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# **The Sticking and Crystallisation of Amorphous Lactose**

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## ABSTRACT

Amorphous lactose has been identified as being one of the major factors in causing stickiness and caking problems when producing and storing dairy powders. Amorphous lactose becomes sticky when its glass transition temperature is exceeded. Above the glass transition temperature it changes to a state where it is a very viscous liquid, and it can flow and build bridges between particles, causing them to become stuck together. Stickiness in amorphous substances depends on the viscosity of the substance, which is a function of how far above the glass transition temperature the actual temperature of the powder is. This work details investigations into the rate and extent of sticking in amorphous lactose, at different temperatures above the glass transition temperature, to find what conditions should be avoided when processing and storing powders containing amorphous lactose.

Methods for predicting the glass transition temperature of amorphous lactose as a function of water activity and moisture content were identified. The glass transition temperature of pure amorphous lactose can be estimated from the moisture content, but in a commercial dairy powder the presence of other components makes this a very difficult exercise. It was concluded that the best way to estimate the glass transition temperature was from a water activity measurement, using a third order model fitted to the available glass transition temperature data.

It was found that the sticking behaviour of amorphous lactose depends on how far above the glass transition temperature it is, irrespective of the temperature and humidity conditions required to achieve this. From investigations into the rate of sticking of amorphous lactose it was found that 25°C above the glass transition temperature amorphous lactose becomes very sticky instantaneously. As such, moisture and temperature conditions that cause the glass transition temperature to be exceeded by this amount should be avoided in all regimes of powder processing. It is also recommended that for processing operations where particle contact times are of the order of a few seconds to a few minutes, the temperature should not be allowed to exceed the glass transition temperature by more than 10°C in order to avoid possible stickiness problems. For long-term storage, powders containing amorphous lactose should be kept in conditions below the glass transition temperature.

Crystallisation of amorphous lactose is recognised as contributing to caking problems, through moisture release and solidification of amorphous bridges. A model for amorphous lactose crystallisation has been confirmed by newly published data. Further crystallisation data is still required at low humidities and high temperatures, but the current model can be used to predict crystallisation rates with reasonable confidence.

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# CHAPTER 1

## PROJECT OVERVIEW

### 1.1 BACKGROUND

Sticking and caking are ongoing problems in the processing and storage of dairy powders, and cause significant economic losses to the manufacturer. While there is knowledge of the reasons for sticking and caking, these problems have traditionally been overcome through experience and trial and error over a number of years, rather than from a mechanistic understanding of the causes. The traditional solutions avoid the majority of problems, but the advent of speciality powders, for which the conditions required to avoid sticking and caking are not known, has made it desirable to have a better understanding of the reasons for these phenomena. Research indicates that amorphous lactose, formed when feed solutions containing lactose are spray dried, is often responsible for problems of sticking and caking in dairy powders.

In order to gain some insight into the sorts of problems experienced with dairy powders in industry, visits were made to various dairy factories in the North Island. The staff involved with powder production at these sites discussed their experiences with powders sticking and caking, with particular reference to processing problems.

Mention was made of high lactose powders blocking cyclones, rotary valves, fines return lines and fluid beds, of powder building up on drier walls and of lumps forming in fluidised beds. When process equipment became blocked the general descriptions indicated that the powder formed a very hard cake and had to be physically chipped away with shovels. Lumps were variously described as being “rock hard” or “able to be crushed by hand”, while some lumps were observed to break up easily in fluid beds. One problematic high lactose powder was described as reaching a stage where it was as bendable and stretchable as chewing gum. The engineer involved felt that this problem was due to lactose being in the rubber state.

Other reasons that staff attributed sticking and caking problems to were ambient weather conditions (particularly during summer) and plant design. The solutions devised to overcome problems included banging the sides of driers with hammers, introducing dry air to the drier chamber, lowering powder throughput, lowering outlet temperatures and drying to lower moisture contents. It is of interest to note that while high fat and high sugar powders often had problems, usually high lactose powders were mentioned as experiencing the most stickiness related problems. It is also interesting that stickiness problems were sometimes observed when a drier was “pushed” to increase throughput by increasing the outlet temperature.

## **1.2 AMORPHOUS LACTOSE STICKING MECHANISM**

The basic theory of sticking due to amorphous lactose is that when the glass transition temperature ( $T_g$ ) is exceeded, the solid can begin to 'flow', like a very thick liquid. This flow can build bridges between particles that causes them to stick together. The presence of water lowers  $T_g$ , leading to sticking problems at lower temperatures. While it is widely accepted that sticking occurs above the glass transition temperature, it is not known for sure whether it depends only on how far above  $T_g$  the ambient conditions are, or whether other factors such as the actual temperature and moisture content are important too. The relationship between sticking and time is also poorly understood. The time that amorphous lactose requires to become sticky under different conditions is not known.

## **1.3 AMORPHOUS LACTOSE CRYSTALLISATION**

Crystallisation is related to sticking and caking for two reasons. The first is that crystallisation of amorphous lactose releases water. The presence of water has been shown to be a major factor in sticking and caking, as it lowers glass transition temperatures and can lead to humidity caking. The second reason is that crystallisation of the interparticle bridges mentioned above can lead to solid crystalline bridges of significant strength, further increasing caking problems.

A model for amorphous lactose crystallisation kinetics exists, which bases crystallisation predictions on the amount that the glass transition temperature is exceeded by. This has been validated by experimental data, but only under certain conditions. Further data is required to confirm the applicability of this model over a broader range of conditions.

## **1.4 PROJECT OBJECTIVES**

The specific objectives of this research were:

- To find the conditions of time, temperature and moisture content under which amorphous lactose becomes sticky and could cause problems in powder processing
- To develop more data for the crystallisation of amorphous lactose, in conditions where little data currently exists
- To recommend the conditions required to avoid stickiness in powders due to amorphous lactose

# CHAPTER 2

## LITERATURE REVIEW

### 2.1 INTRODUCTION

In order to complete the objectives of this work it was necessary to have a basic understanding of several key areas. These included the different forms that lactose exists in and their properties, how the glass transition temperature of amorphous lactose can be measured and predicted as a function of moisture content, and how sticking and crystallisation phenomena can be measured.

### 2.2 LACTOSE

Lactose, or 4-O- $\beta$ -D-galactopyranosyl-D-glucopyranose, is a disaccharide found in the milk of most mammals, hence the often-used term for lactose 'milk sugar'. It can exist in several different forms, outlined below.

#### 2.2.1 FORMS OF LACTOSE

##### 2.2.1.1 Crystalline lactose

Bushill *et al.* (1965) recorded the existence of five different forms of crystalline lactose. The most common form of lactose is  $\alpha$ -lactose monohydrate. This is formed when lactose is crystallised from solution below 93.5°C, and is the form usually produced commercially. The monohydrate refers to the fact that the crystal has one water molecule per molecule of lactose incorporated into the lattice.  $\alpha$ -Lactose can also exist as an anhydride, in both stable and unstable forms (Bushill *et al.* 1965, Jenness and Patton 1959).

$\beta$ -lactose anhydride differs from  $\alpha$ -lactose in the orientation of the hydroxyl group on the number one carbon of the glucose section of the molecule (Jenness and Patton 1959). In addition, it contains no water in its crystal structure.  $\beta$ -Lactose is produced when lactose is crystallised from solution above 93.5°C, and is sweeter to taste than  $\alpha$ -lactose.

In addition, it is reported that lactose can crystallise as a mixture of anhydrous  $\alpha$  and  $\beta$ -lactose. The ratio of  $\alpha$  to  $\beta$  has been given as 5:3 and 4:1, depending on the conditions

of crystallisation (Bushill *et al.* 1965, Jouppila and Roos 1994b, Jouppila *et al.* 1997, 1998).

### 2.2.1.2 Amorphous Lactose

Like many carbohydrates, lactose can exist in an amorphous 'glassy' state, without any ordered crystal structure (Sharp and Doob 1941, Nickerson 1974, Roetman and van Schaik 1975, Bushill *et al.* 1975, Roos and Karel 1990, 1991a, Bronlund 1997). This state is attained when an aqueous lactose solution is concentrated rapidly. During this, the viscosity increases quickly to a value above  $10^{12}$  Pa.s, where the mobility of the lactose molecules is insufficient for crystallisation to occur, and so an amorphous solid containing  $\alpha$  and  $\beta$ -lactose is formed (Roetman and van Schaik 1975, Nickerson 1974, Roos and Karel 1991a).

Amorphous lactose is formed on a large scale in the dairy industry, where the spray drying of various lactose-containing liquid feeds (whey, milk, skim milk) causes the formation of amorphous lactose. As such, amorphous lactose is the principle form in which lactose is present in dairy powders (Lloyd *et al.* 1996, Jouppila and Roos 1994a).

## 2.2.2 LACTOSE CHEMISTRY

### 2.2.2.1 Mutarotation

Regardless of the form of lactose, when it is put into solution one anomer will spontaneously convert into the other until an equilibrium position is reached. This conversion between  $\alpha$  and  $\beta$ -Lactose is termed mutarotation. The equilibrium position depends on the temperature of the solution – at 20°C the ratio of  $\beta$ : $\alpha$  is 1.68, while at 80°C it is 1.45 (Lowe 1993). Mutarotation is a first order reversible reaction, with a rate dependent on temperature and pH (Nickerson 1974).

### 2.2.2.2 Solubility

The solubility of lactose is complicated by the mutarotation reaction. For example, if  $\alpha$ -Lactose is added to excess water, a finite amount will dissolve rapidly. This initial solubility is the true solubility of  $\alpha$ -lactose monohydrate, but as time passes more  $\alpha$ -lactose is slowly dissolved. This is due to the mutarotation of the  $\alpha$ -lactose in solution to  $\beta$ -Lactose. As mutarotation occurs the solution becomes unsaturated with respect to  $\alpha$ -Lactose and thus more  $\alpha$ -Lactose can dissolve. This continues until equilibrium is reached and no more  $\alpha$ -Lactose can dissolve, which defines the final solubility limit (Nickerson 1974).

Below 93.5°C  $\beta$ -lactose is more soluble than  $\alpha$ , and  $\alpha$ -lactose will precipitate first from a saturated solution. Above 93.5°C the reverse is the case, and  $\beta$ -lactose has the limiting solubility (Nickerson 1974).

### 2.2.3 USES OF LACTOSE

Lactose was first isolated in 1633, and during the 1700's became a commercial commodity used mainly in medicine (Nickerson 1974). Today it is commercially extracted from whey by crystallisation, and finds a wide variety of uses, mainly in the Pharmaceutical and Food industries.

#### 2.2.3.1 Pharmaceutical Industry

Lactose has been used in the pharmaceutical industry for many years as a medium for drug delivery. The drug is evenly distributed in lactose powder and is then easily compressed into tablets. These tablets have good dispersing characteristics, which is desirable for the delivery of drugs (Nickerson 1974, Jenness and Patten 1959). The presence of amorphous lactose aids in the formation of stronger tablets (Sebhatu *et al.* 1997).

#### 2.2.3.2 Food Industry

Aside from being found in dairy products, lactose is also used widely in the food industry in many other items. Because human milk contains about 7% lactose whereas cows milk has only 5%, lactose is often added to cows milk for use in infant milk formulas. It can be added to milk based beverages to obtain optimum lactose levels, which improves richness, smoothness and acceptance of the beverage by consumers. Icings, toppings, fillings, candies and beer are other examples where the addition of lactose can improve the products texture, mouth-feel, viscosity, shelf life and overall quality. Because lactose (especially anhydrous lactose) readily absorbs aromas, flavours and colours, it is used as a food additive to retain flavour, gradually release odour and to act as a carrier to disperse colours. Other uses in the food industry include encapsulating products, 'instantising' (increasing the dispersibility) food products, as a dispensing aid to maintain free flowing powders and as a reducing sugar in baked goods (Nickerson 1974, Jenness and Patten 1959).

## 2.3 AMORPHOUS LACTOSE

In order to investigate the rate of sticking and crystallisation of amorphous lactose, knowledge of several important areas is required. These include the moisture sorption

properties of amorphous lactose, the concept of glass transition and how to predict the glass transition temperature of amorphous lactose, and methods for obtaining amorphous lactose for study.

### 2.3.1 MOISTURE SORPTION

As the plasticisation of amorphous sugars by water is important in sticking and crystallisation phenomena (Downton *et al.* 1982, Chuy and Labuza 1994, Roos and Karel 1992), knowledge of the moisture sorption of amorphous lactose is required. The generally accepted method for illustrating the sorption of moisture in foods is through the use of moisture sorption isotherms. These show the amount of water absorbed by the food solid as a function of water activity at constant temperature (Jouppila and Roos 1997). Water activity is defined as the equilibrium ratio of the vapour pressure of a solution to that of pure water (Troller 1983), or in more practical terms as the relative humidity of the air that is in equilibrium with a solid.

