [\text{m}^2 \cdot \text{s}^{-1}]$ is the binary moisture diffusion coefficient of dilute solution at a reference temperature (in this case 303 K) and is an exponential function of moisture content.

$$D_{w,ref} = D_{0,ref} \exp \left(-\frac{a}{b + a u} \right) \quad (A2.31)$$

where u is the droplet moisture content $[(\text{kg water}) \cdot (\text{kg}^{-1} \text{ dry solid})]$ and a and b are constants $[-]$. The parameter $D_{0,ref} [\text{m}^2 \cdot \text{s}^{-1}]$ is the moisture diffusivity [Yamamoto and Sano (1995)] in dilute solution at a reference temperature (in this case 303 K). $D_{0,ref}$ is obtained using the equation for dilute solutions proposed by Wilke and Chang (1955) and modified by Sano and Yamamoto (1993) to apply to dilute sugar and carbohydrate solutions.

$$D_{0,ref} = 1.05263 \times 10^{-14} \frac{T_{ref}}{\mu_{w,ref}} (M_p)^{-1/3} \quad (A2.32)$$

where $T_{ref} [\text{K}]$ is the sample mixture reference temperature, taken to be 303 K in this case. M_p is the molecular weight of the polymer, $3600 \text{ g} \cdot \text{mole}^{-1}$ (for maltodextrin DE5 supplied by Salkat NZ Limited, Auckland, New Zealand and sourced from Grain Processing Corporation, Muscatine, IO, USA) and $\mu_{w,ref} [\text{Pa} \cdot \text{s}]$ the viscosity of water at the reference temperature.

The temperature dependence is expressed by the activation energy, $E_D [\text{kJ} \cdot \text{mole}^{-1}]$, which is also a function of moisture content.

$$E_D = \frac{c + d u}{e + f u} \quad (A2.33)$$

where c , d , e , and f are constants $[-]$. Substitution of Equations (A2.31), (A2.32) and (A2.33) into Equation (A2.30) results in the following working equation for the diffusion coefficient, $D_w [\text{m}^2 \cdot \text{s}^{-1}]$:

$$D_w = D_{w,min} + D_{0,ref} \exp\left(-\frac{a}{b+au}\right) \exp\left[-\frac{1}{R_g}\left(\frac{c+du}{e+fu}\right)\left(\frac{1}{T_d} - \frac{1}{T_{ref}}\right)\right] \quad (A2.34)$$

where T_d is the droplet temperature in K. The values of the coefficients were determined by Adhikari (2002) by fitting Equation (A2.34) using a non-linear least squares technique to calculated diffusion coefficients collected from drying kinetic data and calculated by the method of Yamamoto (1999). Adhikari *et al.* (2002) reviewed the moisture diffusivity calculation procedures of Schoeber (1976), Coumans (1987) and Yamamoto (1999). According to Adhikari (2002), the numerical values for the majority of the parameters were not significantly different to those of Luyben *et al.* (1982) and Sano and Yamamoto (1993).

Equations describing the binary moisture diffusion coefficient are usually fitted to data down to moisture contents of 0.1 (kg water).(kg⁻¹ dry solid). Below this concentration the drying kinetic data used to generate the correlations is unreliable and hidden amongst the noise of the experiment (perturbations in the mass readings in a drying air stream). Because of the exponential nature of the correlation, to obtain reasonable predictions below 0.1 (kg water).(kg⁻¹ dry solid), a minimum binary moisture diffusion coefficient was introduced, $D_{w,min}$ [-]. Inspection of the data in Bruin and Luyben (1980) below 0.1 kg.kg⁻¹ showed that the lowest value of D_w for starch was 10⁻¹⁴ m².s⁻¹. This value was set for $D_{w,min}$ which prevented unreasonably low values of D_w being calculated.

Although, the use of an effective diffusion coefficient with the 6 polymer dependent fitted parameters (a to f), would appear application specific the correlation developed by Adhikari (2002) was valid over wide ranging conditions (63–130 °C, 0.58–1.00 m.s⁻¹, and for solutes encompassing fructose, glucose, sucrose, citric acid and maltodextrin DE6). The values for the curve fitting constants in Equation (A2.34) are: $a = 16$; $b = 1$; $c = 100$; $d = 195$; $e = 1$; $f = 10$.

The binary moisture diffusion coefficient correlation was later modified to include the effect of porosity and air-space as discussed in Section 5.10.

A2.3.6.5 Water activity

Many models have been developed to describe isotherms or parts thereof [Foster (2002)], with the three parameter Guggenheim-Anderson-de Boer (GAB) model being commonly used [Räderer (2001)]. However, Zogzas and Maroulis (1996) found the use of GAB's equation at high water activity values caused unexpected floating point errors during runtime. In addition, the GAB equation also requires an iteration procedure that would slow the simulation time. As a result, the water activity was calculated from a 'best fit' equation to the moisture sorption isotherm data (refer to Figure 4.4) with Equation (A2.35).

$$a_w = a + b \left[\frac{(cd + eu_s^f)}{(d + u_s^f)} \right] \quad (A2.35)$$

where u_s is the moisture content at the droplet surface [(kg water).(kg⁻¹ dry solid)]. The values for the curve fitting constants in Equation (A2.35) are: $a = 4.66 \times 10^{-2}$; $b = 9.38 \times 10^{-1}$; $c = 4.97 \times 10^{-2}$; $d = 1.47 \times 10^{-2}$; $e = 9.82 \times 10^{-1}$; $f = 1.76$. It should be noted that this equation was fitted to data over the moisture content range 0 to 0.3 (kg water).(kg⁻¹ dry solid). At

higher surface moisture contents the equation is still used because it predicts an asymptotic water activity of 0.97, which is close to 1.0, the maximum possible.

According to Kessler (1988), higher temperatures increase the liberation forces, so that less water can be sorbed at the same water activity [as cited in Räderer (2001)]. Foster (2002) stated that, a temperature effect on water activity has been noted for casein, whey protein concentrate, skim milk powder, amorphous sucrose, amorphous glucose among others. Räderer (2001) stated that the Clausius-Claperton equation is widely used to express the temperature variation of the water activity. However, Furuta *et al.* (1984) did not find an appreciable temperature effect for maltodextrin over a 25–45 °C temperature range. The effect of temperature on the moisture sorption isotherm for maltodextrin DE5 was not measured and hence not incorporated into the model.

A2.3.6.6 Glass transition temperature

A number of equations have been used to correlate the T_g [°C] of mixtures. The empirical Gordon-Taylor equation [Gordon and Taylor (1952)] (Equation (A2.36)), is probably the most widely used in the food and polymer fields for predicting the plasticising effect of moisture on a single solute.

$$T_g = \frac{x_p T_{gp} + K x_w T_{gw}}{x_p + K x_w} \quad (\text{A2.36})$$

where x_p and x_w are the mass fractions of polymer (solute) and water respectively [–]. K is a dimensionless proportionality constant [–] which varies with the type of polymer. T_{gp} and T_{gw} are the glass transition temperatures [°C] of the dry solid and of water (–135 °C [Johari *et al.* (1987)]) respectively. The Gordon-Taylor equation is semi-empirical and requires fitting constants so the glass transition temperature data for maltodextrin DE5 from Roos and Karel (1991a) (Figure 4.6) was used to generate the glass transition temperature as a function of water activity, a_w . A better representation of the data was obtained with the 4th order polynomial.

$$T_g = -58.509a_w^4 - 516.17a_w^3 + 874.75a_w^2 - 531.46a_w + 186.49 \quad (\text{A2.37})$$

Similar to the polynomial equation for water activity, Equation (A2.37) must also be used cautiously when predicting near its extremities. At a_w extremes, i.e. $a_w = 0.0$ and 0.97, the equation yields a T_g of 186.5 and -26.7 °C respectively. At high surface water activities, and in particular, at time zero and just after, the real glass transition temperature of the solution is not known. Hence, it was not appropriate to predict the T_g above a surface moisture content of 0.3 (kg water).(kg⁻¹ dry solid) and it was assumed to be -26.7 °C.

A2.3.7 Droplet mixture properties

There are numerous methods for the estimation and prediction of the properties of mixtures. Because, in most cases the physical properties of both the water and the solid were similar, the volume additivity method was used.

The droplet solute concentration, C_s [(kg dry solid).(m⁻³ droplet)], is given by:

$$C_s = \frac{1}{\left(\frac{1}{\rho_p} + \frac{u}{\rho_w} \right)} \quad (\text{A2.38})$$

The droplet density, ρ_d [(kg droplet).(m⁻³ droplet)], is given by:

$$\rho_d = \frac{1+u}{\left(\frac{1}{\rho_p} + \frac{u}{\rho_w} \right)} \quad (\text{A2.39})$$

The droplet specific heat capacity, c_{pd} [J.kg⁻¹.°C⁻¹], is given by:

$$c_{pd} = \frac{1+u}{\left(\frac{1}{\rho_p} + \frac{u}{\rho_w} \right)} \quad (\text{A2.40})$$

The density and specific heat capacity equations were further expanded to include a third component, air, for the ‘dense skin–porous crumb’ model predictions.

There are several methods (serial, parallel or mixed) to predict the thermal conductivity of a substance [Räderer (2001)]. The series model for thermal conductivity λ_{se} [W.m⁻¹.°C⁻¹] would yield the lowest value and takes the form:

$$\frac{1}{\lambda_{se}} = \sum_{i=1}^n \frac{\varepsilon_i}{\lambda_i} \quad (\text{A2.41})$$

where λ_i is the thermal conductivity of the component i and ε_i is the volume fraction [(m³ of component i).(m⁻³ total volume)]. Murakami and Okos (1989) found the parallel model for thermal conductivity, λ_{pa} [W.m⁻¹.°C⁻¹] to be sufficiently accurate for non-porous food systems above the freezing point and is given by Equation (A2.42).

$$\lambda_{pa} = \sum_{i=1}^n \varepsilon_i \lambda_i \quad (\text{A2.42})$$

The parallel model would result in the highest value of the predicted thermal conductivity. According to Räderer (2001), the effective thermal conductivity of non-homogenous substances is between the two cases of serial and parallel heat transfer. As a result, numerous other models exist that include both series and parallel heat transfer character. For example, the Krischer model for thermal conductivity, λ_{Kr} [W.m⁻¹.°C⁻¹] [taken from Rahman (1995)].

$$\lambda_{Kr} = \left[\frac{1-f_k}{\lambda_{pa}} + \frac{f_k}{\lambda_{se}} \right]^{-1} \quad (\text{A2.43})$$

where f_k [–] is the Krischer’s distribution factor which is used to apportion the degree of series or parallel character. Murakami and Okos (1989) used regression analysis to correlate f_k to the moisture content and porosity. The effective medium theory (EMT) thermal conductivity, λ_{EMT} [W.m⁻¹.°C⁻¹] model is also commonly used to describe thermal conductivity of mixtures

of substances and is represented by the mathematical series in Equation (A2.44) [taken from Rahman (1995)].

$$\sum_{i=1}^n \varepsilon_i \frac{\lambda_{EMT} - \lambda_i}{\lambda_i - 2\lambda_{EMT}} = 0 \quad (\text{A2.44})$$

The series is solved to give Equation (A2.45).

$$\lambda_{EMT} = \frac{(V_i \lambda_j + 2V_i \lambda_i + V_j \lambda_i + 2V_j \lambda_j)}{2(2V_i + 2V_j)} + \frac{(V_i \lambda_j - 4V_i^2 \lambda_j \lambda_i - 6V_i \lambda_j V_j \lambda_i + 4V_i \lambda_i^2 V_j + 4V_i^2 \lambda_i^2 + 4V_i \lambda_i^2 V_j + V_j^2 \lambda_i^2 - 4V_j^2 \lambda_i \lambda_j + 4V_j^2 \lambda_j^2)^{1/2}}{2(2V_i + 2V_j)} \quad (\text{A2.45})$$

A2.3.8 Gas side heat and mass transfer coefficients

Gas side heat and mass transfer coefficients are used to help describe the rate of heat transfer from the external environment to the droplet surface and the rate of mass transfer from the droplet surface to the external environment. According to Chen (2004) the adequate matching of the heat and mass transfer correlations is important in predicting the drying kinetics accurately. For this reason it is worthy of a short discussion with respect to a Würster coating operation.