Moisture sorption isotherms are usually obtained by measuring the weight gain of an initially dry solid that is allowed to equilibrate with air of a certain relative humidity (Jouppila and Roos 1994a, 1997, Bronlund 1997, Warburton and Pixton 1978). The data obtained in this way is fitted to a mathematical model. Jouppila and Roos (1997) looked at the various models available for modelling sorption isotherms and their usefulness in modelling real systems. They concluded that the Guggenheim-Anderson-de Boer (GAB) model was the most applicable for dehydrated milk products, including amorphous lactose. The GAB isotherm model is shown in equation 2.1, where  $M$  is the solids moisture content and  $M_0$  is the moisture content when a single layer of water molecules have adsorbed to the surface of the solid. The parameters  $c$  and  $f$  are constants and  $a_w$  is water activity.

$$M = \frac{M_0 c f a_w}{(1 - f a_w)[1 + (c - 1) f a_w]} \quad (2.1)$$

A number of researchers have made measurements of the moisture sorption isotherm of amorphous lactose (Bronlund 1997, Jouppila and Roos 1994a, Roos and Karel 1990, Linko, *et al.* 1981, Warburton and Pixton 1978, Berlin *et al.* 1968). The data of most of these researchers showed significant scatter and little agreement, however Bronlund (1997) measured the moisture sorption isotherm of amorphous lactose at different temperatures and obtained results that agreed closely with those of Jouppila and Roos (1994a). Both researchers fitted GAB isotherm models to their data, which are shown in figure 2.1. In the course of experiments involving amorphous lactose, other researchers (Lloyd *et al.* 1996, Roos and Karel 1990, Sebhatu *et al.* 1997, Hargreaves 1995) have measured the moisture content of amorphous lactose equilibrated at different water

activities. These data points are also included on figure 2.1. Much of this data is significantly higher in moisture content than the measured isotherms predict. The reason for this discrepancy is not clear.

By measuring isotherms at different temperatures, Bronlund (1997) showed that temperature has no significant effect on the isotherm in the range measured (15-40°C). It is also interesting to note that the isotherm measured by Bronlund (1997) was for spray dried lactose, while that measured by Jouppila and Roos (1994a) was for freeze dried lactose. Figure 2.1 indicates that the sorption behaviour of the two types of amorphous lactose is very similar.

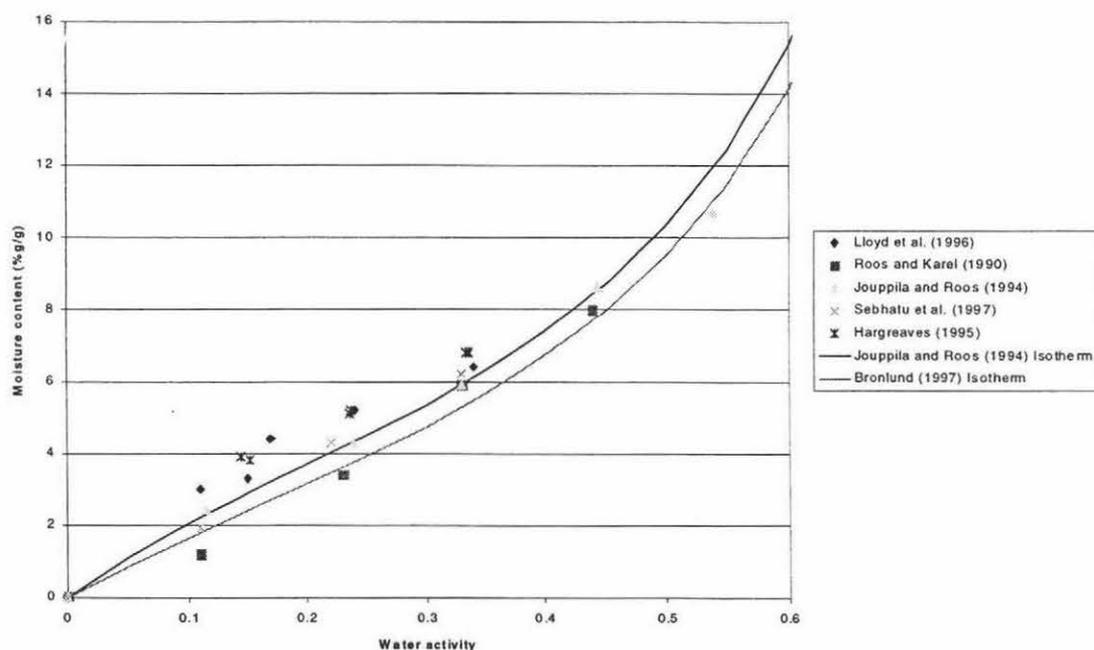


Figure 2.1 Amorphous lactose moisture sorption isotherm

### 2.3.2 GLASS TRANSITION

A 'glass' is defined as a solid material that has an amorphous, liquid-like structure with a viscosity in the order of  $10^{12}$  Pa.s (Noel *et al.* 1990, Downton *et al.* 1982). Examples of food glasses include pasta, confectioneries, some baked products, and the lactose in milk powders (Noel *et al.* 1990). A glass can undergo a second order phase change where it becomes a less viscous, rubber-like substance. The temperature at which this occurs is known as the glass/rubber transition temperature, or simply the glass transition temperature [ $T_g$ ] (Roos and Karel 1990, 1991a,b, 1992, Lloyd *et al.* 1996, Slade and

Levine 1991, Noel *et al.* 1990). The  $T_g$  of amorphous lactose is extremely sensitive to plasticisers, such as water, which lower  $T_g$  (Roos and Karel 1991a).

The glass transition temperature is important to this work as it is widely recognised that phenomena such as sticking, caking, collapse and crystallisation occur at or above  $T_g$  (Roos and Karel 1990, 1991a,b, 1992, Lloyd *et al.* 1996, Chuy and Labuza 1994, Downton *et al.* 1982, Jouppila and Roos 1994b, Jouppila *et al.* 1997, 1998, Bronlund 1997). It is therefore desirable to know what  $T_g$  is at a particular moisture condition, either by measuring it directly or predicting it from the moisture content or water activity.

### 2.3.2.1 Determination of Glass Transition Temperature

There are few methods whereby glass transition temperatures can be directly measured. The usual method is by the use of differential scanning calorimetry (DSC), which measures heat flow as a function of temperature. At  $T_g$  the free volume and the mobility of the molecules in the amorphous matrix increases which causes an endothermic change in the heat flow measured by the DSC apparatus (Roos and Karel 1990). DSC has been the most commonly used method to determine the  $T_g$  of spray-dried and freeze-dried amorphous lactose (Lloyd *et al.* 1996, Roos and Karel 1990, Jouppila and Roos 1994b, Sebhatu *et al.* 1994, 1997, Hargreaves 1995, Schmitt *et al.* 1999, Hill *et al.* 1998, Taylor and Zografi 1996).

Noel *et al.* (1990) reviewed other thermal techniques for measuring the glass transition temperature, including dynamic mechanical analysis and dielectric relaxation. However, the available literature shows that no other thermal method has been used to determine the glass transition temperature of amorphous lactose.

Lloyd *et al.* (1996) investigated the caking of amorphous lactose and the relation of this to the glass transition temperature. As well as determining  $T_g$  using DSC, two other techniques were used. The first was a technique developed by Hargreaves (1995), who used Nuclear Magnetic Resonance (NMR) to measure the relaxation time of lactose protons. At  $T_g$  there is a small discontinuity in the relaxation times, due to the lactose molecules becoming more mobile and the internuclear distances increasing. This method involves highly specialised equipment and is expensive to use. The second method involved incubating lactose in small cylindrical moulds for 3 hours at varying temperatures and measuring the density of the plug that was formed. It was found that the temperature at which the plug densities started to increase corresponded well with the glass transition temperature measured by DSC and NMR. The increase in density was expected to be a consequence of the viscous flow that occurs at and above  $T_g$ . This relatively simple method is disadvantaged by the fact that it takes many samples and a

considerable time to determine the glass transition temperature of lactose at one moisture content.

### 2.3.2.2 Prediction of Glass Transition Temperature

The Gordon and Taylor equation (eq 2.2) can be used to predict  $T_g$  as a function of moisture content, where  $w_1$ ,  $w_2$ ,  $T_{g1}$  and  $T_{g2}$  are the mass fractions and glass transition temperatures of lactose and water respectively, and  $k$  is a constant (Jouppila and Roos 1994b, Jouppila *et al.* 1998, Bronlund 1997, Buckton and Darcy 1996). This equation was originally formulated for calculating  $T_g$  of polymer blends.

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (2.2)$$

$T_{g1}$  and  $T_{g2}$  are usually taken as 101°C for amorphous lactose, and -135°C for amorphous water, and  $k$  values of 6.7 and 7 have been reported (Jouppila and Roos 1994b, Jouppila *et al.* 1997, 1998). Figure 2.2 shows the predictions of the Gordon and Taylor equation and the available literature data for glass transition temperature of amorphous lactose.

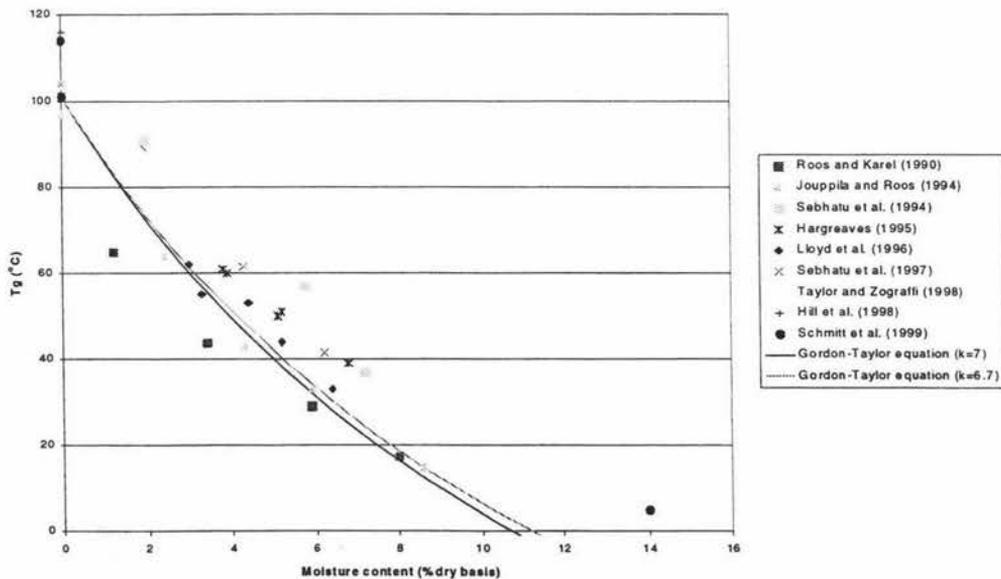


Figure 2.2  $T_g$  versus moisture content for amorphous lactose

It can be seen from figure 2.2 that there is a large degree of variation in the available data. In some cases up to 20°C difference is evident between the data of different researchers at the same moisture content. As such, the predictions of the Gordon and

Taylor equation show poor agreement with the bulk of the experimental data and are not very useful for giving accurate estimates of  $T_g$ .

Since the moisture content of amorphous lactose is difficult to measure in real world situations, for example, when present in a milk powder with other components, it would be desirable to be able to predict  $T_g$  based on water activity. Water activity can be easily measured with an RH probe. If a good estimate of  $T_g$  could be made with a water activity measurement then the problem of knowing how sticky the amorphous lactose might be is made much simpler. Figure 2.3 shows the available data for amorphous lactose  $T_g$  at different water activities. An attempt to predict  $T_g$ , using the GAB isotherm to predict the moisture content and the Gordon and Taylor equation to predict  $T_g$  is also shown on figure 2.3. This method has been used before to try and predict the  $T_g$  of amorphous lactose, given its water activity (Jouppila *et al.* 1998, 1997).

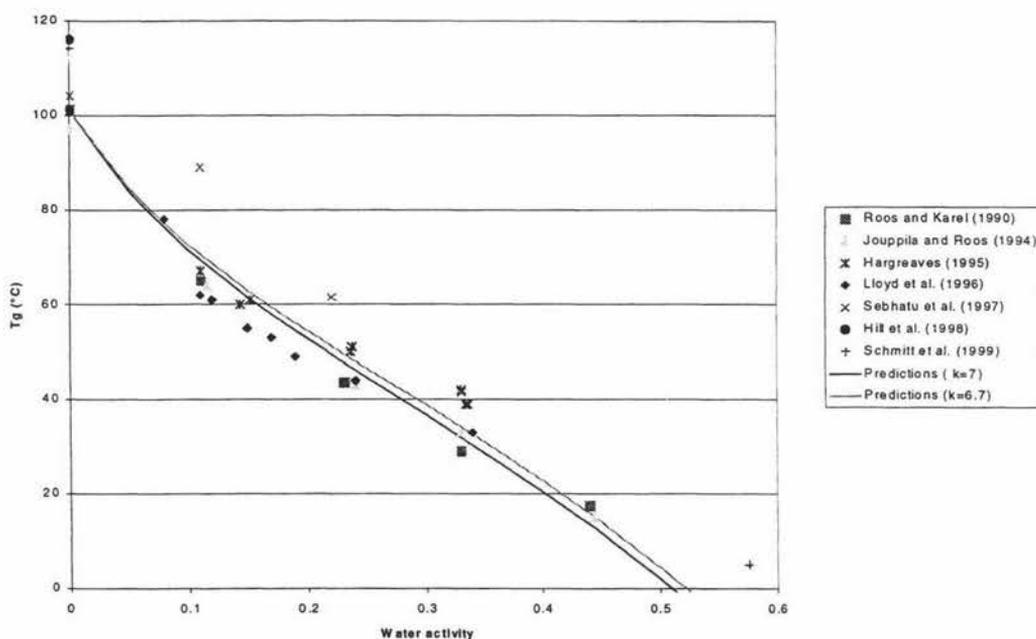


Figure 2.3  $T_g$  versus water activity

The different data sets show better agreement than previously in figure 2.2, although in some cases there is up to 10°C difference in  $T_g$  values, and the data of Sebhatu *et al.* (1997) appears to be radically different from that of any other researchers. The predictions of  $T_g$  do not follow the available data very well, especially in the region of water activities from 0.1 to 0.2 where  $T_g$  is over-predicted by at least 5°C. All things considered, using this model for predicting  $T_g$  would not yield accurate results. As a result, a better way to characterise the  $T_g$  must be found if the stickiness of amorphous lactose powder is to be related to the glass transition temperature.

### 2.3.3 MAKING AMORPHOUS LACTOSE

Making amorphous lactose on a lab scale is required to produce the material to study for this work and also give some insight into the problems of sticking and caking due to amorphous lactose. It was desirable to obtain spray-dried lactose, as this is the form found in dairy powders. Amorphous lactose can also be produced by freeze-drying.

Roos and Karel (1990) made amorphous lactose by freeze-drying a 10% solution of  $\alpha$ -lactose monohydrate in distilled water. 10g lots of the solution were frozen at  $-20^{\circ}\text{C}$  for 24 hours, tempered over dry ice for 3 hrs and freeze-dried on shelves for 24 hrs below 0.1 millibars pressure. The vacuum was broken with dry nitrogen and the portions were transferred to a vacuum desiccator and dried over  $\text{P}_2\text{O}_5$ . This freeze-drying method, or variations of it, has also been used by Tsourouflis *et al.* (1976), Roos and Karel (1991, 1992), Jouppila and Roos (1994, 1997) and Jouppila *et al.* (1997, 1998). Common changes to this procedure are freezing at  $-80^{\circ}\text{C}$  and using a 20% solution of lactose. No publication gives the temperature at which the drying was performed. Roetman and van Schaik (1975) tried to produce amorphous lactose by first freezing a more concentrated (45%) solution in liquid nitrogen, but could not obtain pure amorphous lactose that was free of crystals. This was probably due to spontaneous crystallisation occurring before the solution was completely frozen, as the lactose solution is concentrated by the freezing of water as ice, causing an increase in the driving force for lactose crystallisation.

Lloyd *et al.* (1996) produced spray dried amorphous lactose by dissolving 12 kg of pharmaceutical grade lactose in 80kg of  $80^{\circ}\text{C}$  water, which was then spray dried using a pilot scale drier with disc atomiser and integral fluid bed. The drying conditions are given in Lloyd *et al.* (1996). The product was stored in sealed aluminium foil bags at  $4^{\circ}\text{C}$ , and was confirmed to be amorphous through NMR measurements and observation under a polarising microscope. Lloyd *et al.* (1996) gives the most complete description of spray drying of all the available literature. Other workers (Roetman and van Schaik 1975, Buckton and Darcy 1996, Bushill *et al.* 1965) report spray-drying lactose solutions, but few give specific details of the procedure used. The method of spray drying outlined by Lloyd *et al.* (1996) is therefore the best method to follow for the purposes of this work.

## 2.4 STICKINESS OF AMORPHOUS LACTOSE

### 2.4.1 INTRODUCTION

Stickiness is strongly related to caking, and the two phrases are often used together to describe the phenomena of powder cohesion (Paterson and Bronlund 1997, Wallack and

King 1988, Chuy and Labuza 1994). Aguilera *et al.* (1995) gave a detailed description of caking in amorphous powders, and described it as the transformation of a powder into lumps and then an agglomerated solid. Stages in the caking process were defined, including bridging, agglomeration, compaction and liquefaction. Aguilera *et al.* (1995) assert that the caking of powders occurs “as a result of surface deformation and sticking at contact points between particles”. From this and other works (Tsourouflis *et al.* 1976, Downton *et al.* 1982, Wallack and King 1988, Lloyd *et al.* 1996, Bronlund 1997, Rennie *et al.* 1999, Paterson and Bronlund 1997) it is apparent that caking is the transformation of a free-flowing powder into a solid mass. Also of interest is the term ‘lumping’, which is often used to describe the initial stages of caking, and is simply defined as small masses of powder sticking together to form a lump (Burr 1998). Lumping and caking seem very similar, but Burr (1998) suggests the distinction between the two terms is that in lumping the lumps of powder are easily crushed, whereas when these lumps are difficult to crush the powder can be termed caked.

Downton *et al.* (1982) give the caking of instant coffee and drink powders, and the controlled agglomeration of food powders as examples of stickiness. Other workers give the caking of milk powders (Paterson and Bronlund 1997), fish protein hydrolyzate (Aguilera *et al.* 1995) and infant formulas (Chuy and Labuza 1994) as examples of stickiness problems in food powders. These examples indicate that ‘stickiness’ is the property of powder particles that causes lumping and caking of the bulk powder. Thus, for a powder to cake the particles involved must have already been sticky before caking was observed. It is therefore desirable to have an understanding of the mechanism that causes sticking between particles.

#### 2.4.2 MECHANISM OF STICKING

Caking and sticking in powders is almost always caused by liquid bridging between particles, as opposed to electrostatic or molecular attraction forces (Bronlund 1997, Peleg 1993). For liquid bridging to occur, the surface of the particles must be in a liquid state at a specific site or sites. Peleg (1993) gave the mechanisms by which this may proceed as;

- Accidental wetting, moisture condensation or moisture sorption that causes the surface to dissolve and forms a film of saturated solution around the particle.
- The transformation of the surface of an amorphous material into a highly viscous ‘rubber’ state, by exceeding the glass transition temperature.
- Liberation of absorbed water, which occurs when amorphous glasses re-crystallise.
- Melting of the surface (eg fat melting).

The first mechanism is not appropriate for amorphous lactose, as it is very hygroscopic (Bonelli *et al.* 1997) and any surface moisture would be absorbed into particle rather

than remaining on the outside. Depending on the amount of moisture absorbed and the ambient temperature conditions, this could cause  $T_g$  to be exceeded, giving the second mechanism outlined above. Clearly there is no fat present in amorphous lactose, but the melting of the surface could be an applicable mechanism in powders that do contain fat. For this work on the sticking of amorphous lactose, it would appear that the two mechanisms of liquid bridging involving amorphous solid glass transition and re-crystallisation would be of concern.

#### 2.4.2.1 Viscous Flow

Downton *et al.* (1982) proposed that sticking of hygroscopic amorphous powders occurs by the mechanism of viscous flow, which is driven by surface tension. If two particles come together then they may stick to each other, depending on whether sufficient viscous flow can occur to build an interparticle bridge that can resist subsequent mechanical deformations. The resistance to viscous flow is measured through viscosity, and lower viscosity enables greater flow. Through a simple energy balance Downton *et al.* (1982) obtained equation 2.3, where  $\mu$  is the critical viscosity for sticking in a contact time  $t$ ,  $k$  is a constant ( $\approx 1$ ),  $\sigma$  is surface tension and  $KD$  is the distance over which flow must occur ( $K$  being a constant and  $D$  being particle diameter).

$$\mu = \frac{k\sigma t}{KD} \quad (2.3)$$

Using this equation, Downton *et al.* (1982) predicted the critical viscosity for sticking of a 7:1 w/w sucrose/fructose mixture in a short time period (1-10 seconds) to be between  $10^6 - 10^8$  Pa.s. This critical viscosity range was confirmed experimentally using the sticky point test of Lazar *et al.* (1956).

Wallack and King (1988) used a very similar model, developed by Frenkel in 1945 (equation 2.4), and showed through similar experiments on coffee extract powder and a maltodextrin/sucrose/fructose mixture that this model also predicted the range of critical viscosities for sticking in a short time period. The critical viscosity range for the sugar mixture was the same ( $10^6 - 10^8$  Pa.s) as those predicted by Downton *et al.* (1982), while that for the coffee powder was also similar at  $10^5-10^7$  Pa.s.

$$\mu = \frac{3 \sigma t a}{2 x^2} \quad (2.4)$$

In the Frenkel equation, 'a' is the initial particle radius and 'x' is the radius of the interparticle bridge formed by viscous flow. Wallack and King (1988) used electron microscopy to estimate the bridge radius 'x', by causing a sample to become sticky,

then freeze drying it and taking a scanning electron micrograph. They give a value for 'x/a' (ratio of interparticle bridge radius to particle radius) of 0.1. Downton *et al.* (1982) appear to have estimated the value of K for their work, and they use a range of 0.01-0.001. Both sets of researchers used a value of 70mN/m for surface tension, which is an estimate for interstitial concentrate.

Both Downton *et al.* (1982) and Wallack and King (1988) state that increased contact time and higher surface tension increases sticking tendencies, while greater viscosity or larger particle sizes decrease the tendency for sticking. This is apparent from inspection of the equations. Stickiness was found to be related to moisture content, in that increasing the moisture content decreases the temperature at which powders become sticky (Downton *et al.* 1982, Wallack and King 1988, Tsourouflis *et al.* 1976). The increased moisture lowers  $T_g$  and therefore the temperature at which viscous flow occurs.

Bronlund (1997) stated that crystallisation, as well as releasing moisture that can further contribute to caking problems, causes the rubber bridges between particles to become solid, greatly increasing the strength of the caked powder. However, there is evidence to suggest that powders containing amorphous lactose can form strong cakes with solid bridges without crystallisation taking place. In some cases powders form extremely hard cakes, yet after examination by a variety of methods show no evidence of crystallinity (Lloyd 1999). Part of the reason for this, as well as caking due to other components such as fat, could be that if the ambient temperature falls below  $T_g$  after viscous flow has occurred, any rubber bridges present could solidify without crystallisation to form solid amorphous bridges. Varying temperature or humidity cycles could enhance this. For example, if during the day a stored powder experienced temperatures above  $T_g$  but during the night was sufficiently cool so that  $T_g$  was not exceeded, viscous flow could occur during the day but be halted at night. As long as crystallisation occurred slower than about 12 hours, no crystals would be formed, and the next day more flow could occur, increasing the bridges between particles still further, and so on. For a powder being shipped around the world, or perhaps stored in a desert country where there are large diurnal temperature variations, the cumulative viscous flow could be quite substantial.

#### 2.4.2.2 Viscosity Of Amorphous Lactose

Since the mechanism outlined above depends on the viscosity of the material in question, it is desirable to know the viscosity of amorphous lactose as a function of temperature. No experimental data is available in the literature for the viscosity of highly concentrated lactose solutions.

Downton *et al.* (1982) and Wallack and King (1988) experimentally measured the viscosities of super-concentrated solutions of sucrose/fructose and maltodextrin/sucrose/fructose mixtures respectively, by the falling ball method. This method involved concentrating solutions by evaporation to 93-98% solids, which would not be possible for amorphous lactose, due to the difficulty of forming such a solution without crystallisation taking place.

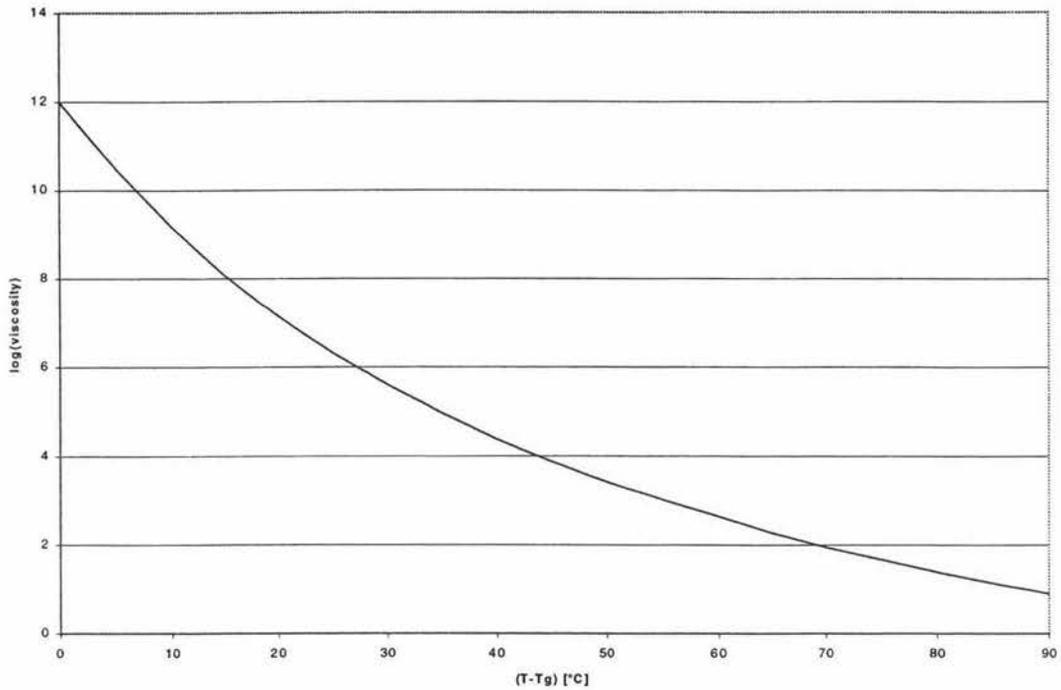
Williams *et al.* (1955) proposed the Williams-Landel-Ferry (WLF) equation, which relates the relaxation time of mechanical properties to the temperature above glass transition. Since viscosity is governed by the relaxation of the amorphous structure (Bronlund 1997), the WLF equation (equation 2.5) has been used to describe the temperature dependence of viscosity for sugar solutions above the glass transition temperature (Soesanto and Williams 1981, Downton *et al.* 1982).

$$\log \frac{\mu}{\mu_s} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \quad (2.5)$$

The measured viscosity data of Downton *et al.* (1982) was found to agree well with the predictions of the WLF equation, and Soesanto and Williams (1981) also found that it adequately described the viscosity of sugar solutions. Both of these researchers used the values of constants  $C_1$  and  $C_2$  reported by Williams *et al.* (1955) [-17.44 and 51.6 respectively]. These constants are reported as universal constants, which apply for many materials. Figure 2.4 shows the viscosity predictions of the WLF equation using the universal constants.