The determination of the heat transfer coefficients is viewed as a problem of convection [Incropera and DeWitt (1981b)] and depend on the fluid properties, surface geometry and flow conditions. The type of flow in the Würster coater will determine the thickness of the stagnant boundary layer around a pneumatically transported droplet/particle. The gas side heat transfer coefficient is therefore a function of the hydrodynamics and can be written in terms of the Nusselt number. The Nusselt number characterises the external heat transfer conditions.

$$Nu = \frac{\text{total heat transfer}}{\text{molecular heat transfer (conductive)}} = \frac{h_g L_c}{\lambda_a} \quad (\text{A2.46})$$

where L_c is the characteristic length of the object (in this case droplet diameter, d_d) [m] and λ_a is the thermal conductivity of the fluid (air) [$\text{W.m}^{-1}.\text{°C}^{-1}$]. Experimental data [Marshall (1955) as cited in Masters (1991)] have shown that heat transfer to a spherical droplet in still air ($Re = 0$) and in the absence of natural convection [Ranz and Marshall (1952a); Rowe *et al.* (1965)] can be expressed as $Nu = 2.0$. With the minimal Nusselt number $Nu = 2.0$ for a motionless fluid, the Nusselt number can be expressed with the often used form [Bird *et al.* (1960); Rädlerer (2001)]:

$$Nu = 2 + k_1 Re^{x_1} Pr^{y_1} \quad (\text{A2.47})$$

The factor k_1 may vary between 0.552–0.664 [Rädlerer (2001)]. The values proposed by Ranz and Marshall (1952a) are, however, most widely used being $k_1 = 0.6$, $x_1 = 0.5$, $y_1 = 0.33$. Variations are described in the Ranz-Marshall equation that allows an uncertainty of about 20% [Weiss (1987) and Taniguchi and Asano (1994) both cited in Rädlerer (2001)]. Das *et al.*

(1984) and Gosman and Clerides (1997) [as cited in Räderer (2001)] show differences of 50% to 100%. However, these differences are in part due to the widely varying experimental conditions used in their evaluation. It should be noted that these values are usually based upon experiments conducted in aeronautic wind tunnels where the turbulence intensity is close to 0% [Kondjoyan *et al.* (1993) as cited in Räderer (2001)]. In reality, high turbulence in a coater could bring about an increase in these values.

The Reynolds number, Re [–], characterises the flow and the Prandtl number, Pr [–], describes the material by the following equations:

$$Re = \frac{\text{total momentum transfer (inertial)}}{\text{molecular momentum transfer (viscous)}} = \frac{\rho_a v_a d_d}{\mu_a} \quad (\text{A2.48})$$

$$Pr = \frac{\text{molecular momentum transfer (viscous)}}{\text{molecular heat transfer (conduction)}} = \frac{c_{pa} \mu_a}{\lambda_a} \quad (\text{A2.49})$$

where ρ_a , v_a , d_d , c_{pa} , μ_a and λ_a are the air density [kg.m^{-3}], the air velocity [m.s^{-1}], the droplet diameter [m], the air specific heat capacity [$\text{J.kg}^{-1}.\text{°C}^{-1}$], the air viscosity [Pa.s], the specific heat capacity of air [$\text{J.kg}^{-1}.\text{°C}^{-1}$], the air viscosity [Pa.s] and the air thermal conductivity [$\text{W.m}^{-1}.\text{°C}^{-1}$] respectively.

During spray drying, droplets (diameters < 100 μm) released from an atomiser decelerate rapidly to become completely influenced by the surrounding air flow [Masters (1991)]. During droplet deceleration considerable evaporation can occur for pure water droplets. According to Masters (1991), equations by Frössling (1938) express evaporation during this period. These equations are of the same form as Equation (A2.47) and the values are not significantly different to those proposed by Ranz and Marshall (1952a). As a result, the Ranz and Marshall (1952a) correlation was chosen for use in this work. The limitations are acknowledged as only applying over moderate relative velocities and air temperatures. According to Das *et al.* (1984), the Ranz and Marshall (1952a) correlations are only valid for droplets less than 3 mm in diameter [as cited in Räderer (2001)].

The effect of mass flux on the rates of heat and mass transfer is limited in the case of evaporation of water at moderate evaporating conditions which are expected in air-suspension coating of dairy powders. High mass transfer rates cause a decrease in the heat transfer rate as well as in the apparent mass transfer coefficient. Crosby and Stewart (1970) [as cited in Lijn (1976)] showed that application of the correction factor predicted by the film theory presented in Bird *et al.* (1960) gives acceptable results. These heat and mass transfer corrections were also applied in the work of Luyben *et al.* (1982) and Lin and Chen (2002). To extend the Ranz and Marshall (1952a) correlation to high flux conditions requires the introduction of the gas side heat transfer coefficient correction factor, β [–] presented by Bird *et al.* (1960).

$$\beta = \frac{\frac{F_{wvR} c_{p w v}}{h_g}}{\exp\left(\frac{F_{wvR} c_{p w v}}{h_g}\right) - 1} \quad (\text{A2.50})$$

where F_{wvR} is the water-vapour flux from the droplet surface [$\text{kg.m}^{-2}.\text{s}^{-1}$] and $c_{p_{wv}}$ is the specific heat capacity of water-vapour [$\text{J.kg}^{-1}.\text{°C}^{-1}$] at the boundary film temperature, T_f . This means the corrected gas side heat transfer coefficient, h_g^* [$\text{W.m}^{-2}.\text{°C}^{-1}$] takes the form:

$$h_g^* = \beta \left(\frac{\lambda_a}{d_d} \right) (2 + 0.6 Re^{1/2} Pr^{1/3}) \quad (\text{A2.51})$$

This equation is then used in Equation (A2.83).

Similarly, the gas side mass transfer coefficient can be factored out using the Sherwood number, Sh [–], which is analogous to the Nusselt number for heat transfer. The Sh number is also characterised by the kind of fluid, surface and type of flow.

$$Sh = \frac{\text{total mass transfer}}{\text{molecular mass transfer (diffusion)}} = \frac{k_g d_d}{D_v} \quad (\text{A2.52})$$

Generally accepted correlations for mass transfer from single spheres in a gas stream were first given by Frössling (1938) [as cited in Lijn (1976)] and later with slightly different coefficients by Ranz and Marshall (1952a). The correlation for the Sherwood number is also taken for an isolated sphere in a moving air stream and bears similar resemblance to the Nusselt number.

$$Sh = 2 + k_2 Re^{x_2} Sc^{y_2} \quad (\text{A2.53})$$

where the Schmidt number, Sc [–], characterises the kinematic (momentum) to mass diffusivities and takes the form:

$$Sc = \frac{\text{molecular momentum transfer (viscous)}}{\text{molecular mass transfer (diffusion)}} = \frac{\mu_a}{D_v \rho_a} \quad (\text{A2.54})$$

Again there is much debate over the value of the constants appearing in Equation (A2.53), which is most likely a result of the different experimental conditions for which the equations were developed. Rowe *et al.* (1965) [as cited in Masters (1991)] determined values of the above powers and constants for spherical droplets/particles and by comparison of data from other investigations concluded that as with the Nusselt number the widely accepted values of the Ranz-Marshall equation of $k_2 = 0.6$, $x_2 = 0.5$, $y_2 = 0.33$ should be used. These values represent the average value, since the power of the Reynolds number increases with Reynolds number from above 0.4 at $Re = -1$ to 0.6 at $Re = 104$. The value of x_2 generally accepted for evaporation conditions in spray drying is 0.5. This is applicable to a Re number range between 100 and 1000. Motion of small droplets in this range occurs only in the first fractions of a second of travel, and thus much of the evaporation occurs at droplet Re numbers far below 100.

The correlation for the Sherwood number was obtained under low mass flux conditions. When there is a large concentration gradient and hence a high surface mass flux, a correction to the gas side mass transfer coefficient is essential. The correction factor, α [–] presented by Bird *et al.* (1960) using film theory was used in this work to account for the dependence of the gas side mass transfer coefficient on mass flux.

$$\alpha = \frac{\ln \left[\frac{P_{vs}/P_T - P_v/P_T}{1 - P_{vs}/P_T} + 1 \right]}{\left[\frac{P_{vs}/P_T - P_v/P_T}{1 - P_{vs}/P_T} \right]} \quad (\text{A2.55})$$

From the Ranz and Marshall (1952a) correlation and incorporation of the correction factor α , the corrected gas side mass transfer coefficient takes the form:

$$k_g^* = \alpha \left(\frac{D_v}{d_d} \right) (2 + 0.6 Re^{1/2} Sc^{1/3}) \quad (\text{A2.56})$$

This equation is then used in Equation (A2.81).

It should be noted that in the determination of h_g^* and k_g^* for a non-stationary droplet, Re should be replaced with Re_r (Equation (A2.10)) to account for the relative velocity between the droplet and air.

A2.4 IMPLEMENTATION OF THE DROPLET DRYING MODEL

According to Lijn (1976), the solution of the coupled heat and mass transfer case of an evaporating droplet, is complicated by two key factors:

1. The differential equation describing moisture transfer is highly non-linear in character because the binary moisture diffusion coefficient over the expected range of water concentrations and temperatures varies by several orders of magnitude.
2. Boundary conditions are time and concentration dependent. This character is caused by the non-linear moisture sorption isotherms of many liquid foods and the change in water-vapour pressure with changing temperature.

For these reasons the analytical solution of the diffusion equations with boundary conditions is restricted to very simple situations. Hence, a numerical scheme was sought.

A2.4.1 Numerical solution type and computer program

According to Bronlund (1997), the most common methods available for the numerical solution of PDE's are:

- Explicit finite differences schemes.
- Implicit finite differences schemes (e.g. Lee's or Crank-Nicholson).
- Finite elements methods.

Bronlund (1997) discussed the advantages and disadvantages of each method. The explicit finite differences scheme was the preferred numerical solution for this problem due to its ease of implementation as the predictions of the dependent variables are made based on already known values.

The computer software package Matlab® 7 (The Mathworks, Inc., Natick, MA) was selected to numerically solve the formulated problem due to its availability and library of useful ODE functions to make the implementation easier.

The central differences technique was used to discretise space and is discussed in Section A2.4.2. The discretisation of time was handled by Matlab® 7 using the ODE15s solver. This solver routine is used for ‘stiff’ problems in which diffusion is often considered to fall [Frias *et al.* (2001)]. These are problems in which the solution of a differential equation contains components which change at significantly different rates for given changes in the independent variable [Lindfield and Penny (1995)]. This is the case for the binary moisture diffusion coefficient in that it can change up to 2 or 3 orders of magnitude with water concentration (which is a function of time). In order to avoid instability, a smaller time-step is usually selected to avoid large numerical error carry-over. However, this comes at the expense of computation time. ODE15s avoids this by altering the size of the time-step, which is dependent on the proximity to the solution and results in significantly improved simulation times.

A2.4.2 Definition of finite difference grid

The partial differential equations for droplet moisture content and droplet temperature were approximated using the expanded Taylor series to yield finite difference equations. The spatial central differences technique was selected over the forward and backward differences technique because of its higher degree of accuracy (i.e. truncation error $\approx \Delta x^2$). The droplet was divided into J nodes ($J-1$ control volumes), each containing the same amount of solute, $4\pi\Delta z$ [kg], as shown in Figure A2.3.