#### 2.4.2.3 $(T - T_g)$ as a Parameter for measuring stickiness

The sticking mechanisms outlined in this section depend on the viscosity of the amorphous substance, which varies as a function of how much the temperature is above  $T_g$ , or  $(T - T_g)$ . Since  $T_g$  depends on the moisture content of the amorphous material,  $(T - T_g)$  combines the parameters of temperature and moisture content into one. If sticking depends only on the viscosity it implies that only  $(T - T_g)$  is important, not the actual temperature and moisture conditions required to achieve it. Bhandari *et al.* (1997), Roos and Karel (1991a) and Dumoulin and Bimbenet (1998) have all used the concept of  $(T - T_g)$  to describe the sticking behaviour of amorphous powders.



**Figure 2.4 Viscosity predictions of the WLF equation**

### 2.4.3 MEASUREMENT OF STICKING PHENOMENA

There are several methods covered in the literature for the observation of stickiness in powders. A review of the most relevant methods follows.

#### 2.4.3.1 Sticky Point Temperature

The most widely used test reported in the literature is the so-called ‘sticky-point temperature’ test, originally developed by Lazar *et al.* (1956) and since used by Downton *et al.* (1982), Wallack and King (1988) and Chuy and Labuza (1994). This test involves placing a sample of powder with a known moisture content into a boiling tube, which is immersed in a temperature controlled water or oil bath. The tube is closed to the atmosphere with a rotating mercury seal, and a small hand turned propeller is embedded in the sample. The temperature of the bath is slowly raised while the propeller is turned about a quarter turn at regular intervals. The temperature at which the force required to turn the propeller increases sharply is recorded as the sticky-point temperature. Both Downton *et al.* (1982) and Wallack and King (1988) report sticky-point measurements to be clearly defined and repeatable to  $\pm 1$  K. Within 5°C of the sticky point, slight resistance to stirring is noted, and within 2-3°C the powder is observed to form small lumps which easily fall apart (Wallack and King 1988).

Lazar *et al.* (1956) does not give the heating rate used for sticky-point determinations. Downton *et al.* (1982) and Wallack and King (1988) used a temperature ramp of 1°C/3min then 1°C/5min as the sticky point was approached. Chuy and Labuza (1994) looked at the effect of different temperature ramps (1°C/3min, 5°C/min and 10°C/min) on the values obtained for the sticky-point, and found that the temperatures were generally lower for the lower heating rates. The reason put forward for this was that at slow heating rates the sample had a longer residence time at any given temperature, increasing the probability for viscous flow. This would seem a reasonable explanation, but it should be noted that Chuy and Labuza (1994) only stirred the powder sample every 5°C, giving contact times for the particles of 15 minutes at the lowest heating rate, and 30 seconds at the fastest. From the mechanisms outlined above it is apparent that longer contact times mean that the more flow between particles can occur, and hence the sticky-point would be observed at a lower temperature. Thus, if the runs performed at 1°C/3min were stirred at the same time interval as the runs at 10°C/min (30 seconds instead of 15 minutes) then it is expected that similar sticky-point temperatures would be obtained. Any flow that occurs during the 30 seconds available at lower temperatures might be insufficient to form bridges that can resist breaking, however if 15 minutes were available then the bridges could be sufficiently strong.

Downton *et al.* (1982) and Wallack and King (1988) related the sticky-point temperatures they obtained to viscosity/temperature data. The results of Downton *et al.* (1982) gave experimental viscosity values of  $0.32 \times 10^7$  to  $4 \times 10^7$  Pa.s, well within the predicted range of  $10^6$  to  $10^8$  Pa.s. The results of Wallack and King (1988) gave similar agreement with the predicted range. These results indicate it may be possible to predict the time for a powder to become sticky at a certain temperature, using the WLF equation for predicting viscosity and equation 2.3 or 2.4 for predicting time required for sticking.

The sticky-point test measures a very advanced stage of stickiness (Chuy and Labuza 1994), and the observation of lumps and slight resistance to stirring before the sticky-point indicate that there is an appreciable amount of sticking occurring before this point. The test offers no quantitative information about the cohesive strength of a powder, just a temperature above which the powder becomes very sticky (Papadakis and Bahu 1992). It would be useful to look at less developed stages of stickiness with a more quantitative test. The earlier stages of sticking may still be a problem in real world situations, particularly under storage conditions, where the time in which sticking can occur can be very large.

Another problem with the sticky-point test is the contact times it achieves. Downton *et al.* (1982) and Wallack and King (1988) use contact times of 1-10s in their calculations, which is probably a good approximation considering that the stirrer is turned a quarter

turn every other second. In this way some particles (those near the propeller) will be disturbed every second, while others near the edge of the test tube may only be disturbed every 10 seconds. A better experiment would have a way of obtaining a bigger range of contact times, from seconds up to hours, so that the effect of different contact times (and hence time for viscous flow to occur) can be observed.

A modification to the sticky point test could be made to overcome these problems. This test would involve a viscometer inserted into a small fluidised bed of amorphous lactose, using air with controlled relative humidity and temperature for fluidisation. The torque required to turn the spindle could be used to indicate the stickiness between the particles.

The main advantages anticipated for this method are that it would directly measure the surface of the particles, and that response to relative humidity and temperature changes would be quick. Bronlund (1997) and O'Donnell (1998) reported that absorption of moisture by amorphous lactose particles is very fast, and that the moisture sorption is limited by diffusion through a packed bed. In a fluidised bed amorphous lactose could therefore absorb water very quickly. This means the time consuming process of humidifying samples over saturated salts could be avoided, and the time taken to heat the sample to the temperature of interest could be greatly reduced, due to better heat transfer in a fluidised bed.

The contact time of particles in a fluidised bed is short, so this test will not give an indication of how stickiness progresses with time. However, as sticky particles collide and require more force to be separated, the viscometer should indicate a resulting increase in torque. This modified sticky point temperature test requires testing as it should provide several advantages over the traditional methods reported in the literature.

#### 2.4.3.2 Surface Caking Temperature

In their study of the sticking of several dairy-based food powders, Chuy and Labuza (1994) defined two temperatures for measuring the stickiness of the powders. One was the sticky-point temperature described above, and the other was the "surface caking temperature" ( $T_{sc}$ ). The test for  $T_{sc}$  was a modified version of the test used by Tsourouflis *et al.* (1976) to measure the "collapse temperature" of freeze dried carbohydrates. The procedure, as used by Chuy and Labuza (1994), involved sealing 1g samples of powders inside glass ampoules and immersing them in a controlled temperature oil bath. The temperature was raised at the same rates as for the sticky-point tests and the ampoules were removed from the bath every 5°C to be shaken and tapped on a hard surface.  $T_{sc}$  was defined as the temperature at which the powder failed to separate into finite particles and appeared as clumps.

The reported surface caking temperatures were lower than the sticky-point temperatures, while both were above  $T_g$ . Both measure the same phenomena, and only differ in that they observe different degrees of viscous flow (Chuy and Labuza 1994). Thus, the surface caking test may be useful for measuring an earlier stage of stickiness. The biggest problem with this test is that the endpoint is very subjective, and depends to a large degree on the judgment of the experimenter, and the force with which the samples are agitated.

#### 2.4.3.3 Blow Test

Paterson and Bronlund (1997) measured the caking strength of milk powder with a “blow test”. In this test, air was passed through a small diameter tube held at a fixed angle and constant height above a bed of powder. The powder beds had been stored at 20°C at different humidities. The flowrate of air was increased until a channel was formed in the bed and this flowrate recorded as a measure of the caking strength (and hence stickiness) of the powder. It was found that for the particular milk powder there was a linear relationship between the airflow required to carve a channel and the relative humidity that the powder had been stored at. Burr (1998) also used this test for the investigation of caking in cheese powders.

The advantage of the blow test is that it is more quantitative than the previous two tests. It gives a measure of how sticky the sample is after a contact period, rather than depending on a specific endpoint like the sticky-point or surface caking tests. For example, a powder sample at a certain temperature and relative humidity might not have reached its sticky-point after 5 minutes, but the blow test might show that the particles have become slightly sticky and an appreciable flow of air is required to form a channel.

Experiments involving the blow test could use individual dishes for each measurement, or one large bed of powder with the tester used on different portions of the bed over time.

#### 2.4.3.4 Caking Index

Aguilera *et al.* (1995) defined the caking index of a powder as the weight fraction of a sample retained by a screen with a certain opening size. The problem with this test is that small samples might limit its sensitivity, and using large samples might not be possible considering the amount of amorphous lactose available. If this test is performed in open air, the possibility exists for the amorphous lactose to absorb moisture and become sticky during the test, giving meaningless results.

#### 2.4.3.5 Flowability

The discharge rate from a funnel or bin is a measure of the cohesive strength of a powder (Peleg 1993, Aguilera *et al.* 1995). The problems of a large sample requirement and the absorption of moisture from the air again limit the usefulness of this test.

#### 2.4.3.6 Angle of Repose

The angle formed between the side of a heap of powder and the horizontal surface it is resting on is termed the angle of repose (Aguilera *et al.* 1995). The stickier the powder is, the greater the angle will be. Aguilera *et al.* (1995) report that the angle of repose is less than 40° for a free flowing powder. This is a simple test, but controlling the RH and the temperature of the testing environment would prove difficult.

#### 2.4.3.7 Cohesion Tests

The extrapolated stress required to cause failure of a particulate mass for a normal stress of zero is a measure of the cohesion of a powder (Aguilera *et al.* 1995). Pasley *et al.* (1995) looked at different cohesion tests for stickiness and concluded that the tests that gave the most consistent and repeatable results were the Jenike Flow Factor Tester and the Warren Spring Cohesion Tester. The Jenike Flow Factor Tester uses a cell comprised of two metal rings. This is filled with powder with one ring on top of the other, and weighted so the top ring is pushed against the lower ring. The force required to cause shearing of the powder is used as a measure of the caking strength.

The Warren Spring Laboratory (WSL) cohesion tester determines the cohesion of a sample of powder by measuring the torque applied, at failure, to a vaned paddle resting in a bed of powder. This is a relatively simple idea, and could probably be adapted for use in this work if required.

#### 2.4.3.8 Tests for use in this work

For the investigation of the time, temperature and moisture conditions under which amorphous lactose becomes sticky it appears that of all the methods reviewed the modified sticky point test and the blow test could be of the most use. These tests are relatively simple, although both are quite new and required some development before being used. While the sticky-point temperature test has been widely used in the past to investigate stickiness, it has been discounted here as it is not quantitative enough and is only of use for short contact times.

## 2.5 AMORPHOUS LACTOSE CRYSTALLISATION

### 2.5.1 INTRODUCTION

The crystallisation of amorphous lactose has been of interest for many years to both the food and pharmaceutical industries. The crystallisation of lactose in ice cream, condensed milk and milk powders is undesirable, as it degrades the product and causes it to be rejected by the consumer (Kedward *et al.* 1998). In pharmaceutical preparations the dissolution rate and bioavailability of poorly soluble drugs may be improved by dispersing the drug in an amorphous solid such as amorphous lactose, however problems with the crystallisation of such formulations has been encountered (Schmitt *et al.* 1999), causing product failure.

In the sticking and caking of dairy powders, amorphous lactose crystallisation is of interest because it releases water that can accelerate caking problems, and after viscous flow it is one mechanism for the formation of solid bridges between particles (Bronlund 1997). While work on the crystallisation of amorphous lactose has been ongoing since the 1940's (Sharp and Doob 1941) it has not been until the last decade that significant progress in predicting crystallisation rates has been made and models of amorphous lactose crystallisation have been put forward.

Important concepts in the crystallisation of amorphous lactose are the products formed during crystallisation, the rate of moisture sorption and desorption and the conversion of  $\beta$ -anhydride to  $\alpha$ -lactose monohydrate in the products.

#### 2.5.1.1 Product Of Crystallisation Of Amorphous Lactose

Amorphous lactose may crystallise to several different crystal forms, depending on the temperature and water activity conditions (Jouppila *et al.* 1997). The possibilities are  $\alpha$ -lactose monohydrate, anhydrous  $\beta$ -lactose, stable and unstable anhydrous  $\alpha$ -lactose and mixtures of anhydrous  $\alpha$ - and  $\beta$ -lactose. These forms have been identified using X-ray diffraction techniques (Jouppila *et al.* 1997, Bushill *et al.* 1965).

Bronlund (1997) conducted an extensive review of the literature in this area, and concluded that at water activities less than 0.55 either  $\beta$ -lactose or stable  $\alpha$ -lactose anhydride is formed. Above this value there is enough water present to form  $\alpha$ -lactose monohydrate crystals, but until the lactose reaches this level of water activity (if for example adsorption is still taking place as crystallisation starts) it may partially crystallise as the anhydrous product. This was confirmed in recent work by Schmitt *et al.* (1999), which showed that at a relative humidity of 57.5% amorphous lactose crystallised as a mixture of  $\alpha$ -lactose monohydrate and  $\beta$ -lactose anhydride. At high

water activities crystallisation to  $\alpha$ -lactose monohydrate takes place, and solid state conversion from anhydrous to hydrous crystals can also occur. The final product of amorphous lactose crystallisation will therefore vary depending on the conditions it is carried out under.

### 2.5.1.2 Sorption and Desorption Effects

In most experiments of amorphous lactose crystallisation the temperature and moisture conditions must change from those where crystallisation cannot occur to those that can cause nucleation and crystal growth. This has often been achieved by increasing the moisture content of the amorphous lactose so that it will crystallise at ambient temperature (Bronlund 1997, Schmitt *et al.* 1999). In any such experiment care must be taken to ensure that the rate of sorption is faster than the rate of crystallisation (Bronlund 1997). If this is not the case then the experiment will merely be measuring the rate of moisture sorption and not the rate of amorphous lactose crystallisation. The same is true of the rate of moisture desorption, especially if crystallisation is being followed by loss of water (Schmitt *et al.* 1999).

Bronlund (1997) and O'Donnell (1998) showed that moisture sorption into a bed of amorphous lactose is limited by diffusion through the bed. Thus, a shallow bed of lactose would give quicker sorption times than a deeper bed, indicating that one way to ensure quick sorption is to use a small sample spread thinly in the measuring device. This has physical limitations, such as the area available to spread the sample, and the sample weight required to obtain useful results. Another way to cut out the effect of moisture sorption altogether is to humidify the sample at a low temperature then begin crystallisation by raising the temperature (Bronlund 1997). In this way heat transfer becomes the limiting factor.

Little or no data is available on the rate of moisture desorption during amorphous lactose crystallisation. The relative humidity of the air around the sample and the temperature both affect how fast water is lost, with hot dry conditions being best for fast desorption. Schmitt *et al.* (1999) checked that water desorption was not limiting their crystallisation experiment by making sure that the crystallisation rate constant increased with increasing relative humidity at a constant temperature. It was found that water desorption was not limiting at 57.5% relative humidity and 25°C.

### 2.5.1.3 Conversion of $\beta$ to $\alpha$ -lactose

Buckton *et al.* (1998) found that anhydrous  $\beta$ -Lactose could convert to  $\alpha$ -Lactose monohydrate in the solid state. This conversion could interfere with the observation of crystallisation by weight loss because it involves weight gain, (by incorporating a

molecule of water) reducing the apparent rate of crystallisation. This means that it is desirable to perform the crystallisation experiment under conditions where this conversion is negligible.

In order to model this solid state conversion, Bronlund (1997) used mutarotation kinetics, assuming that the system could be viewed as a saturated solution of  $\beta$ -Lactose. Using this approach, it was predicted that after one month at a relative humidity of 80% and a temperature of 30°C, only 15% of the  $\beta$ -Lactose would convert to  $\alpha$ -lactose monohydrate. This agreed with the results of the  $\beta$ -Lactose sorption isotherm measured in the same work, where conversion to  $\alpha$ -lactose monohydrate was suspected.

It is therefore evident that for crystallisation experiments occurring over short time periods (in the order of a fortnight or less) and at relative humidities of 80%, conversion of  $\beta$  to  $\alpha$ -lactose monohydrate should not cause any problems.

## 2.5.2 PREVIOUS WORK ON AMORPHOUS LACTOSE CRYSTALLISATION

In the determination of the kinetics of amorphous lactose crystallisation there have been two main methods used. These have been differential scanning calorimetry (DSC) and gravimetric analysis. In addition, x-ray diffraction has been used, and in some cases infra red techniques. This section looks at the previous work on the crystallisation of amorphous lactose and the experimental techniques used.

### 2.5.2.1 Differential Scanning Calorimetry (DSC)

Roos and Karel (1990, 1991a, 1992) used isothermal DSC to follow the progress of amorphous lactose crystallisation. Isothermal DSC measures the heat flow from a sample sealed in an aluminium pan at constant temperature, with crystallisation being observed as a large exotherm. Since crystallisation occurs when the mobility of the lactose molecules is sufficient to allow alignment into a lattice, and mobility is related to viscosity, Roos and Karel (1990, 1991a, 1992) used the WLF equation (equation 2.5) to predict crystallisation times for amorphous lactose at different values of  $(T-T_g)$ . Although they found that completely dry amorphous lactose followed the WLF equation well at high values of  $(T-T_g)$ , samples equilibrated at increasingly high relative humidities required less and less time to crystallise. Different constants for the WLF equation had to be used for different moisture contents, even when the value of  $(T-T_g)$  was the same. The explanation given by the authors, and Bronlund (1997), was that in the sealed DSC pans the moisture released by crystallisation was available to increase the moisture content of the remaining amorphous material. This lowered  $T_g$ , increasing  $(T-T_g)$  and therefore increasing the crystallisation rate throughout the experiments. Hence, of the data of Roos and Karel (1990), only that for dry amorphous lactose can be

considered to have taken place at constant  $(T-T_g)$ . Roos and Karel (1992) performed an experiment at constant relative humidities, whereby amorphous lactose was stored inside jars over saturated salt solutions and samples were taken periodically to be checked for crystallinity. Using this method the data was obtained at constant  $(T-T_g)$  values. The constant  $(T-T_g)$  data and the WLF equation from Roos and Karel (1990) is shown on figure 2.5.

Kedward *et al.* (1998) used isothermal DSC to investigate the crystallisation of amorphous lactose at high temperatures, where the value of  $(T-T_g)$  ranged between 40-130°C and crystallisation times were in the range of 20-140 seconds. The data of Kedward *et al.* (1998) can be seen in figure 2.5 as being significantly different from any model predictions or the data of any other workers. This could be due to the fact that they used non-dry amorphous lactose in sealed DSC pans, giving rise to the same problems of lowering  $T_g$ , as mentioned for the work of Roos and Karel (1990, 1991, 1992). What is particularly confusing about this is that the samples of amorphous lactose were stored over phosphorous pentoxide, a method that is usually used for complete drying of a sample (Bronlund 1997, Jouppila and Roos 1994a), yet the 'dry' moisture content was measured by Kedward *et al.* (1998) as being 3.2%. The glass transition temperature for this lactose was measured by the authors as 57°C, far below the  $T_g$  for dry amorphous lactose of 101°C (Roos and Karel 1990, Lloyd *et al.* 1996), indicating that there was in fact moisture present. With moisture present in the sealed pans the data of Kedward *et al.* (1998) cannot be considered as having been obtained at constant  $(T-T_g)$ .

#### 2.5.2.2 Gravimetric Studies

When amorphous lactose crystallises the moisture in it is driven out (Bronlund 1997, Schmitt *et al.* 1999). Gravimetry involves measuring this weight loss with time, the change in weight being an indication of the progress of crystallisation. This method is most accurate in situations where the crystallisation time is greater than merely a few minutes (Kedward *et al.* 1998), and so is not of use for  $(T-T_g)$  values of 40°C or greater. Bronlund (1997) conducted a gravimetric study to follow the crystallisation of amorphous lactose at 30°C and 45 and 43.5% relative humidity, choosing these conditions so that the product of crystallisation was known, sorption effects were not limiting, and conversion of  $\beta$ -lactose to  $\alpha$ -lactose monohydrate was negligible. The samples of lactose were placed on a sensitive balance, which was enclosed by a plastic chamber through which controlled humidity air was sparged. The change in weight with time was logged by computer.

### 2.5.2.3 Crystallisation Model

Bronlund (1997) analysed data obtained with a gravimetric study with the Avrami equation (equation 2.6), where  $Y(t)$  is the crystallinity of the sample at time  $t$ ,  $k$  is the crystallisation rate constant containing both nucleation and growth rates, and  $n$  is the Avrami index.

$$Y(t) = 1 - e^{-kt^n} \quad (2.6)$$

Equation 2.6 can be linearised to give:

$$\log[-\ln(Y)] = n \log(t) + \log(k) \quad (2.7)$$

From equation 2.7 a plot of  $\log[-\ln(Y)]$  versus  $\log(t)$  gave a straight line with a slope  $n$  and intercept of  $\log(k)$ . Bronlund (1997) showed that  $n$  was equal to 3, which corresponds to linear growth in three dimensions. This was confirmed by Schmitt *et al.* (1999) who found  $n$  equal to 3 also.

Bronlund (1997) determined an equation for  $k$  (equation 2.8), by incorporating the WLF equation to describe the change in viscosity of amorphous lactose with  $(T-T_g)$ . It was also assumed that the rate of nucleation was not rate limiting, hence the nucleation parameter in  $k$  tended to zero.

$$k = C_C \left( e^{\frac{-C_A}{R[C_B + T - T_g]}} \right)^3 \quad (2.8)$$

The values of the constants  $C_A$ ,  $C_B$  and  $C_C$  ( $3.54 \times 10^4$ , 108.9 and  $3 \times 10^{27}$  respectively) were determined by fitting the equation to the experimental data obtained by Bronlund (1997), and that obtained by Roos and Karel (1990, 1992) at constant  $(T-T_g)$ . Combined with the Avrami equation, this gave a model of crystallisation that fitted the experimental data much better than the WLF model put forward by Roos and Karel (1990, 1992). Using this model, if the values of  $(T-T_g)$  and  $n$  are known, then the actual crystallisation rate can be predicted as a function of time using the differentiated form of the Avrami equation, equation 2.9 (Bronlund 1997).

$$\frac{d(1-Y)}{dt} = nkY \left[ \frac{-\ln(Y)}{k} \right]^{\frac{n-1}{n}} \quad (2.9)$$

Figure 2.5 shows both the WLF model (Roos and Karel 1990, 1992) and the mixed Avrami/WLF model (Bronlund 1997) predictions for the time taken to reach 90% crystallinity, as well as the available experimental data.

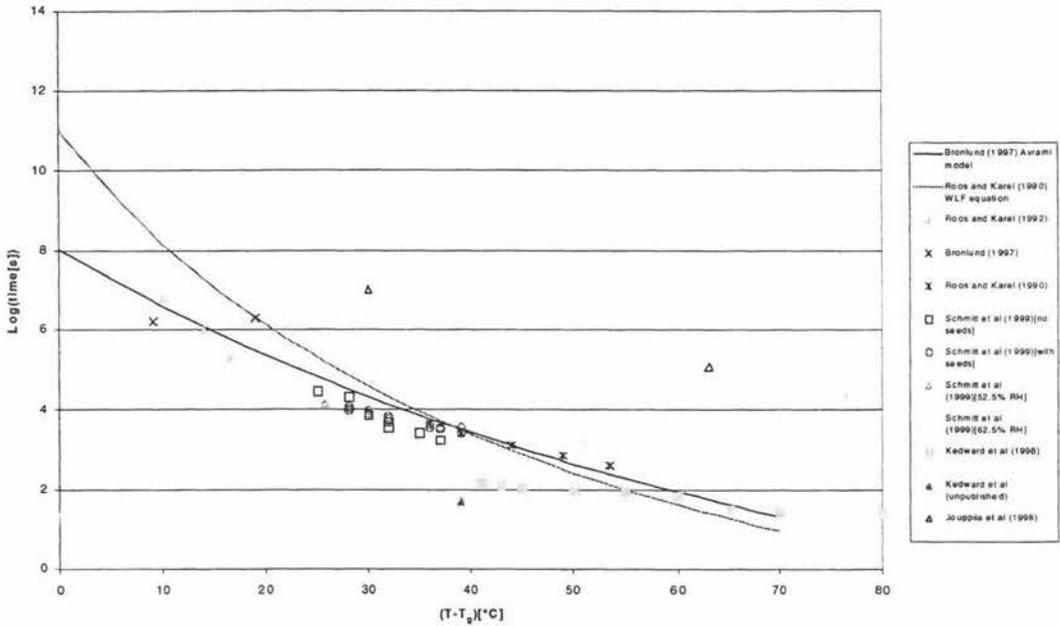


Figure 2.5 Time to 90% crystallinity versus  $(T-T_g)$

Bronlund (1997) concluded that more data for crystallisation in the intermediary  $(T-T_g)$  range was required. Such data has recently been published by Schmitt *et al.* (1999). This group conducted gravimetric experiments on amorphous lactose at 57.5% relative humidity and a range of temperatures giving  $(T-T_g)$  values of 25°C to 40°C. While Schmitt *et al.* (1999) did not appear to be concerned with  $(T-T_g)$ , sufficient data is presented for their work to be of use here. Values of  $k$ , determined from the Avrami equation, were given as functions of temperature. Using these, the Avrami equation, and  $T_g$  for a relative humidity of 57.5%, the time to reach 90% crystallinity was calculated and plotted on figure 2.5. It can be seen that while the agreement of this data with the model of Bronlund (1997) is not perfect, but is very close. The disagreement could be explained by the error inherent in estimating  $T_g$ , which was shown in section 2.3.2.2 to be quite large. Also, crystallisation times could be shortened if crystallisation started before moisture sorption onto the samples was finished, as time was corrected by subtracting the time for moisture sorption. From an inspection of representative raw data presented in Schmitt *et al.* (1999) it would appear that this was not the case.