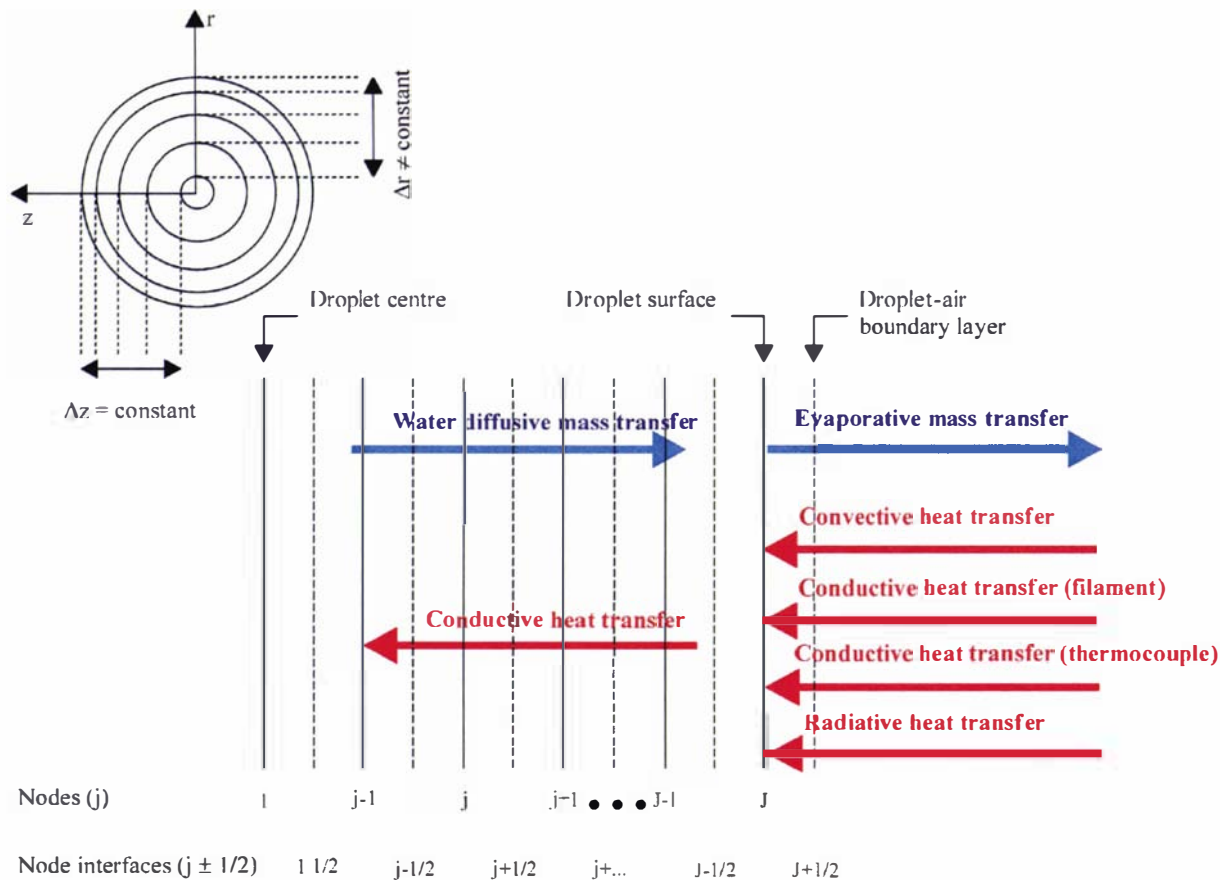


Figure A2.3: Finite difference grid for droplet drying model.

The central node is denoted node 1 rather than node 0 for indexing simplicity.

To convert between the two coordinate systems, and determine both the moisture content and temperature as a function of position and time, the transformation given by Equation (A2.3) is used. For a finite volume the mass of solute, m_s [kg], in a shell of radial thickness, Δr is:

$$m_s = 4\pi\Delta z = 4\pi C_s r^2 \Delta r \quad (\text{A2.57})$$

Upon integration of Equation (A2.3), the total mass of solute in a droplet, m_{sd} [kg], at $t = 0$ and C_s is constant throughout r , is therefore:

$$m_{sd} = 4\pi Z = 4\pi \int_0^R C_s r^2 dr = \frac{4}{3} \pi C_s R^3 \quad (\text{A2.58})$$

When $t > 0$, the solid concentration, C_s is a function of both r and t . This means that at the first time-step, $t = t_1$:

$$m_{sd} = 4\pi Z = 4\pi \int_0^{R_1} C_s(r, t) r^2 dr \quad (\text{A2.59})$$

where R_1 is the radius of the droplet radius [m] at the first time-step. Thus, while m_{sd} and Z are known, the integral is not easily calculated because both $C_s(r, t)$ and R_1 must be numerically evaluated. Hence, the radius and solids content relationship described by Equation (A2.60) was used to convert between the two coordinates systems for the internal nodes.

$$4\pi\Delta z = \frac{m_{sd}}{J-1} = \frac{4\pi}{3} C_s(r_{j+1/2}, t)(r_{j+1}^3 - r_j^3) \quad (\text{A2.60})$$

The central and surface nodal volumes contain half ($2\pi\Delta z$) the amount of solids as an internal node.

A2.4.3 Physical properties

The algebraic equations describing the diffusivity properties i.e. the binary moisture diffusion coefficient and the droplet thermal conductivity were calculated at the adjacent node interfaces ($j-1/2$ and $j+1/2$) in the solute-fixed coordinate system. This was done to better represent the transport properties across the node. These properties were calculated by taking the arithmetic average of the moisture content and temperature between each node. This was especially important in the case of the binary moisture diffusion coefficient because of its exponential relationship with moisture content. Failure to define both the moisture content and the binary moisture diffusion coefficient at the node interfaces can result in large inaccuracies, particularly close to the droplet surface where the moisture gradient is significant.

A2.4.4 Initial conditions

At time zero the droplet is assumed to have a uniform initial moisture content and temperature distribution and to have a known initial droplet velocity (i.e. exiting the atomiser).

$$u = u_i \quad \text{for } 0 < z < Z \text{ at } t = 0 \quad (\text{A2.61})$$

$$T_d = T_{di} \quad \text{for } 0 < r < R \text{ at } t = 0 \quad (\text{A2.62})$$

$$v_d = v_{di} \quad \text{at } t = 0 \quad (\text{A2.63})$$

A2.4.5 Boundary conditions

A2.4.5.1 Inner boundary conditions

A Neumann boundary condition (2nd type) was used to reflect the symmetry at the droplet centre ($j = 1$), i.e. no flow across the boundary to give a one dimensional modelling scenario for both mass and heat transfer.

$$\frac{\partial u_1}{\partial z} = 0 \quad \text{for } t > 0 \text{ at } z = 0 \quad (\text{A2.64})$$

$$\frac{\partial T_1}{\partial r} = 0 \quad \text{for } t > 0 \text{ at } r = 0 \quad (\text{A2.65})$$

where u_1 and T_1 are the droplet moisture content [(kg water).(kg⁻¹ dry solid)] and the droplet temperature [°C] at the central node.

A2.4.5.2 Outer boundary conditions

A Robbins (3rd type) boundary condition was used to describe both mass and enthalpy conservation at the droplet surface given by Equations (A2.66) and (A2.67) respectively.

$$D_{ws}(u_s, T_s) C_{ss}^2 R^2 \frac{\partial u}{\partial z} = -F_{wvR} \quad \text{for } t > 0 \text{ at } z = Z \quad (\text{A2.66})$$

where $D_{ws}(u_s, T_s)$, u_s , T_s , C_{ss} , R and F_{wvR} are the binary moisture diffusion coefficient at the droplet surface [$\text{m}^2.\text{s}^{-1}$], the surface moisture content [(kg water).(kg⁻¹ dry solid)], the surface temperature [°C], the surface solids concentration [(kg water).(m⁻³ of droplet)], the droplet radius [m] and the water-vapour flux from the droplet surface [$\text{kg}.\text{m}^{-2}.\text{s}^{-1}$] respectively.

$$\lambda_{ds} \frac{dT_s}{dr} + \Delta H_v F_{wvR} = -h_g^*(T_a - T_s) \quad \text{for } t > 0 \text{ at } r = R \quad (\text{A2.67})$$

where λ_{ds} , ΔH_v , h_g^* and T_a are the thermal conductivity at the droplet surface [$\text{W}.\text{m}^{-1}.\text{°C}^{-1}$], the latent heat of water vaporisation [$\text{J}.\text{kg}^{-1}$], the corrected gas side heat transfer coefficient [$\text{W}.\text{m}^{-2}.\text{°C}^{-1}$] and the air temperature [°C] respectively.

Equations (A2.66) and (A2.67) were numerically approximated with ODE's which are derived in the following two sections. The error from the approximation of the surface having a finite volume decreases as the nodal volume decreases. Numerical error checks were made in Section A2.5.5 to establish an acceptable level of numerical error in the predicted surface conditions.

A2.4.5.3 ODE for surface moisture content

A moisture balance around the surface control volume (shell) of an evaporating droplet can be written as:

$$\left[\begin{array}{l} \text{Rate of accumulation of} \\ \text{moisture in the droplet} \\ \text{surface shell volume} \end{array} \right] = \left[\begin{array}{l} \text{Rate of moisture inflow} \\ \text{from the inside shell surface} \\ \text{of droplet by diffusion} \end{array} \right] - \left[\begin{array}{l} \text{Rate of moisture outflow} \\ \text{from the outside shell} \\ \text{surface by evaporation} \end{array} \right] \quad (\text{A2.68})$$

Mathematical conversion of the word balance yields Equation (A2.69).

$$\frac{dm_{ws}}{dt} = \underbrace{D_{ws,i} A_c \frac{dC_w}{dr}}_{\text{Internal moisture diffusion}} - \underbrace{F_{wvR} A_d}_{\text{Evaporation and water-vapour diffusion}} \quad (\text{A2.69})$$

where m_{ws} , t , $D_{ws,i}$, A_c , C_w , r , F_{wvR} and A_d are the mass of water in droplet shell surface [kg], time [s], binary moisture diffusion coefficient at the inside surface of the shell [$\text{m}^2 \cdot \text{s}^{-1}$], the area through which water diffuses (inside surface of the shell) [m^2], the moisture content [(kg water).(m^{-3} of droplet)], the droplet radial position through which water is transported [m], the water-vapour flux from the droplet surface [$\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$] and the droplet surface area [m^2] respectively. Equation (A2.69) is described by the finite difference approximation in solute-fixed coordinates by Equation (A2.92).

Because no assumption on the rate controlling mechanism is made, the simplifying assumption that the droplet surface is in equilibrium with the bulk air conditions is not made. Audu and Jeffreys (1975) observed that the larger proportion of resistance to mass transfer in small solute containing droplets was in the gas film. Hence, the mass transport of water-vapour from the droplet surface through the droplet surface–boundary layer to the bulk air must be considered. The rate of moisture removed as water-vapour from the droplet surface can be derived by considering a second shell balance around the droplet surface and the stagnant air boundary layer through which the moisture diffuses to the well mixed surrounding air. This can be written as:

$$\left[\begin{array}{l} \text{Rate of accumulation} \\ \text{of moisture in the} \\ \text{droplet-air boundary} \\ \text{layer surface shell volume} \end{array} \right] = \left[\begin{array}{l} \text{Rate of moisture inflow} \\ \text{from the surface by} \\ \text{evaporation} \end{array} \right] - \left[\begin{array}{l} \text{Rate of moisture outflow} \\ \text{from the boundary layer} \\ \text{to the bulk air by diffusion} \end{array} \right] \quad (\text{A2.70})$$

Conversion to mathematical form gives:

$$R_{wv} = 4\pi r^2 F_{wv} \Big|_r - 4\pi r^2 F_{wv} \Big|_{r+\Delta r} \quad (\text{A2.71})$$

where R_{wv} , r , F_{wv} , and Δr are the rate of water-vapour transfer [$\text{moles} \cdot \text{s}^{-1}$], the radial position of the shrinking droplet [m], the water-vapour flux [$\text{moles} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$] and a small increment in distance along the radial dimension to the stagnant air boundary layer [m]. To find the flux through the stagnant air boundary layer, steady-state conditions are assumed (i.e. no moisture

accumulation in the stagnant air boundary layer). Dividing through by $4\pi\Delta r$ and taking the limit as Δr approaches zero gives:

$$\left\{ \lim_{\Delta r \rightarrow 0} \frac{r^2 F_{wv} \Big|_r - r^2 F_{wv} \Big|_{r+\Delta r}}{\Delta r} \right\} = 0 \quad (\text{A2.72})$$

The expression in Equation (A2.72) is the first derivative of $r^2 F_{wv}$ with respect to Δr , which is also given by:

$$\frac{d(-r^2 F_{wv})}{dr} = 0 \quad (\text{A2.73})$$

Integration, with respect to r , of this first order differential equation for water-vapour flux, F_{wvr} , yields:

$$-r^2 F_{wvr} = C_1 \quad (\text{A2.74})$$

Hence, the water-vapour flux, F_{wvr} , can be rewritten as:

$$F_{wvr} = -\frac{C_1}{r^2} \quad (\text{A2.75})$$

The flux is inversely proportional to the square of the radius but the value of the integration constant, C_1 [moles.s⁻¹] is not known. However, the water-vapour flux through the boundary layer can also be described by molecular diffusion of a gas (water-vapour) in a gas (air) by Equation (A2.76) taken from Incropera and DeWitt (1981a).

$$F_{wvr} = -CD_v \frac{dx_{wvr}}{dr} + x_{wvr}(F_{wvr} + F_{ar}) \quad (\text{A2.76})$$

where F_{wvr} , C , D_v , x_{wvr} , r and F_{ar} are the water-vapour flux [mole.m⁻².s⁻¹], the total molar concentration of gas (water-vapour and air) [(moles of gas).(m⁻³ of gas)], the diffusivity of water-vapour in air [m².s⁻¹], the mole fraction of water-vapour [(moles water-vapour).(total⁻¹ moles of gas)], the radial position from the surface to the edge of the boundary layer [m] and the flux of air through the air–water-vapour system [moles.m⁻².s⁻¹]. The subscript r , refers to the values being dependent on the radial position from the surface to the edge of the boundary layer. Using a unimolal, unidirectional mass diffusivity case (i.e. air flux through the interface is negligible or essentially stationary compared to the water-vapour flux) as outlined in Skelland (1974), F_{ar} reduces to zero and Equation (A2.76) simplifies to:

$$F_{wvr} = -\frac{CD_v}{(1-x_{wvr})} \frac{dx_{wvr}}{dr} \quad (\text{A2.77})$$

At steady-state, Equation (A2.77) is balanced with Equation (A2.75) and separation of variables followed by integration from the droplet surface to the radial boundary layer (i.e. at $r = r_s$, $x_{wvr} = x_{wvs}$ and $r = r_b$, $x_{wvr} = x_{wvb}$) to give:

$$CD_s \ln \left(\frac{(1-x_{vvb})}{(1-x_{vvs})} \right) = C_1 \left(\frac{1}{r_s} - \frac{1}{r_b} \right) \quad (\text{A2.78})$$

Rearrangement of Equation (A2.78) yields an expression for C_1 , which is then substituted back into Equation (A2.75) to give:

$$F_{wvR} = -\frac{1}{r^2} \frac{CD_v}{\left(\frac{1}{r_s} - \frac{1}{r_b} \right)} \ln \left(\frac{(1-x_{vvb})}{(1-x_{vvs})} \right) \quad (\text{A2.79})$$

Equation (A2.79) is now of the form of various researchers [Downing (1966); Lijn (1976); Incropera and DeWitt (1981a); Sano and Keey (1982); Coumans (1987); Adhikari (2002)] having a logarithmic water-vapour concentration driving force. Assuming $r_s \ll r_b$, (made by Skelland (1974)), evaluating $r = r_s = R$, conversion of mole fractions to pressures and substitution of the ideal gas law for C gives:

$$F_{wvR} = \frac{1}{R} \frac{1}{R_g} \frac{P_T D_v}{(T_f + 273.15)} \ln \left(\frac{1 - P_v / P_T}{1 - P_{vs} / P_T} \right) \quad (\text{A2.80})$$

The negative sign is dropped as it refers only to the direction of mass transfer, i.e. a mass loss from the droplet. F_{wvR} , R , R_g , T_f , P_T , P_v and P_{vs} are the water-vapour flux at the droplet surface [moles.m⁻².s⁻¹], the droplet radius [m], the universal gas constant [8.314 J.mole⁻¹.K⁻¹], the film temperature (arithmetic average of T_s and T_a) [°C], the total system air pressure [101 325 Pa], the water-vapour partial pressure at the dry bulb air temperature [Pa] and the saturated water-vapour pressure at the droplet surface temperature [Pa]. The gas side mass transfer coefficient can be defined as $k_g = D_v/R$ [m.s⁻¹] to yield Equation (A2.81). To extend to high mass flux conditions k_g is replaced by $k_g^* = \alpha.k_g$.

$$F_{wvR} = \frac{k_g^*}{1000} \frac{M_w}{R_g} \frac{P_T}{(T_f + 273.15)} \ln \left(\frac{1 - P_v / P_T}{1 - a_w P_{vs} / P_T} \right) \quad (\text{A2.81})$$

where the flux, F_{wvR} has units of [kg.m⁻².s⁻¹] and M_w is the molecular mass of water [18 g.mole⁻¹]. Realising the diminished water-vapour pressure at the surface resulting from the presence of solute at the surface, the water activity coefficient, $a_w = f(C_{ws}, T_s)$ [-], is substituted into Equation (A2.81). This is incorporated into the solution scheme through the appropriate moisture sorption isotherm (Section A2.3.6.5).

A2.4.5.4 ODE for surface temperature

An enthalpy balance around the surface control volume (shell) of an evaporating droplet can be written as:

$$\begin{aligned}
 \left[\begin{array}{l} \text{Rate of accumulation} \\ \text{of heat in the droplet} \\ \text{surface shell volume} \end{array} \right] &= \left[\begin{array}{l} \text{Rate of heat inflow from} \\ \text{drying air by convection} \end{array} \right] + \left[\begin{array}{l} \text{Rate of heat inflow} \\ \text{from external sources} \end{array} \right] - \\
 &\quad \left[\begin{array}{l} \text{Rate of heat outflow to} \\ \text{droplet centre by} \\ \text{conduction} \end{array} \right] - \left[\begin{array}{l} \text{Rate of heat outflow} \\ \text{by evaporative cooling} \end{array} \right]
 \end{aligned}
 \tag{A2.82}$$

Mathematical conversion of the word balance yields Equation (A2.83).

$$\underbrace{m_{ds} c_{pds} \frac{dT_s}{dt}}_{\text{Surface shell}} = \underbrace{h_g^* A_d (T_a - T_s)}_{\text{Convection}} + \underbrace{\dot{Q}_{\text{filament}} + \dot{Q}_{\text{thermocouple}} + \dot{Q}_{\text{radiation}}}_{\text{External heat sources}} - \underbrace{\lambda_{dsi} A_c \frac{dT_{si}}{dr}}_{\text{Conduction}} \bigg|_{\text{internal interface}} - \underbrace{A_d F_{wvR} \Delta H_v}_{\text{Evaporation}}
 \tag{A2.83}$$

where m_{ds} , c_{pds} , t , T_s , h_g^* , A_d , T_a , λ_{dsi} , A_c , T_{si} , r , ΔH_v and $m_{w,s}$ are the droplet surface shell total mass [kg droplet], the specific heat capacity of the droplet surface shell [$\text{J.kg}^{-1}.\text{°C}^{-1}$], time [s], the droplet surface temperature [°C], the corrected gas side heat transfer coefficient [$\text{W.m}^{-2}.\text{°C}^{-1}$], the droplet surface area [m^2], the air temperature [°C], the thermal conductivity at the inside surface of the shell [$\text{W.m}^{-1}.\text{°C}^{-1}$], the area of conductive heat transfer (inside surface of the shell) [m^2], the droplet temperature at the inside surface of the shell [°C], the droplet radial position [m], the latent heat of water vaporisation [J.kg^{-1}] and the water-vapour flux from the droplet surface [$\text{kg.m}^{-2}.\text{s}^{-1}$] respectively.

The term representing conduction in Equation (A2.83) is described by the finite difference approximation in spatial coordinates by Equation (A2.93).

Three external heat sources, $\dot{Q}_{\text{filament}}$ [W], $\dot{Q}_{\text{thermocouple}}$ [W] and $\dot{Q}_{\text{radiation}}$ [W] require inclusion when verifying the model with the experimental data collected due to the by experimental set-up. The $\dot{Q}$ quantities are incorporated into the heat transfer equation separately so they can be turned on and off in the model to validate experimental data or to simulate an industrial-scale spray droplet drying process. The single droplet drying experiments had the droplet suspended from a glass filament. The heat conducted through the filament was accounted for by considering the one-dimensional heat transfer through a fin of constant cross-sectional area [Incropera and DeWitt (1981b)] described by Equation (A2.84). The filament had a tapered cross-sectional diameter (0.4 mm down to 0.2 mm). For model predictions, the filament diameter was taken to be the volume weighted diameter which was 0.31 mm.

$$\dot{Q}_{\text{filament}} = 0.5\pi d_f \sqrt{h_g d_f \lambda_f} (T_a - T_s)
 \tag{A2.84}$$

where d_f is the glass filament diameter [m] and λ_f is the glass filament thermal conductivity [$1.14 \text{ W.m}^{-1}.\text{°C}^{-1}$]. The h_g for the $\dot{Q}_{\text{filament}}$ term applies to the filament not the droplet, which will be geometry and flow dependent. Since this is unknown and not likely to be significantly different to that of the droplet [Trommelen and Crosby (1970)], the uncorrected h_g determined

for droplet evaporation from Ranz and Marshall (1952a) correlation was used in the calculation of $\dot{Q}_{filament}$.

Regarding the temperature history in the single droplet drying experiments a 70 μm diameter K-type thermocouple wire entered from the bottom of the suspended droplet with the bulb sitting in the droplet centre. Thus, the model has to be run twice when validating predictions against experimental data, once to validate against the mass transfer histories and again to account for the heat contribution from the thermocouple wire when validating the temperature histories. This heat source was also modelled by assuming it behaves as a one-dimensional fin. Hence, Equation (A2.84) was employed again but the equation was multiplied by a factor of 2 because two wires make up the thermocouple. The thermal conductivity was calculated based on the mass weighted average thermal conductivities of the K-type thermocouple wires; Chromega® (90% Ni, 10% Cr) and Alomega® (95% Ni, 2% Mn, 2% Al, 1% Si) to give a thermal conductivity of $91.7 \text{ W.m}^{-1}.\text{C}^{-1}$.

The third heat source, $\dot{Q}_{radiation}$ is that supplied by environmental radiation to the droplet and is given by:

$$\dot{Q}_{radiation} = \varepsilon_{enviro} A_d \sigma_{sb} F_{12} (T_{wall}^4 - T_s^4) \quad (\text{A2.85})$$

where T_{wall} is the drying chamber wall temperature which is taken to be the air temperature, $T_a [\text{K}]$. T_s is also in K. The environmental emissivity, $\varepsilon_{enviro} [-]$ accounts for the difference in radiation between a black body and another material. The emissivity for foodstuffs can be assumed between 0.8–0.9 [Räderer (2001)]. A value of 0.95 was taken for environmental radiation (inside of the glass insulated drying chamber) to the droplet. σ_{sb} is the Stefan-Boltzmann constant [$5.669 \times 10^{-8} \text{ W.m}^{-2}.\text{K}^{-4}$]. A droplet–environment view factor, $F_{12} [-]$, of 0.95 was used [Trommelen and Crosby (1970)].

A2.4.6 Internal nodes ($2 < j < J-1$)

Figure A2.4 presents the finite difference grid for an internal node calculation ($2 < j < J-1$).

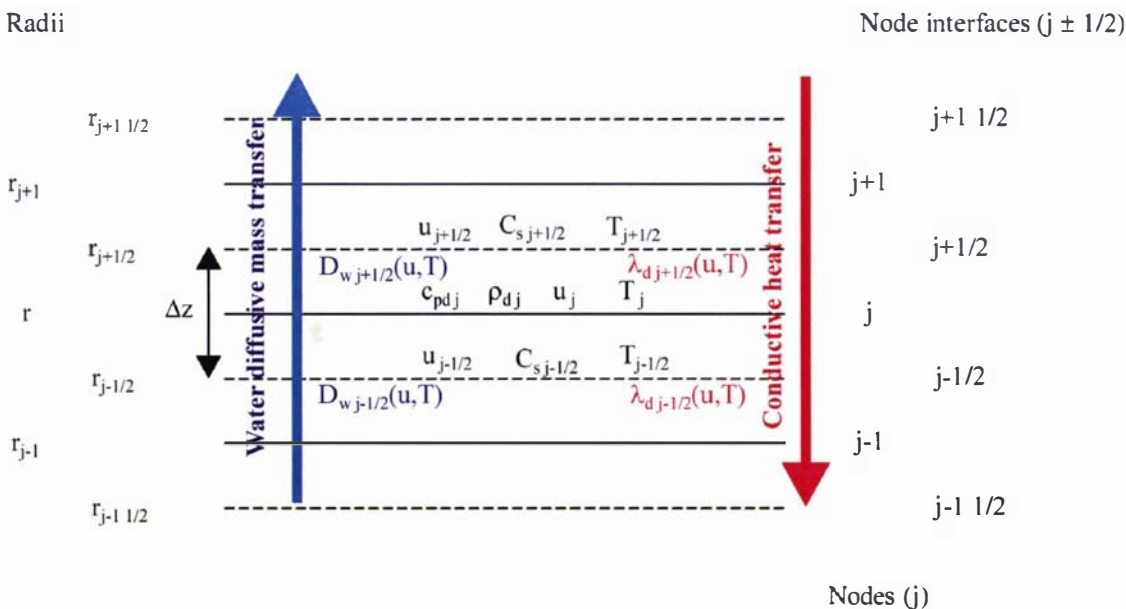


Figure A2.4: Finite difference grid for an internal node calculation ($2 < j < J-1$).