Since the data of Schmitt *et al.* (1999) seems to show a close fit with the best current model, and is in a  $(T-T_g)$  range where no previous data existed, the model should be

refitted to the available data, including the work of Roos and Karel (1990, 1992), Bronlund (1997) and Schmitt *et al.* (1999). In this way the constants of the model could be made more accurate, giving a better model of amorphous lactose crystallisation. Care needs to be taken with the value of  $T_g$  used in the calculation of  $(T-T_g)$ , and if a more accurate way of estimating  $T_g$  can be found then the data presented in figure 2.5 should be reassessed.

From the available literature data it appears that crystallisation depends on the value of  $(T-T_g)$ . Data has been collected at 150°C and 0%RH, and at 18-32°C and 57.5%RH with the same  $(T-T_g)$  which agrees with follows the model formulated by Bronlund (1997). Other data that follows this model has been collected at relatively low temperatures and higher humidities (25-45°C, 30-53%RH). The only gap in the data, which would confirm that only  $(T-T_g)$  is important and not the conditions required to achieve it, is at humidities around 20% and temperatures around 70°C.

#### 2.5.2.4 Other Methods

Jouppila *et al.* (1997, 1998) followed amorphous lactose crystallisation using x-ray diffraction. This method measures the intensities of peaks in x-ray diffraction patterns. As the sample becomes more crystalline the intensity of the peaks increases, giving an indication of the progress of crystallisation.

The data of Jouppila *et al.* (1998) is plotted on figure 2.5. It is obvious that this data shows little agreement with any of the other data or models presented here. The data of Jouppila *et al.* (1997) has not been included on figure 2.5 for reasons of maintaining a reasonable scale on the graph. It is sufficient to say that this data does not even agree with that of Jouppila *et al.* (1998). For example, at a condition of 66.2% relative humidity and 24°C, Jouppila *et al.* (1997, 1998) give half time values of 42 and 3.4 hours respectively for the observation of the same peak in the x-ray diffraction pattern. This suggests that this method of following amorphous lactose crystallisation has some large errors associated with it, and is not very reproducible. The authors found that amorphous lactose was crystallising mainly as a mixture of  $\alpha$ -lactose monohydrate and anhydrous crystals with  $\alpha$ - and  $\beta$ -lactose in a molar ratio of 5:3. They also suggested that the nuclei formed initially were the determinants of the ratio of the various crystals formed. Since Jouppila *et al.* (1997, 1998) used only the x-ray diffraction peak at 20° to follow crystallisation, variations in the types of crystals formed and their relative amounts could make the x-ray diffraction data difficult to interpret in a quantitative sense, leading to the observed discrepancies.

Buckton *et al.* (1998) report the use of near infra-red spectroscopy (NIR) to observe crystallisation in amorphous lactose. This was possible by studying the region of the

NIR spectrum where water shows stretching frequencies (1825 – 1975nm) and the region where  $\beta$ -lactose shows characteristic peaks (2075 – 2160nm). Water shows as a broad peak at about 1925nm, which reaches a maximum intensity when the maximum amount of water is absorbed. When crystallisation starts a peak at about 1935nm due to crystal water in  $\alpha$ -lactose monohydrate is observed, as well as peaks around 2100nm due to  $\beta$ -lactose. These peaks increase in intensity as crystallisation proceeds. While Buckton et al. (1998) concluded that this method was a valuable tool for following crystallisation and the solid state conversion of  $\beta$ - to  $\alpha$ -lactose monohydrate, there is no evidence presented for its use in a quantitative sense – ie, for determining rates. The nature of infra-red spectra often precludes their use for such studies.

## 2.6 CONCLUSIONS

Sticking of amorphous lactose occurs through a viscous flow mechanism, when it experiences conditions of moisture and temperature that put it above the glass transition temperature. Bridges between particles form over time and bind them together. The size, and therefore the strength of these bridges depends on how long they have had to form, and how far above  $T_g$  the conditions are. Several experimental methods for investigating the conditions under which amorphous lactose becomes sticky have been identified. Of particular importance to sticking is the concept of the glass transition temperature. However, the disagreement and scatter amongst the available  $T_g$  data for amorphous lactose means that it is impossible to confidently predict  $T_g$  from the moisture content or water activity of a sample. Work attempting to reduce the variability of  $T_g$  prediction from moisture content or water activity is the focus of chapter 3.

New crystallisation data has recently been published that helps confirm the best available model for amorphous lactose crystallisation. Interpretation of this new data, and attempts to fill the gaps in the available data at higher temperatures are the focus of chapter 4. Chapters 5 and 6 deal with the development of a reliable method for predicting the rate of stickiness formation in amorphous lactose powder. In this way some recommendations on how to avoid industrial sticking and caking problems were possible.

# CHAPTER 3

## PREDICTING $T_g$

### 3.1 INTRODUCTION

The glass transition temperature ( $T_g$ ) is important to the study of sticking and crystallisation phenomena. It is the temperature at which significant numbers of lactose molecules can begin to move past each other within the amorphous matrix. The amount that  $T_g$  is exceeded by, the value of  $(T-T_g)$ , determines the viscosity of amorphous lactose in the rubber state, and so determines how fast and to what extent it becomes sticky, and the rate at which it crystallises. Before  $(T-T_g)$  can be calculated,  $T_g$  must be known with reasonable accuracy. The key requirement for this work is to have some method of predicting the potential for sticking or crystallisation based on a measurement that can be easily taken for a milk powder, such as a moisture content or the air humidity at the drier outlet. Thus, a way of accurately predicting  $T_g$  from the water activity or moisture content of amorphous lactose is needed.

Many researchers have collected data on the glass transition temperature of amorphous lactose at different moisture conditions, and it would seem reasonable to be able to predict  $T_g$  based on this data. However, as outlined in the previous chapter, this leads to large errors because of the differences between the data of the different publications.

This chapter focuses on ways of predicting the  $T_g$  of amorphous lactose, by examining the available data and looking for possible explanations for the poor agreement of the different data sets.

### 3.2 RESIDUAL MOISTURE

#### 3.2.1 RESIDUAL MOISTURE IN FREEZE-DRIED SUGARS

Amorphous sugars are often prepared by freeze-drying solutions, as outlined in section 2.3.3. The moisture content after freeze-drying is affected by the particular drying conditions used, and there is usually a small amount of moisture left. Desiccation for a week or more over a strong desiccant, such as phosphorous pentoxide, is often used to complete the drying process and remove this moisture (Bonelli *et al.* 1997, Arvanitoyannis and Blanshard 1994). Although this is used as a conventional method to give completely dry material, it does not guarantee that there is no residual moisture present (Roos and Karel 1991a,b). Roos (1993) noted that differences in reported 'dry'

glass transition temperatures for sugars could be due to residual moisture that is not removed by desiccation over phosphorous pentoxide.

Bonelli *et al.* (1997) found that freeze-dried amorphous sugars (lactose, trehalose, sucrose, and maltose) still contained a small amount of residual moisture, even after extended desiccation over phosphorous pentoxide. The sugars were freeze-dried, then further dehydrated over phosphorous pentoxide for one week at 25, 35 and 45°C. The residual moisture contents of the sugars were determined by oven drying the samples at 105°C, followed by a period at 120°C.

The results of Bonelli *et al.* (1997) are shown in table 3.1. It can be seen that freeze-dried lactose desiccated over phosphorous pentoxide at 25°C contained 2% residual moisture, and that the amount of residual moisture decreased with increasing desiccation temperature.

**Table 3.1 Lactose residual moisture results (Bonelli *et al.* 1997)**

Desiccation temp. (°C)	25	35	45
Residual moisture content (% dry basis)	2.0	1.6	1.3

Further indication of residual moisture was given when desiccated samples were heated at temperatures slightly above the reported 'dry' glass transition temperatures. Lactose samples heated to 105°C in sealed vials exhibited structural collapse, while those in open vials did not. The authors attributed this to the residual moisture being released from the open vials, causing  $T_g$  to be raised above the published 'dry' value of 101°C given by Roos and Karel (1990). Any residual moisture present could not escape from the sealed vials and remained as a plasticiser, keeping the glass transition temperature at about 101°C – thus at 105°C the  $T_g$  of the sample was exceeded and collapse occurred. Collapse is a structural change exhibited by amorphous freeze-dried materials that involves shrinkage of the solid matrix, occurring at temperatures above  $T_g$  (To and Flink 1978, Tsourouflis *et al.* 1976).

### 3.2.2 IMPLICATIONS FOR THE GLASS TRANSITION TEMPERATURE

The glass transition temperature of 'dry' amorphous lactose has been reported as 97°C (Jouppila and Roos 1994), 101°C (Roos and Karel 1990, Lloyd *et al.* 1996), 104°C (Sebhatu *et al.* 1997), 114°C (Schmitt *et al.* 1999, Taylor and Zografis 1998) and 116°C (Hill *et al.* 1998). The value of 114°C obtained by Schmitt *et al.* (1999) was measured in an open pan using differential scanning calorimetry (DSC). Taylor and Zografis (1998) attributed their high  $T_g$  value of 114°C to the fact that they performed the DSC runs in

non-sealed pans, allowing residual moisture to be driven off. Further examination of the different publications reveals that the highest values for the dry  $T_g$  were obtained using open DSC pans, while all the lower values were measured using hermetically sealed pans. For these lower values the actual moisture content was assumed to be zero in each case, and was not actually measured. Using the same argument as Bonelli *et al.* (1997), it is likely that in open DSC pans any residual moisture can escape during the determination, raising  $T_g$  compared to the determinations in sealed pans. This implies that on a  $T_g$ /moisture content graph, the values obtained in sealed pans at a moisture content of zero should be shifted to the right slightly, in recognition of the fact that the samples contained some moisture. Just how much moisture they contained is unknown, but a good approximation would be 2%, as measured by Bonelli *et al.* (1997) for freeze-dried amorphous lactose.

One method that has been used to measure the moisture content of amorphous lactose is the gravimetric method (Bronlund 1997, Roos and Karel 1990, Jouppila and Roos 1994a, Sebhatu *et al.* 1997). This involves measuring the weight change of samples equilibrated at different humidities, using a sample dried over phosphorous pentoxide as the reference for zero moisture content. The fact that some moisture may not be removed by desiccation over phosphorous pentoxide means that there is a systematic error inherent in using the gravimetric method to determine moisture contents, and all these moisture contents should be higher. This could be corrected for by adding a value for residual moisture to all the moisture contents determined gravimetrically. Other methods for moisture content determination, such as Karl Fischer titration (Lloyd *et al.* 1996, Hargreaves 1995) and oven drying determine total moisture and avoid this residual moisture problem. This could explain why, in figure 2.1, the sorption isotherms measured using the gravimetric method disagree with the experimental values obtained by Lloyd *et al.* (1996) and Hargreaves (1995) using Karl Fischer titration.

This work used spray-dried lactose. It was desirable to find how much residual moisture was present in spray-dried lactose, as it may not be the same as for freeze-dried lactose. Once the amount of residual moisture present was known the available data could be re-evaluated to obtain better predictions of  $T_g$ .

The available data for  $T_g$  includes measurements obtained with both spray and freeze-dried amorphous lactose. Different structural features, such as different porosities and surface areas, may mean that the two types of lactose retain different amounts of residual moisture, affecting the  $T_g$  results accordingly.

### 3.2.3 RESIDUAL MOISTURE MEASUREMENTS

An experiment was performed to measure the amount of residual moisture present in spray-dried amorphous lactose after desiccation over phosphorous pentoxide. This was done for desiccation times of 1, 2 and 3 weeks to gain an understanding of the kinetics of moisture removal. In addition, the experiment was also performed with freeze-dried amorphous lactose, to see if there was any difference in residual moisture content between the two types of material.