Conversion of Equation (A2.4), describing the change in moisture content with time of an internal node to the finite difference numerical approximation yields:

$$\frac{du_j}{dt} = \left(\frac{1}{\Delta z^2} \right) \left(D_{w,j-1/2} C_s^2{}_{j-1/2} r^4{}_{j-1/2} (u_{j-1} - u_j) - D_{w,j+1/2} C_s^2{}_{j+1/2} r^4{}_{j+1/2} (u_j - u_{j+1}) \right) \quad (\text{A2.86})$$

Similarly for Equation (A2.5), the finite difference approximation for the change in temperature with time of an internal node is:

$$\frac{dT_j}{dt} = \left(\frac{1}{V_{tj} \rho_d c_{pdj}} \right) \left(A_{d,j+1/2} \lambda_{d,j+1/2} \frac{T_{j+1} - T_j}{r_{j+1} - r_j} - A_{d,j-1/2} \lambda_{d,j-1/2} \frac{T_j - T_{j-1}}{r_j - r_{j-1}} \right) \quad (\text{A2.87})$$

The droplet thermal conductivity, λ_d , is evaluated at the node interfaces ($j-1/2$ and $j+1/2$), whereas the droplet density, ρ_d , and specific heat capacity, c_{pd} , are evaluated at the nodes (j). The volume of the node, V_{tj} [m^3], is given by Equation (A2.88).

$$V_{tj} = \frac{4}{3} \pi (r_{j+1/2}^3 - r_{j-1/2}^3) \quad (\text{A2.88})$$

A2.4.7 Central boundary node ($j = 1$)

Figure A2.5 presents the FD grid for a central node calculation.

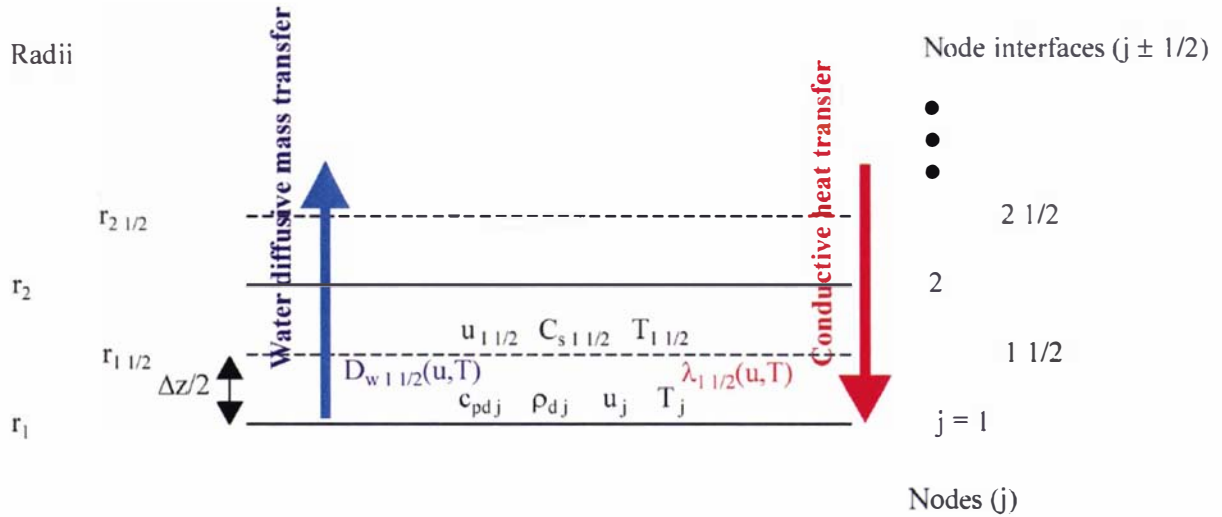


Figure A2.5: Finite difference grid for a central node calculation ($j = 1$).

The ODE for the change in droplet moisture content with time at the central node is given by:

$$\frac{du_1}{dt} = - \left(\frac{2}{\Delta z^2} \right) \left(D_{j+1/2} C_s^2{}_{j+1/2} r^4{}_{j+1/2} (u_1 - u_2) \right) \quad (\text{A2.89})$$

A factor of 2 is required to account for the fact that this control volume is half the volume of an internal shell. The ODE for the change in droplet temperature with time at the central node is given by:

$$\frac{dT_1}{dt} = \left(\frac{1}{V_{t1} \rho_{d1} c_{pd1}} \right) \left(A_{dj+1/2} \lambda_{dj+1/2} \frac{T_2 - T_1}{r_2 - r_1} \right) \quad (\text{A2.90})$$

where $V_{t1} [\text{m}^3]$ is the central node volume given by Equation (A2.91).

$$V_{t1} = \frac{4}{3} \pi (r_{j+1/2}^3 - 0^3) \quad (\text{A2.91})$$

A2.4.8 Surface boundary node ($j = J$)

Figure A2.6 presents the finite difference grid for the surface node calculation.

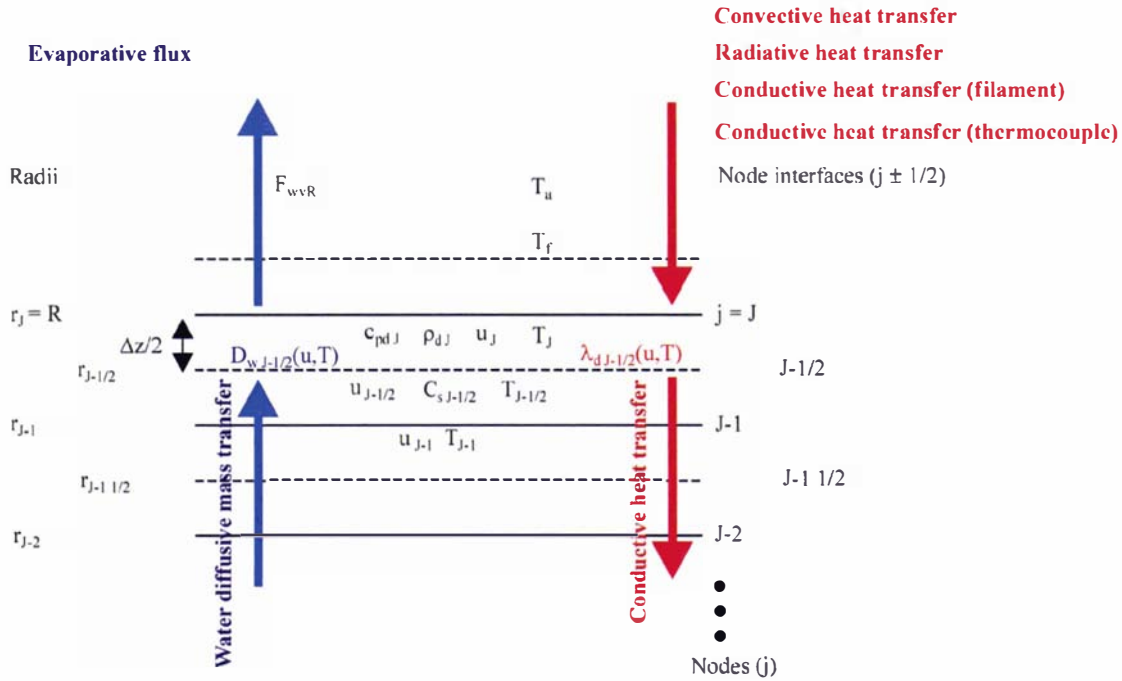


Figure A2.6: Finite difference grid for the surface node calculation ($j = J$).

The ODE for the change in droplet moisture content with time at the surface node is given by:

$$\frac{du_J}{dt} = \left(\frac{2}{\Delta z^2} \right) \left(D_{wJ-1/2} C_{sJ-1/2}^2 r_{J-1/2}^4 (u_{J-1} - u_J) \right) - \frac{2F_{wvR} A_d}{4\pi \Delta z} \quad (\text{A2.92})$$

A factor of 2 is required to account for the fact that the control volume at the surface is half the volume of an internal shell. The ODE for the change in droplet temperature with time at the surface node is given by:

$$\frac{dT_J}{dt} = \left(\frac{1}{V_{tJ} c_{pdJ} \rho_{dJ}} \right) \left[h_g^* A_d (T_a - T_J) - A_d F_{wvR} \Delta H_v + \dot{Q}_{radiation} + \dot{Q}_{filament} + \dot{Q}_{thermocouple} - \left(A_{dJ-1/2} \lambda_{dJ-1/2} \frac{T_J - T_{J-1}}{r_J - r_{J-1}} \right) \right] \quad (\text{A2.93})$$

where $V_{tJ} [\text{m}^3]$ is the surface node volume given by Equation (A2.94).

$$V_{t,j} = \frac{4}{3} \pi (r_j^3 - r_{j-1/2}^3) \quad (\text{A2.94})$$

A2.4.9 Numerical solution procedure

The numerical solution procedure is schematically represented in Figure A2.7.

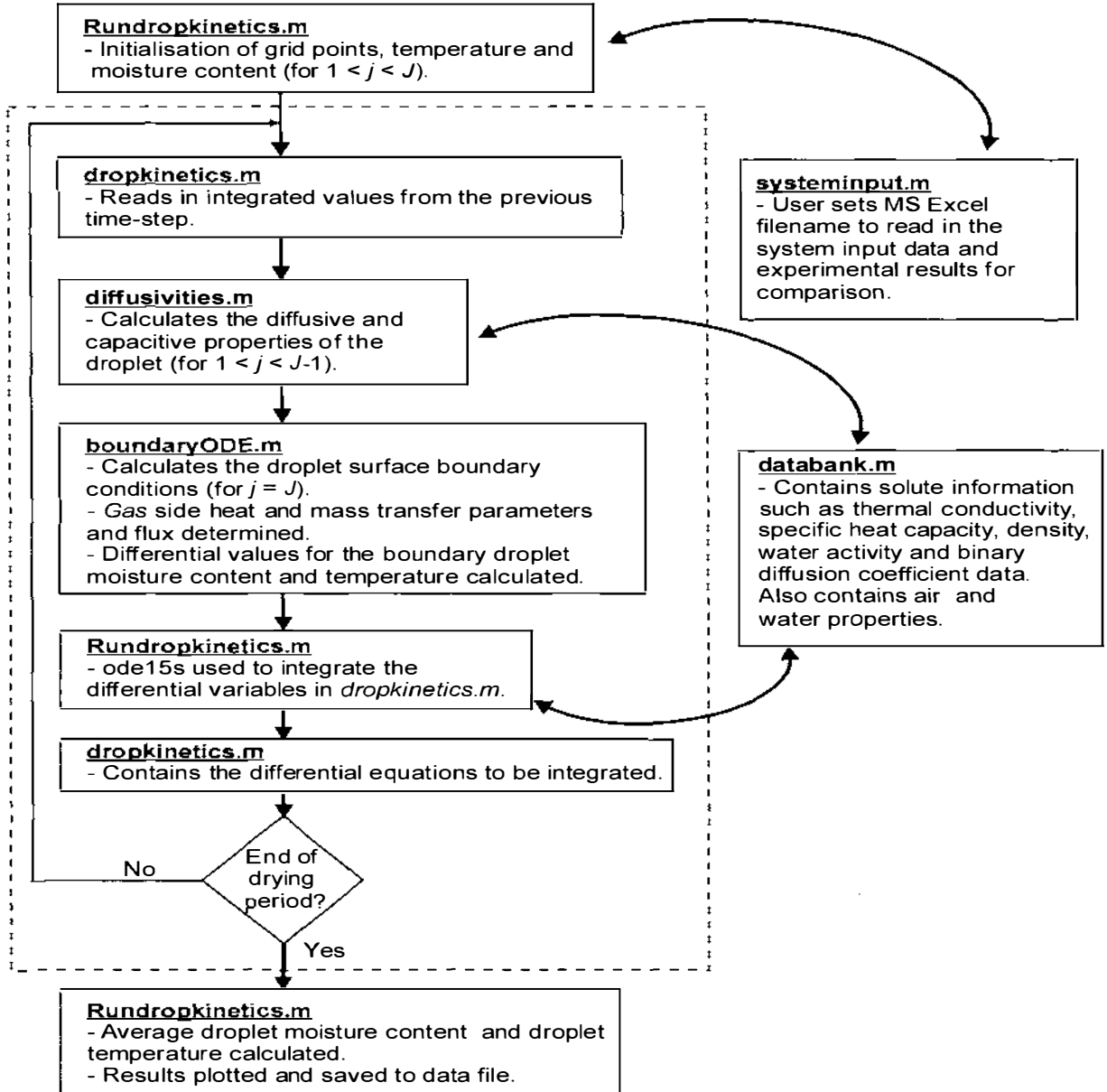


Figure A2.7: Program flow chart for single droplet drying mathematical model predictions.

The program flow chart consists of five function files and a script/driver file ('Rundropkinetics.m'). Two additional function files, 'analytical.m' and 'SphereBm.m' are also included (but not shown) that can be run to analytically validate simplified simulations.

A2.5 MATHEMATICAL MODEL EVALUATION

A2.5.1 Maths checking

Maths checking is an essential element of any mathematical modelling exercise. The maths checking of existing single droplet drying mathematical models has not been reported in the literature. Maths checking was undertaken to ensure that the numerically implemented model was that which was actually formulated. This is usually done by comparison with existing solutions which have already been validated. Although numerical solutions already exist for single droplet drying models, actual programs are rarely given in the literature, only the results of the simulations are presented. In addition, no models exist based on the effective diffusion model that also incorporates temperature discretisation, so a direct comparison could not be made. Instead, the model was simplified to see if it predicted commonly available analytical solutions for simplified situations. This involved ‘turning off’ (essentially setting to zero) part of the model to factor it out and set conditions such that the simplifying assumptions of the analytical solution are met. In these cases, two additional Matlab® function files ‘analytical.m’ and ‘SphereBm.m’ were used to generate the analytical solutions. In all cases, the full numerical model was run with the average data values contained in Table A2.2.

A2.5.2 Internal and external heat transfer side numerical check with analytical solution

The internal temperature history prediction was validated against a simplified analytical solution for heat transfer in a sphere under a third-type boundary condition. Being a third-type boundary condition the analytical solution simultaneously tested the validity of the internal and external heat transfer sides of the model. The analytical solution was that given in Cleland (2004). The fractional accomplished temperature change (LHS) was equated with the mathematical series (RHS) in Equation (A2.95) from which the internal droplet temperature, T_j [°C] at the internal nodes ($2 < j < J-1$) can be calculated.

$$\frac{T_j - T_{di}}{T_a - T_{di}} = \sum_{m=1}^{\infty} 2Bi_h \frac{R}{r} \frac{\beta_m^2 + (Bi_h - 1)^2}{\beta_m^2(\beta_m^2 + (Bi_h - 1)Bi_h)} \sin(\beta_m) \sin(\beta_m \frac{r}{R}) \exp(-\beta_m^2 Fo) \quad (A2.95)$$

where T_j , T_a , T_{di} , m , R , and r are the droplet temperature [°C] at position, r , the air temperature [°C], the initial droplet temperature [°C], the number of roots calculated in Equation (A2.97), the droplet radius [m] and the radial position inside the droplet [m] respectively. For the surface position, T_j , a value of $r/R = 1$ is used. For the central position, T_1 , a value of $r/R = 1/100 * \Delta r_1$ was used because the equation has no solution at $r/R = 0$.

The Biot number for heat transfer, Bi_h [–] was that given by Equation (5.1). The Fourier number, Fo [–] for heat transfer is defined by Equation (A2.96).

$$Fo = \frac{t \lambda_d}{c_{pd} R^2} \quad (A2.96)$$

where t , λ_d , and c_{pd} are time [s], the droplet thermal conductivity [$W.m^{-1}.^{\circ}C^{-1}$] and the droplet specific heat capacity [$J.kg^{-1}.^{\circ}C^{-1}$] respectively. The β_m values are the roots of Equation (A2.97) generated by the function file ‘SphereBm.m’.

$$\beta_m \cot \beta_m + (Bi_h - 1) = 0 \quad (\text{A2.97})$$

For the predictions the number of significant terms, $m = 50$ gave acceptable results (i.e. $m_{50} \gg m_{51}$). The mass averaged droplet temperature, T_{dav} [°C] was calculated with Equation (A2.98) [Cleland (2004)].

$$\frac{T_{dav} - T_{di}}{T_a - T_{di}} = \sum_{m=1}^{\infty} Bi_h \frac{6Bi_h^2}{\beta_m^2(\beta_m^2 + (Bi_h - 1)Bi_h)} \exp(-\beta_m^2 Fo) \quad (\text{A2.98})$$

A number of simplifying assumptions were required to develop the analytical solution for temperature. These assumptions were incorporated into the numerical model predictions by setting various parameters to values that would satisfy these assumptions. The assumptions and the corresponding method used to meet the assumptions for the numerical predictions are described below.

To meet the conditions specified by the third-type boundary required ‘turning off’ the internal mass diffusion side of the model. The following changes to the program were made. To meet the specification of a non-shrinking system, the flux was set to zero by setting the ODE for the surface moisture content (du/dt) to zero. This ensured that there was no driving force for moisture loss, keeping the droplet mass, droplet density and droplet radius constant. Heat transfer by convection only, meant that the $\dot{Q}$ quantities (radiation, thermocouple conduction, filament conduction) were set to zero. The term representing evaporation in Equation (A2.93) was also set to zero. The values of the other parameters set to be constants for the simulation were: $h_g^* = 65 \text{ W.m}^{-2}.\text{°C}^{-1}$ to give constant convection coefficient; $c_{pd} = 3012 \text{ J.kg}^{-1}.\text{°C}^{-1}$ to give constant thermal diffusion properties; $\lambda_d = 0.5513 \text{ W.m}^{-1}.\text{°C}^{-1}$ to give constant thermal diffusion properties; $\rho_d = 998.5 \text{ kg.m}^{-3}$ to give both constant thermal diffusion properties and a constant droplet radius. These values were all calculated at the initial system input conditions given in Table A2.2.

Figure A2.8 compares the numerical model predictions with the analytical solution for the third-type heat transfer boundary condition. J was set to 100.

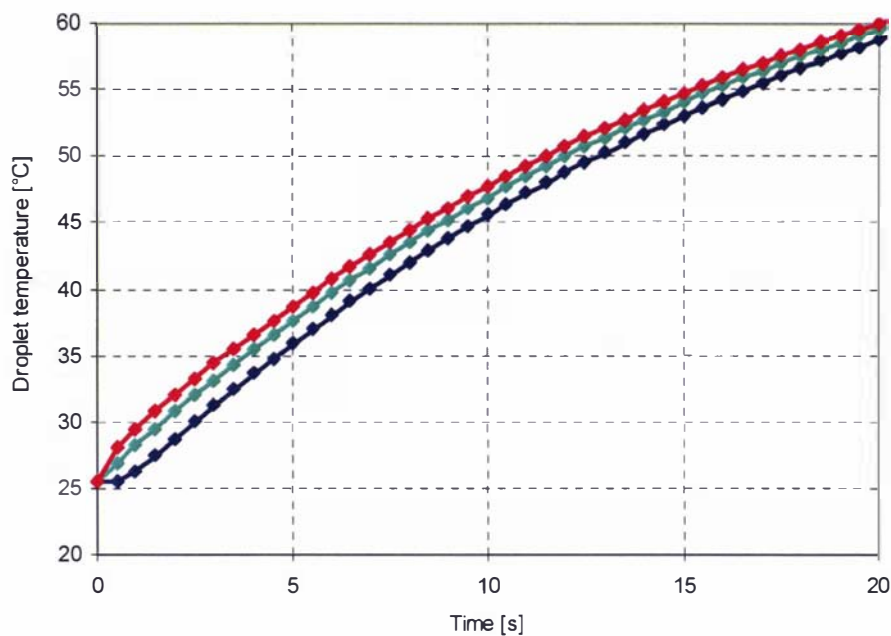


Figure A2.8: Comparison of the numerical model predictions with the analytical solution for the centre, mass average and surface temperatures of a 2.4 mm diameter droplet of 40% w/w maltodextrin DE5 drying under a heat transfer third-type boundary condition. Temperatures: — numerical centre; — numerical average; — numerical surface; ♦ analytical centre; ♦ analytical average; ♦ analytical surface.

The simplified analytical solutions fall on the numerical predictions indicating that the formulated mathematical model for internal thermal diffusion and external heat transfer was correctly implemented. Both the numerical and analytical predictions show that over the first 20 s of drying, a 2.5 °C temperature gradient exists across the droplet which is contrary to the simplifying assumption of constant internal droplet temperature gradient made by previous researchers. However, these results are only applicable to the assumptions made here and the non-shrinking droplet assumption would not be valid in a real drying situation.

A2.5.3 Internal moisture diffusion side numerical check with analytical solution

Analytical solutions of the diffusion equation with a constant binary moisture diffusion coefficient for numerous initial and boundary conditions are available [Crank (1956); Carslaw and Jaeger (1959)]. However, for a shrinking sphere no general solutions are available [van der Lijn (1976)]. A third-type boundary condition is not trivial to formulate because of the difficulty in developing a mass transfer Biot number using consistent units. As a result, a simple first-type boundary condition was enforced and the model predictions validated against the simplified analytical solution.

For a drying sphere of constant radius, assuming uniform initial moisture distribution, negligible external resistance to moisture transfer, constant surface moisture content, constant binary moisture diffusion coefficient, unidirectional moisture movement (centre to surface) and isothermal process conditions, Equation (A2.1) has been solved analytically [e.g. Cleland (2004)]. The fractional accomplished moisture content change (LHS) is equated with the mathematical series (RHS) in Equations (A2.99), (A2.100) and (A2.101) from which the centre, internal and average droplet moisture contents can be calculated respectively.

$$\frac{C_{wc} - C_{wi}}{C_{wa} - C_{wi}} = \sum_{m=1}^{\infty} 2(-1)^{(m-1)} \exp(-m^2 \pi^2 Fo) \quad (A2.99)$$

where C_{wc} is the moisture content at the centre node ($j = 1$) [(kg water).(m⁻³ droplet)]. C_{wi} and C_{wa} are the droplet initial moisture content and the droplet surface concentration in equilibrium with the ambient surroundings both in (kg water).(m⁻³ droplet).

$$\frac{C_{wj} - C_{wi}}{C_{wa} - C_{wi}} = \sum_{m=1}^{\infty} \frac{2}{\pi} \frac{R}{r} \left(\frac{-1}{m}\right)^{(m-1)} \sin(m\pi \frac{r}{R}) \exp(-m^2 \pi^2 Fo) \quad (A2.100)$$

where C_{wj} is the moisture content at nodes ($2 < j < J-1$) [(kg water).(m⁻³ droplet)].

$$\frac{C_{w,av} - C_{wi}}{C_{wa} - C_{wi}} = \sum_{m=1}^{\infty} \frac{6}{\pi^2} \frac{1}{m^2} \exp(-m^2 \pi^2 Fo) \quad (A2.101)$$

where $C_{w,av}$ is the droplet mass average moisture content [(kg water).(m⁻³ droplet)]. In all cases the analytical solution was solved in terms of C_{wj} and converted to u_j knowing the values of V_j and $m_{s,j}$.

The Fourier number, Fo [–] for mass transfer is given by Equation (A2.102).

$$Fo = \frac{D_w t}{R^2} \quad (A2.102)$$

To meet the first-type boundary conditions required ‘turning off’ the internal thermal diffusion side of the model. The following changes were made to the program. To ensure negligible external mass transfer resistance k_g^* can be set to a high number (99 999 m.s⁻¹). However, the ODE15s solver was unable to meet the tolerances with the minimum allowable time-step because of the very steep slope calculated by the surface moisture content ODE. To get around this, a constant surface moisture content was set by determining the surface moisture content at $t \rightarrow \infty$ (i.e. when $T_{d,J} = T_a$). This gave an imaginary boundary layer moisture content (at $J+1/2$) of $u_J = 0.0055$ (kg water).(kg⁻¹ dry solid). The numerical value u_J had the equivalent analytical value of C_{wa} . The values of the other parameters set to be constants for the simulation were: $D_w = 1.55 \times 10^{-10}$ m².s⁻¹ to give constant mass diffusion properties. The density could not be set constant because it changes as moisture is lost from the droplet. However, as the droplet radius and hence volume of each shell must remain constant for the numerical and analytical solutions to be compared, the density was allowed to change by re-calculating the mass of water at each time-step but holding the volume of each shell constant. The internal temperature side was factored out by setting the surface ODE ($dT_{d,J}/dt$) to zero and the initial droplet temperature, T_{di} to T_a .

Figure A2.9 compares the numerical model predictions with the analytical solution for a mass transfer first-type boundary condition. J was set to 100.