#### 3.2.3.1 Preparation Of Amorphous Lactose

##### 3.2.3.1.1 *Spray-dried lactose*

Amorphous lactose was spray-dried using the method outlined by Lloyd *et al.* (1996) as a guide.  $\alpha$ -Lactose monohydrate (200 mesh, Lactose New Zealand Ltd.) was dissolved in distilled water to make a solution of approximately 300g/L, which was then used as the feed to an Anhydro Lab S.1 spray drier. The drying conditions were; feed temperature 80°C, inlet air temperature 200°C, outlet air temperature 96°C (maintained by varying the feed flow-rate). A disc atomiser was used for feed atomisation, and the solids were collected in a cyclone as a fine white powder with roughly the same consistency as icing sugar. A small flow of cool dry air (20°C, 15% relative humidity) was introduced to the collection vessel at the bottom of the cyclone in order to cool the product and prevent any stickiness from occurring in the fresh powder. It was stored under dry air in sealed plastic bags inside an airtight container.

The product was confirmed amorphous by observation under a polarising microscope, and by the gravimetric test developed by O'Donnell (1998). Both tests showed no signs of any crystallisation, so the product was assumed to be 100% amorphous. Particle size analysis was carried out at the New Zealand Dairy Research Institute, using a Malvern particle size analyser. The average particle diameter was 27 $\mu$ m.

##### 3.2.3.1.2 *Freeze-dried lactose*

A 10% solution of  $\alpha$ -lactose monohydrate was shell frozen at -25°C, then stored at -80°C overnight. Freeze-drying was carried out in a Virtis 10-020 lab freeze-drier at -55°C and 250 millitorr over 48 hours. The freeze-dried materials were broken up under dry air and used immediately.

The freeze-dried product appeared similar to the spray-dried lactose, but examination under a polarising microscope showed that some crystals were present. These appear as bright spots in the otherwise dark amorphous material. If these crystals had precipitated before freezing was complete then they would be in the form of  $\alpha$ -lactose monohydrate.

If they had formed during drying then the type of crystals would depend on the humidity conditions in the drying vessel. As no indication of collapse or bubbling was evident in the freeze-dried samples, it is most likely that the crystals appeared during freezing and were therefore  $\alpha$ -lactose monohydrate crystals. Shell freezing took place with relatively large (200mL) samples, so the freezing was probably not fast enough to freeze the sample completely before crystallisation took place.

### 3.2.3.2 Moisture Content Determination

To test for the presence of residual moisture, samples of spray and freeze-dried amorphous lactose were dehydrated at 20°C over phosphorous pentoxide for periods of 1, 2 and 3 weeks, then weighed. These 'dry' samples were then placed in a forced convection oven at 120°C for 24hrs, after which time they were weighed, then placed back in the oven for a further 24hrs and reweighed to check for any additional weight loss. The observed weight loss during oven drying was attributed to the loss of residual moisture.

The oven drying was carried out at 120°C because at this temperature all the water of crystallisation is removed (Bronlund 1997). This fact means that moisture content determinations using this method for powders containing crystalline lactose are unreliable. However, when measuring the moisture content of pure amorphous lactose it is desirable to remove the water of crystallisation from any  $\alpha$ -lactose monohydrate that is formed during heating in the oven, so that the true moisture content is measured. As long as the sample is completely amorphous to start with, and all the crystal water is removed from any  $\alpha$ -lactose monohydrate formed during drying, this method will give accurate moisture content measurements.

A possible problem with this method is that of sample weight loss through mechanisms other than drying. This includes the possibility of the lactose decomposing to form other products, some of which may be lost as gases.  $\alpha$ -Lactose monohydrate decomposes just above its melting point at 202°C, while  $\beta$ -lactose does the same at 252°C (Pritzwald-Stegmann 1986). Therefore, at 120°C, decomposition is unlikely to occur. The flow of air inside the oven could physically remove some of the lactose particles. To prevent this the samples were covered with inverted beakers. The hot air could still circulate through the wire tray of the oven, but only very slowly. Reweighing the samples after the second period in the oven showed no significant weight loss, indicating that drying was complete and no lactose was blown out of the moisture dishes.

The phosphorous pentoxide desiccator was opened under dry air to avoid any moisture sorption. Samples in the oven were sealed as quickly as possible after opening the oven for the same reason. It is possible that the amorphous lactose samples could absorb

moisture once the air trapped with the sample cools below 100°C. Taking into account the headspace in the moisture dish and the absolute humidity of the air in the oven, it was calculated that in a worst case scenario a 5g sample would absorb around 0.00006g water/g lactose. The residual moisture being measured is in the order of 0.02g/g, so it is reasonable to assume that any moisture absorbed in this way will be negligible. Further evidence for the validity of this assumption comes from Bonelli *et al.* (1997), who found that when amorphous lactose stored over phosphorous pentoxide was exposed to 84% RH for 10 minutes the moisture pick-up was only 0.002g/g. During weighing in this experiment, the air in the headspace of the moisture dishes, once cooled, could reach a maximum of about 50% RH, and the exposure time was in the order of 2-3 minutes.

### 3.2.3.3 Results and Discussion

The results of the residual moisture experiment are shown in table 3.2 below. Values are shown with their 95% confidence interval, and are the average of 4 replicates.

**Table 3.2 Residual moisture experiment results**

Weeks over P <sub>2</sub> O <sub>5</sub>	Residual Moisture Content (g water/g dry lactose)	
	Spray-dried lactose	Freeze-dried lactose
0	0.0375 ±0.0004	0.063 ±0.001
1	0.0165 ±0.0003	0.033 ±0.001
2	0.011 ±0.001	0.026 ±0.001
3	0.0101 ±0.0005	0.024 ±0.001

It is obvious from table 3.2 that the freeze-dried amorphous lactose contained more residual moisture than the spray-dried variety. This could indicate that the freeze-dried product tends to hold more residual moisture than the spray-dried. However, the polarising microscope observations showed that the freeze-dried lactose was partially crystalline. If these crystals were  $\alpha$ -lactose monohydrate, the water of crystallisation would then be driven off in the 120°C oven and measured as residual moisture, explaining the high moisture content results.

It is reasonable to assume that the residual moisture measured in the spray-dried lactose did not come from the crystal water of  $\alpha$ -lactose monohydrate, as the gravimetric test gave a result of 0% crystallinity, and the polarising microscope failed to detect any crystals. For crystalline  $\alpha$ -lactose monohydrate to account for the residual moisture measured here after 1 week the samples would have to be approximately 40% crystalline.

The average residual moisture content of 0.0165 g/g for spray-dried lactose after 1 week is only slightly lower than that measured by Bonelli *et al.* (1997) for freeze-dried lactose after the same time period (0.02 g/g). If the freeze-dried results here are discounted due to non-amorphous samples, then this comparison is the only one possible. From this, it would have to be concluded that spray-dried and freeze-dried lactose tend to retain similar amounts of residual moisture, despite their likely structural differences.

The effect that time over phosphorous pentoxide has on residual moisture content is shown in figure 3.1. It can be seen that moisture removal is rapid in the first week, slows significantly over the second, and is very slow in the third week. The two curves in figure 3.1 for the two types of amorphous lactose are of very similar shapes, although the freeze-dried curve is much higher than the spray-dried curve. The reason for the higher moisture content in the freeze-dried lactose has already been discussed – the likely presence of  $\alpha$ -lactose monohydrate. The similar shape of the two curves indicates that the kinetics of moisture removal are the same for the two types. Considering that the only reliable data for freeze-dried amorphous lactose shows a similar amount of residual moisture as that measured here, it can be concluded that after the same period of desiccation in the same conditions, both spray and freeze-dried amorphous lactose will contain the same amount of residual moisture. Therefore, the  $T_g$  will be affected by the same amount in each case.

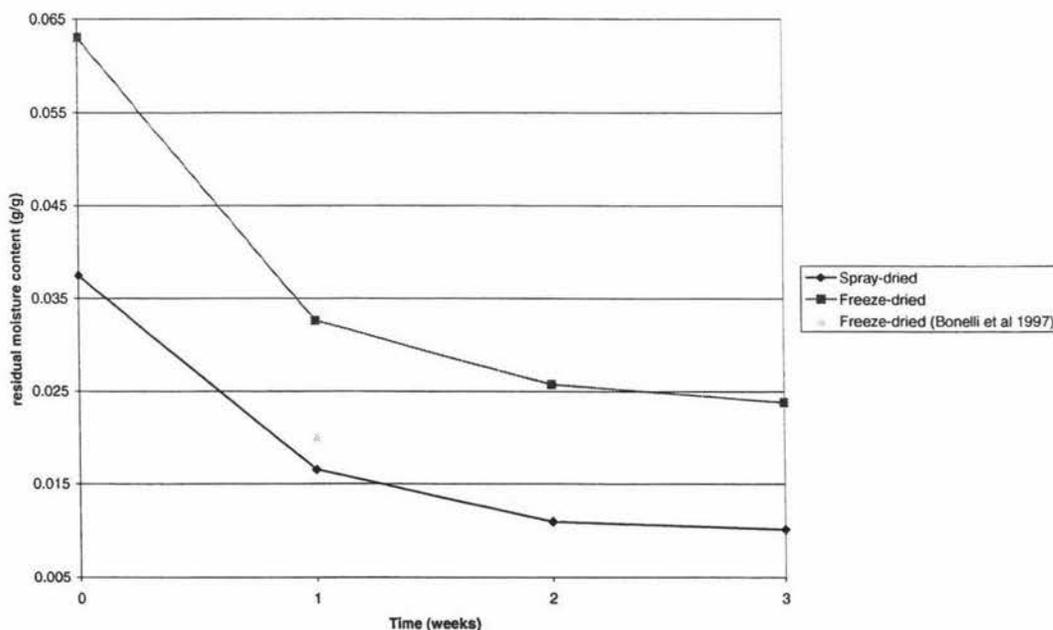


Figure 3.1 Effect of desiccation time on residual moisture content

While Bonelli *et al.* (1997) concluded that freeze-dried sugars contained residual moisture, they did not give any explanation as to why this moisture is so strongly held that phosphorous pentoxide cannot remove it. Although there is no crystalline  $\alpha$ -lactose monohydrate in pure amorphous lactose, amorphous  $\alpha$ -lactose is present. The  $\beta$ - to  $\alpha$ -lactose ratio in a lactose solution that has been allowed to reach equilibrium is 1.45 at 80°C (Lowe 1993). Given that the ratio of  $\beta$ - to  $\alpha$ -lactose in the amorphous lactose is the same as in the feed solution before spray or freeze-drying (Lowe 1993) there is about 40%  $\alpha$ -lactose in amorphous lactose. If each  $\alpha$ -lactose molecule were to associate with one water molecule then the moisture content would be 0.021g/g dry lactose. This is only slightly higher than the residual moisture content measured in this work after 1 week, and agrees within errors with the value measured by Bonelli *et al.* (1997) after the same period. Thus it seems possible that the residual moisture remaining after 1 week of desiccation could be due to a water molecule being weakly bound to each  $\alpha$ -lactose molecule and therefore being harder to remove. However, it could also be possible that the low driving force for moisture removal at these low moisture contents means that moisture removal is just very slow, and the  $\alpha$ -lactose molecules have no effect. Figure 3.1 shows that half of the moisture remaining after 1 week of desiccation is removed very slowly over the next 2 weeks, with the last 0.01g/g appearing to be very hard to remove.

### 3.3 RE-EXAMINATION OF LITERATURE DATA

#### 3.3.1 MOISTURE SORPTION

Figure 2.1 shows the available data for moisture sorption of amorphous lactose, along with the two GAB isotherms fitted by previous workers. It is apparent from figure 2.1 that publications where moisture contents were determined with a “total moisture” method like Karl Fischer titration give significantly higher moisture contents than those determined gravimetrically. With a measured value for residual moisture, the moisture contents determined gravimetrically (Roos and Karel 1990, Jouppila and Roos 1994b, Bronlund 1997) can be corrected. Figure 3.2 shows the corrected data.

With this correction applied, the two isotherms and the gravimetric data are much similar to the data where moisture contents were determined via Karl Fischer Titration (Lloyd *et al.* 1996, Hargreaves 1995). The data points where the fit with the isotherms is poor could be explained by experimental error and/or the different treatments that the amorphous lactose samples received, leading to differing amounts of residual moisture.