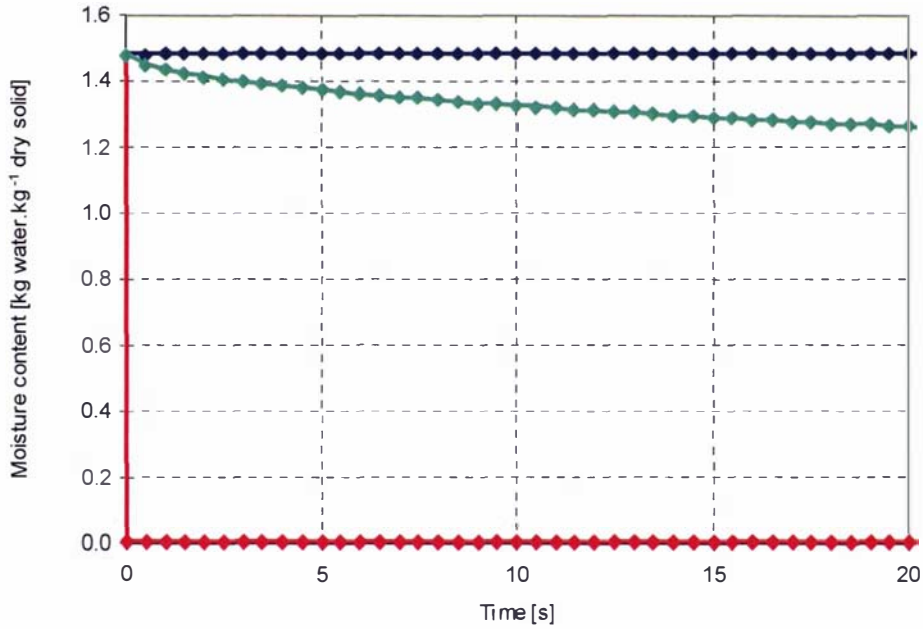


Figure A2.9: Comparison of the numerical model predictions with the analytical solution for the centre, mass average and surface temperatures of a 2.4 mm diameter droplet of 40% w/w maltodextrin DE5 drying under a mass transfer first-type boundary condition. Moisture contents: — numerical centre; — numerical average; — numerical surface; ♦ analytical centre; ♦ analytical average; ♦ analytical surface.

The simplified analytical solutions fall on the numerical predictions suggesting that the formulated mathematical model for internal moisture diffusion was correctly implemented. There is a significant droplet internal moisture content gradient over the entire drying time, which is in agreement with the numerous researchers who discretised droplet moisture content in their mathematical models.

A2.5.4 External mass transfer and volume contraction check with analytical solution

The simplified analytical solutions were developed using a constant volume assumption (i.e. fixed radius). To ensure external mass transfer flux and volume contraction was implemented correctly, an analytical solution for droplet radius (Equation (A2.103)) was derived. The following changes were made to the program. The assumption of constant thermal properties was made by setting the initial droplet temperature to the air temperature. The internal moisture transport was factored out by setting the binary moisture diffusion coefficient to $99\,999\text{ m}^2\cdot\text{s}^{-1}$. The Reynolds number was allowed to change as a function of droplet radius. The only simplifying assumption made was that heat transfer coefficient correction factor was set to be constant (i.e. $\alpha = 1$), which is a reasonable assumption given that it does not change significantly under these conditions.

$$\frac{dR}{dt} = \frac{-\alpha(2 + 0.6 \times 2^{1/2}(\rho_a(v_a - v_d)R / \mu_a)^{1/2} Sc^{1/3}) D_v \Delta C}{2R\rho_d} \quad (\text{A2.103})$$

where ΔC is the driving force for evaporation [$\text{kg}\cdot\text{m}^{-3}$] which was that taken from the water-vapour flux equation (Equation (A2.81)).

$$\Delta C = \frac{1}{1000} \frac{M_w}{R_g} \frac{P_T}{(T_f + 273.15)} \ln \left(\frac{1 - P_v / P_T}{1 - a_w P_{vs} / P_T} \right) \quad (\text{A2.104})$$

Equation (A2.103) was analytically integrated by Matlab® and solved for time, t [s]. The numerically calculated radius was substituted in to the simplified analytical equation and the numerical time, t_{num} [s] and analytical time, t_{anal} [s] were compared. Figure A2.10 shows the numerically predicted droplet radius and the simplified analytical prediction via Equation (A2.103).

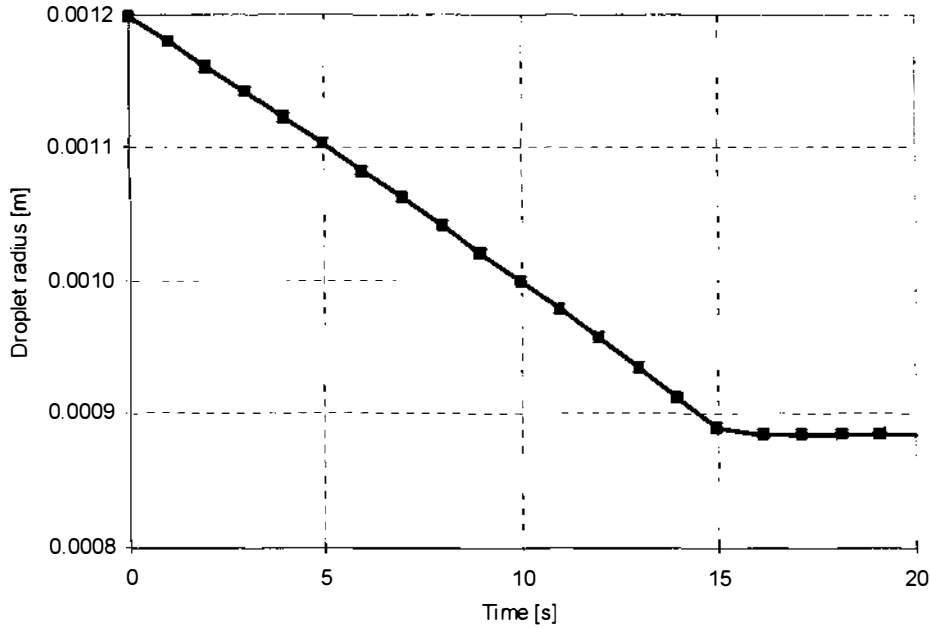


Figure A2.10: Comparison of the numerical model predictions with the analytical solution for the droplet radius. — numerical radius; ■ analytical radius.

The numerical droplet radius prediction accurately follows the simplified analytical solution. The droplet dries rapidly because it immediately attains the drying air temperature (78 °C) and the high k_g^* means the droplet essentially evaporates as if it were a pure water droplet. The final droplet radius agrees with the amount of solid remaining in the droplet.

In conclusion, the mathematical model describing external heat and mass transfer was adequately formulated and implemented. The level of numerical error accumulating in the discretised solution required checking.

A2.5.5 Numerical error checking

The fundamental principle which forms the finite difference numerical scheme used in this work to solve the coupled heat and moisture transport equations is the discretisation of both time and space, by cutting continua of time and space into a series of time-steps and nodes, over which the properties of the material are averaged [Bronlund (1997)]. As the time-step approaches zero and the number of spatial nodes approaches infinity, the real continua are more closely modelled. Reducing the time-step and node size has the effect of rapidly increasing simulation time and introduces rounding errors which accumulate in the calculated results. A trade-off is therefore required so numerical errors are acceptable and simulation times are also sensible [Bronlund (1997)].

A series of simulations were run using the average values for system inputs shown in Table A2.2. The Matlab® function ODE15s controlled the size of the time-steps. The relative (RelTol) and absolute tolerances (AbsTol) were each changed from their default value settings of 10^{-3} and 10^{-6} respectively, by two orders of magnitude to increase the precision of the model predictions. This resulted in a 10 fold decrease in the standard deviation (0.03 to 0.003) of the residuals between surface moisture content predictions relative to the highest precision predictions using RelTol = 10^{-5} and AbsTol = 10^{-8} . The default value settings were acceptable for model predictions.

The effect changing the number of spatial nodes, J , on the numerical error accumulating in the solution was investigated. Sano and Kee (1982) used 21 space increments for a droplet initially 2 mm in diameter. The mathematical model was run with 10, 30 and 100 nodes. Table A2.1 shows the percentage error in the moisture content and temperature predictions at the centre, average and surface nodes along with the predicted averages. The errors are given relative to the values obtained with the 100 node simulation. The amount of real computing time for the 1000 s simulations is also given.

Table A2.1: Average and maximum percentage errors in moisture content and temperature predictions as a function of the number of nodes

Nodes [#]	Real time [s]	Moisture content [% Error] ¹			Temperature [% Error] ¹		
		u_1	u_{av}	u_J	T_{d1}	T_{dav}	T_{dJ}
10	9	2.4(5.2)	0.4(1.3)	-0.4(-92)	0.08(8.8)	0.07(8.7)	0.07(8.7)
30	15	0.6(1.4)	-0.3(-0.7)	0.04(-19)	-0.003(1.9)	-0.007(1.8)	-0.007(1.9)
100	52	—	—	—	—	—	—

¹ % Error is calculated as the percentage deviation from a simulation with $J = 100$ nodes. Note: the unbracketed number is the average percentage error and the bracketed number is the maximum percentage error. u_1 , u_{av} , u_J , T_{d1} , T_{dav} , T_{dJ} are the centre, average and surface moisture contents [(kg water).(kg⁻¹ dry solid)] and the centre, average and surface temperatures [°C] respectively.

In all cases, increasing the number of nodes from 10 to 30 decreases the percentage error in the simulation variables but at the expense of real processing time. Even with 10 nodes the average error in the predictions is acceptable. However, the surface conditions are of importance to this work and a maximum error of -92% (under-prediction) occurs in the surface moisture content prediction for the simulation using 10 nodes. Hence, the surface node calculations are sensitive to volume of the node. Inspection of the data shows that this discrepancy occurs at $t = 16$ s and diminishes to insignificance at $t = 60$ s. Increasing the number of nodes to 30 reduces the discrepancy to -19%. Increasing the number of nodes to 100 increased the real time to 52 s to simulate 1000 s of droplet drying. 30 nodes was considered to give adequate results.

A2.5.6 Maths checking summary

The model describing both the internal and external transport of heat and moisture through the drying droplet was shown to give sensible predictions and followed simplified analytical solutions. This indicated that the implementation of the formulated model was performed correctly.

Checks on the level of numerical errors accumulating in the solution of the model indicated that a minimum of 30 spatial nodes was required to obtain accurate predictions. Under these conditions, it took the model and PC (2.4 GHz, Intel Pentium 4) 15 s of real time to simulate 1000 s of drying.

A2.5.7 Mathematical model predictions against experimental drying kinetics and sensitivity analysis

Figure A2.11 shows the model predictions of the drying kinetics of a 2.4 mm diameter maltodextrin DE5 droplet drying under the average conditions given in Table A2.2.

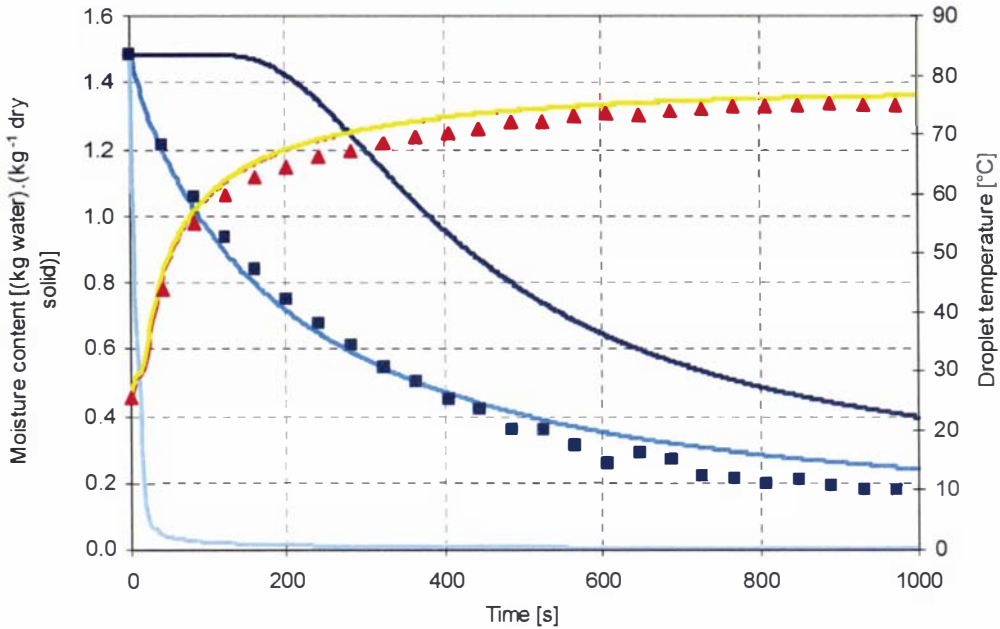


Figure A2.11: Moisture content and temperature histories of 40% w/w maltodextrin DE5 droplet along with model predictions: ■ experimental moisture content history; ▲ experimental temperature history; — predicted centre moisture content; — predicted bulk moisture content; — predicted surface moisture content; — predicted centre temperature; — predicted bulk temperature; — predicted surface temperature.

The model follows the experimental data well. There is no sign of a constant rate drying period which is in agreement with numerous researchers for concentrated foodstuffs [Cheong *et al.* (1986); Zogzas and Maroulis (1996); Dolinsky (2001); Räderer (2001)]. The droplet surface rapidly decreases very near to the surface equilibrium moisture content within 100 s. Overall there is no significant difference in the predicted droplet surface and centre temperatures, although a 1 °C temperature difference between the surface and centre is predicted between 18 and 40 s (scale does not permit observation). A slight over-prediction in the temperature history occurred which is probably because of the inaccuracy in the mathematical terms describing the heat transfer in the glass filament and wire thermocouple (approximated as one-dimensional fins). The moisture content history is under-predicted towards the end of the drying. At this time, the surface skin was observed to be rigid and significantly warped. The surface morphological changes with time are shown in Figure 5.32(k–o). The excessive surface wrinkling and indentations (similar to that in observed for industrial spray-dried droplets by Rosenberg *et al.* (1985) in Figure 5.3) could serve to increase the evaporation rate through increased surface area and reduced radial distance for moisture transport which are not predicted due to the ‘ideal shrinkage’ assumption made. Alternatively, it is also possible that small fissures could have developed allowing preferential moisture transport to the surface, resulting in a faster moisture loss than that predicted. It is also notable that the droplet radius remains largely fixed soon after 2 mins of drying. It is possible that the actual drying process could be better modelled using a mixture of both the effective diffusion model to account for ‘ideal shrinkage’ early in the drying process and then

the receding interface model to account for skin formation and a fixed radius later in the drying process. This is discussed in Section 5.10.

Having implemented the numerical solution correctly, the accuracy of the drying model predictions are determined by the accuracy of the (measured and estimated) physical parameters. A sensitivity analysis was conducted to determine the system input values and constitutive equations that were critical to achieving the desired accuracy for model predictions. High and low estimates of the system input values were determined from experimental error analysis and the observed variability in the experimental set-point parameters over the course of a drying experiment. According to Meerdink (1993), the important physical parameters for drying model predictions are, the binary moisture diffusion coefficient, the moisture sorption isotherm and the external mass and heat transfer coefficients. High and low values of these algebraic equations were generated by multiplying the parameter by a scaling factor. For example, Adhikari (2002) found his calculated binary moisture diffusion coefficient data for sucrose to be $\pm 10\%$ of that measured by Henrion (1964). Hence, scaling factors of 0.9 and 1.1 were used to generate the respective low and high values of the binary moisture diffusion coefficient. Variations are described in the Ranz-Marshall equation that allows an uncertainty of about 20% [Weiss (1987); Taniguchi and Asano (1994) both cited in Räderer (2001)]. Hence, scaling factors of 0.8 and 1.2 were used. The moisture sorption isotherm data for maltodextrins vary significantly depending on the degree of hydrolysis and the supplier. A 10% discrepancy in the water activity values was assumed for this analysis.

Table A2.2 gives the values of system input parameter values used to test the sensitivity of the model predictions. 30 nodes were used for the sensitivity analysis predictions.

Table A2.2: System input values used in the model sensitivity analysis

System input parameter	Low value	Average value	High value
Initial solids concentration [% w/w]	38.9	40.2	40.9
Initial droplet mass [mg]	7.18	7.21	7.28
Initial droplet temperature [°C]	25.4	25.6	26.9
Air temperature [°C]	77.4	77.8	78.0
Air velocity [m.s^{-1}]	0.29	0.31	0.32
Relative humidity [% RH]	0.5	0.7	0.9
Diffusion coefficient [$\text{m}^2.\text{s}^{-1}$]	$0.9D_w$	$1.0D_w$	$1.1D_w$
Water activity [–]	$0.9a_w$	$1.0a_w$	$1.1a_w$
Heat transfer coefficient [$\text{W.m}^{-2}.\text{°C}^{-1}$]	$0.8h_g^*$	$1.0h_g^*$	$1.2h_g^*$
Mass transfer coefficient [m.s^{-1}]	$0.8k_g^*$	$1.0k_g^*$	$1.2k_g^*$

The sensitivity of the model predictions to the low values of the system input data were tested one at a time. The model was relatively insensitive to system input data, because of the small ranges in the observed data variability. The most sensitive parameter was the initial solids concentration which gave an average relative error of 1.8% in the average moisture content. The drying air temperature was the second most sensitive variable which gave an average relative error of 0.7% in the average moisture content. The errors in the average temperature predictions were lower for all cases. Given the low sensitivity of the model predictions to the system input values under these ranges, no further sensitivity analysis was performed with the system input data.

The model predictions were also relatively insensitive to the key constitutive equations, the most significant being the heat transfer coefficient which is shown in Figure A2.12.

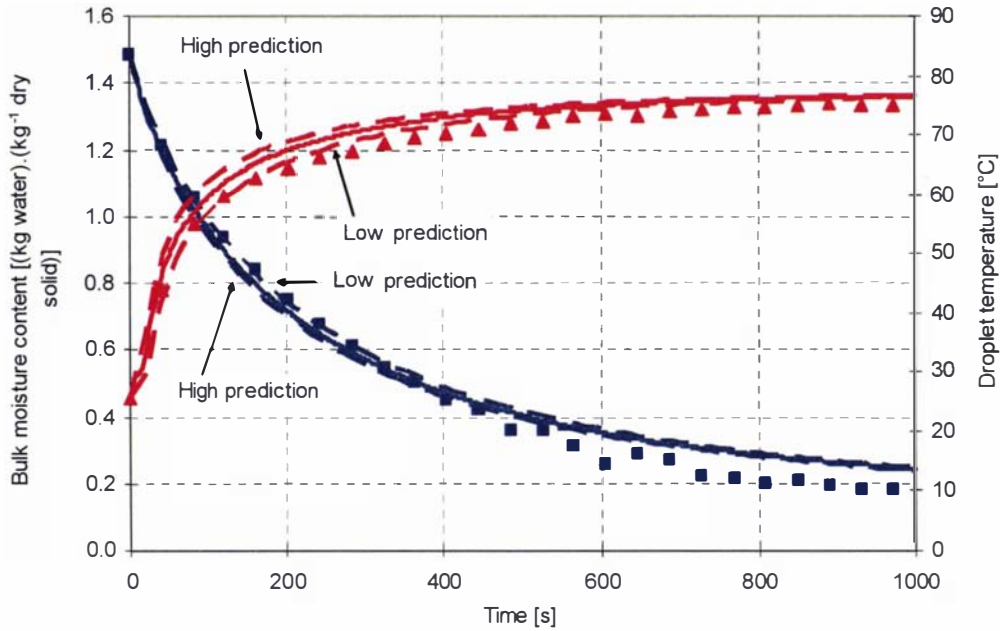


Figure A2.12: Moisture content and temperature histories of 40% w/w maltodextrin DE5 droplet along with model predictions: ■ experimental moisture content history; ▲ experimental temperature history; — bulk moisture content prediction; — bulk temperature prediction; — — low and high bulk moisture content and bulk temperature predictions (blue and red respectively).

A 20% decrease in the heat transfer coefficient resulted in a better average temperature prediction and reduced the average predicted droplet temperature deviation from the experimental data from -2 to -0.8 °C. However, there was no significant increase in the accuracy of the predicted average moisture content.

In conclusion, the model was relatively insensitive to the variability in the system input data and the mathematical descriptions describing the binary moisture diffusion coefficient, heat and mass transfer coefficients and the water activity. The small discrepancy remaining in the experimental and model predicted data probably arises from the significant morphological development of the droplet surface and the incorrect assumption of ‘ideal shrinkage’. These issues are addressed in Chapter 5.

As an assumption check, the heat and mass transfer Biot numbers (Figure A2.13) were determined for the average moisture content history predictions using the average values given in Table A2.2. The temperature difference between the centre and the surface of the droplet, ΔT_d [°C] is also plotted.

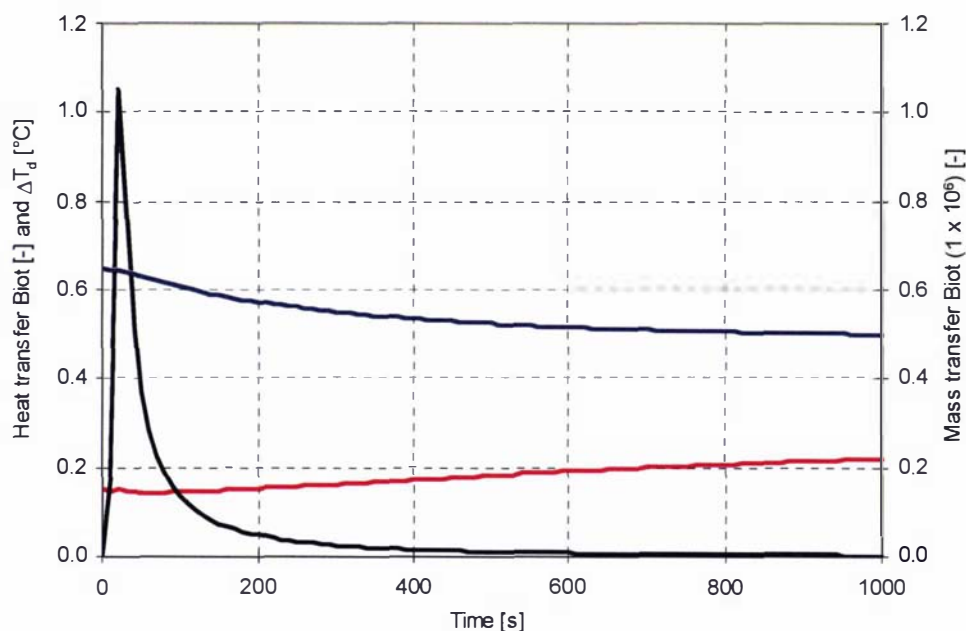


Figure A2.13: Heat and mass transfer Biot numbers for a 40% w/w maltodextrin DE5 droplet drying at 78 °C. — heat transfer Biot number; — mass transfer Biot number; — temperature difference between the droplet centre and droplet surface, ΔT_d .

Given that the critical heat transfer Biot number is 0.3 (radius being the critical dimension), the assumption of constant internal droplet temperature is valid under these conditions and discretisation of the internal droplet temperature is not required. It is clear that internal mass transfer controls the drying kinetics of single droplets containing high molecular weight solutes. Despite this a temperature gradient does exist and at its greatest reaches 1 °C. Depending on the accuracy required, larger droplet diameters and less severe drying conditions may require droplet discretisation.

A2.6 CONCLUSIONS

A mathematical model to predict the drying kinetics of a single droplet drying was formulated and implemented in to Matlab®. The model was based on the effective moisture diffusion model employing a solute-fixed coordinate system and including both moisture content and temperature discretisation to more accurately depict the drying process. The numerical model accurately predicted simplified analytical solutions for both internal and external heat and mass transfer. The model accurately predicted the drying kinetics of a single droplet containing 40% w/w maltodextrin DE5 drying at 78 °C. The model was relatively insensitive to the system input data and key constitutive equations. The flexibility of the model is validated under a variety of conditions in Chapter 5.

APPENDIX A3

PROGRAM SOURCE CODE

A3.1 NOTES FOR USERS

The program source code, written in Matlab® 7 (The Mathworks, Inc., Natick, MA, USA) is contained in 8 separate Matlab® files ('Rundropkinetics.m', 'dropkinetics.m', 'diffusivities.m', 'boundaryODE.m', 'systeminput.m', 'analytical.m', 'SphereBm.m') in the folder 'Solute droplet drying model' on the CD inside the back cover insert. Eight Microsoft® Excel (2002) spreadsheet files (Microsoft Corporation, Redmond, WA, USA) containing the system input data for the drying experiments modelled in Chapter 5 are also included in this folder as well as system input data spreadsheets for the analytical checks and the industrial-scale simulations. The user need only open the driver file called 'systeminput.m' and enter the experimental spreadsheet name (contained in this file) into the *exptfilename* handle to select the drying scenario for simulation.

The mathematical model was only validated for maltodextrin DE5 and hence contains the thermophysical and chemical properties of this substance in a file called 'databank.m'. It serves as the beginnings of a comprehensive database of physical properties for potential coating materials of interest to the dairy industry. This makes the task of running simulations much easier, as the user simply selects the material, as opposed to entering all the constants, chemical and physical relationships before each simulation.

Incorporation of the simplified analytical solutions and the parameter values necessary to numerically predict these have resulted in a large and complex mathematical code. The program can be considered a work in progress and contains numerous evolutionary additions of code that could be rationalised at a later date. The code is annotated for the user to make necessary changes.