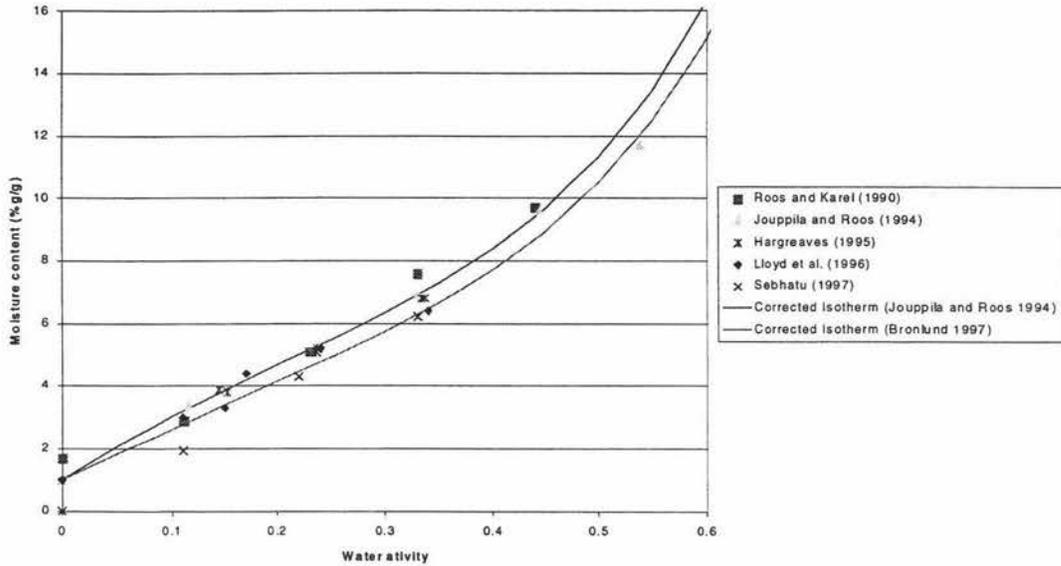
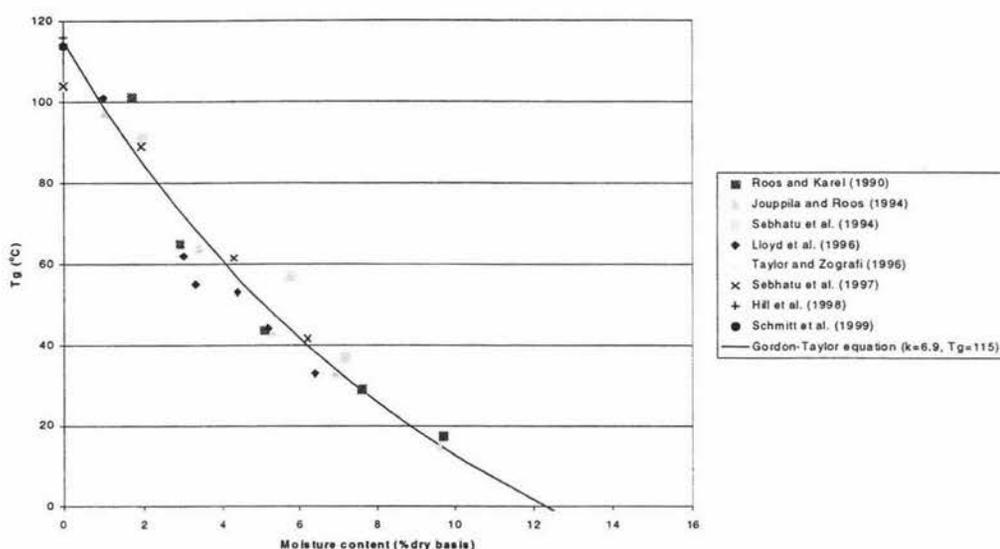


Figure 3.2 Corrected sorption data

### 3.3.2 $T_g$ /MOISTURE CONTENT

The value for residual moisture measured here can be applied to the available  $T_g$ /moisture content data to correct the moisture contents which were determined gravimetrically. Figure 3.3 shows the data with these corrections made.

Roos and Karel (1990), Jouppila and Roos (1994b) and Sebhatu *et al.* (1997) used the gravimetric method to determine moisture contents. Roos and Karel (1990) stored over phosphorous pentoxide for “at least one week”, so in the absence of more specific information this data has been corrected using a value for residual moisture of 0.0165 g/g. Jouppila and Roos (1994b) desiccated for only 24 hours in a vacuum desiccator at 24°C. The effect of a vacuum desiccator on residual moisture is unknown. As a best guess this data was corrected by a value of 0.01 g/g. Sebhatu *et al.* (1997) stored amorphous lactose over phosphorous pentoxide at 60°C for 2 weeks. The work of Bonelli *et al.* (1997) showed that increasing the desiccation temperature decreased the amount of residual moisture present (table 3.1 above), so desiccation at 60°C for two weeks may have removed all the residual moisture. The data from this publication was not corrected, and it showed good agreement with the data from other work. The remainder of the researchers used a method for determining moisture content that measures total moisture. Lloyd *et al.* (1996) did not measure the moisture content of amorphous lactose stored over phosphorous pentoxide for three weeks, and assumed no moisture was present (Lloyd 1999). Data presented in this publication as having zero moisture has therefore been corrected by the residual moisture value measured here.



**Figure 3.3 Glass transition temperature versus moisture content, corrected for residual moisture**

The corrected data in figure 3.3 shows much better agreement with the rest of the available data than previously in figure 2.2. Figure 3.3 also shows the Gordon-Taylor equation (equation 2.2) with a new value for the  $T_g$  of dry amorphous lactose of 115°C. The Gordon-Taylor equation was re-fitted to the available data to obtain a new  $k$  value of 6.9. Overall the fit of the Gordon-Taylor equation with the corrected data is far more acceptable than it was previously. There are still several data points which seem to fall a long way from the equation predictions, but these could be explained as outliers. The values for residual moisture used to correct the data are estimates based on residual moisture measurements made under certain experimental conditions – 1,2 or 3 weeks, 20°C, no vacuum. The actual residual moisture values in different publications will depend greatly on the conditions that were used, especially the temperature that desiccation occurred at.

The glass transition temperature data collected by Hargreaves (1995) has been left out of figure 3.3. This data was not collected as the onset  $T_g$ , but as the intercept of the baseline and the slope of the initial rise of the DSC trace (Hargreaves 2000). Since the bulk of the data is for the onset  $T_g$ , or the initial rise from the DSC baseline, the data of Hargreaves (1995) could not be accurately compared to it. Other publications (Taylor and Zografis 1996, Sebhatu *et al.* 1994, 1997) do not specify which  $T_g$  they measured, but in the absence of any other information this data has been included.

While moisture content is simple to measure in pure amorphous lactose, commercial dairy powders contain other components such as fat, protein and ash. With these

components present, determining the moisture content of the amorphous lactose in the powder becomes very difficult, as the other components affect the equilibrium moisture content of the lactose. It is therefore difficult to predict the  $T_g$  of the amorphous lactose part of a commercial powder from a moisture content measurement. Water activity would be a better measurement to use. It is easily measured and it better reflects the  $T_g$  of amorphous lactose, without being affected by the other components of the powder.

### 3.3.3 $T_g$ /WATER ACTIVITY

Now that the fit of the Gordon-Taylor equation and the moisture sorption isotherms has been improved through including the effect of residual moisture, it is worthwhile looking at the fit of the combined model for predicting  $T_g$  as a function of water activity. Figure 3.4 shows this plot, using the corrected Gordon-Taylor equation and the corrected isotherms.

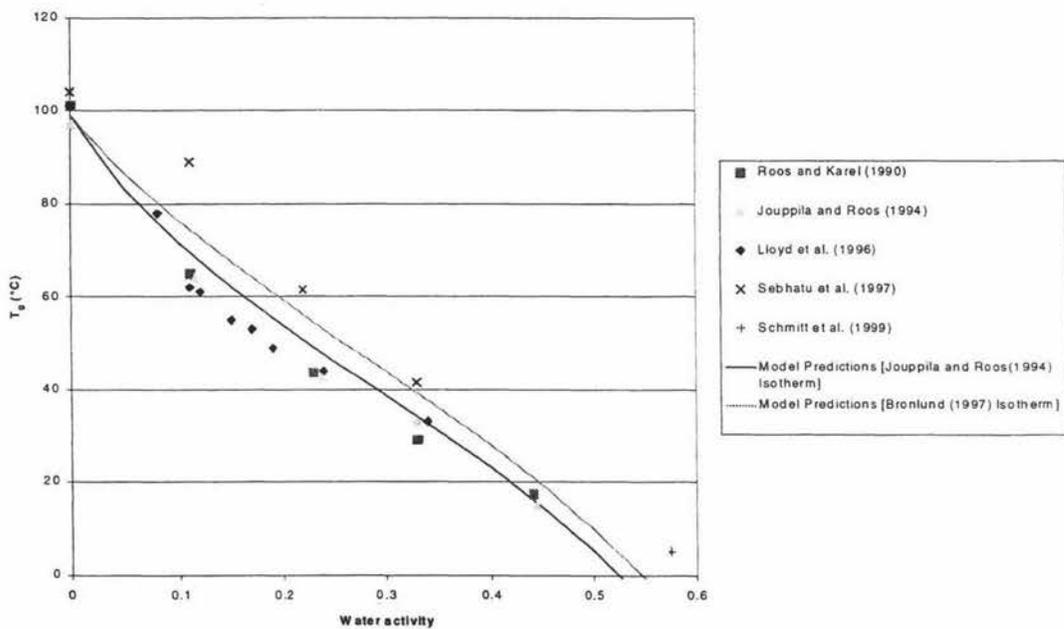


Figure 3.4  $T_g$  versus water activity

The graph of figure 3.4 gives no better predictions for  $T_g$  than the graph of figure 2.3. The two graphs are in fact very similar. While the changes to the sorption isotherms increase the moisture content at a given water activity, the changes to the Gordon-Taylor equation increase  $T_g$  for a given moisture content. The two effects cancel out, leaving the predictions of  $T_g$  substantially unchanged. The residual moisture correction has no effect on the  $T_g$ /water activity data, as it only corrects the moisture content. The reason for the lack of fit of this combined model is most likely that the errors in the two

models, which are accurate enough by themselves, add up to produce unacceptable disagreement with the literature data when they are combined.

Though the combined model does not give very good predictions, another possibility is fitting a non-mechanistic equation to describe the data. Lloyd *et al.* (1996) fit a cubic function to their  $T_g$ /water activity data. Figure 3.5 shows attempts to fit cubic, quadratic and sinusoidal equations to the available  $T_g$  measurements.

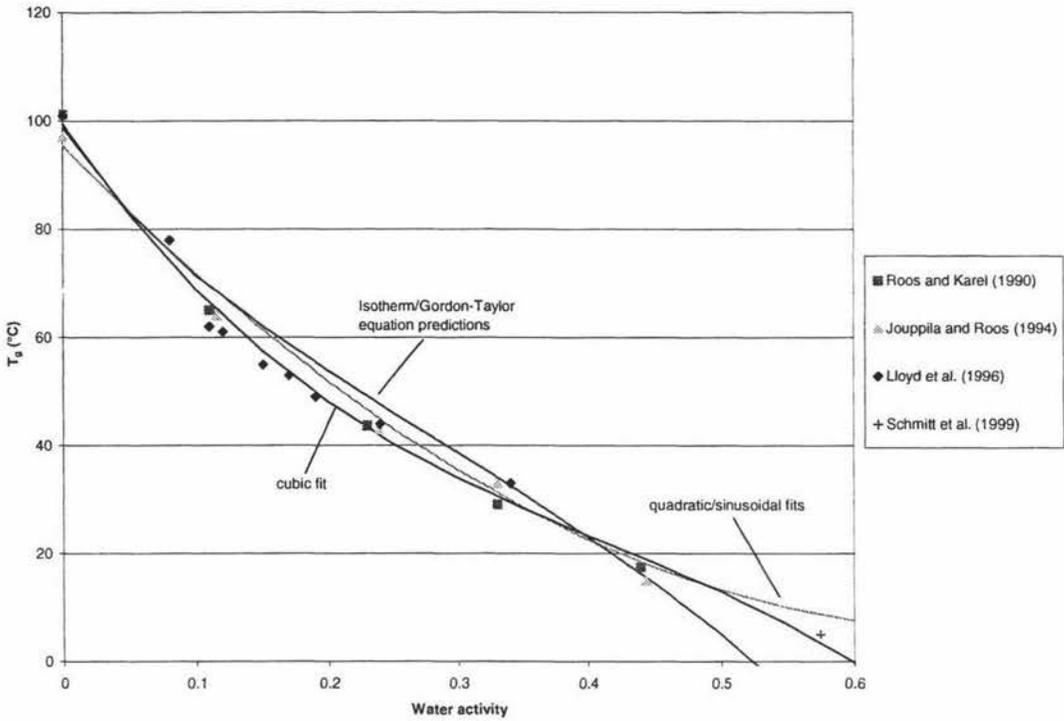


Figure 3.5 Fitting equations to  $T_g$  versus water activity data

In figure 3.5, any point plotted with a water activity of zero has been desiccated over phosphorous pentoxide, and had  $T_g$  determined in a sealed pan. Including  $T_g$  values determined in open pans would be misleading, as these samples were subject to different treatment than the bulk of the data. Thus the data of Schmitt *et al.* (1999), Taylor and Zografis (1998) and Hill *et al.* (1998) have been left out. The data of Sebhata *et al.* (1997) were also left out, as this can be seen in figure 3.4 to be very different from the majority of the data.

Figure 3.5 shows that the sinusoidal and quadratic equations give essentially the same fit – these two lines are so close as to be the same. The cubic fit (equation 3.1) gives an  $R^2$  value of 0.99, and follows the data very closely, much better than the sinusoidal and quadratic equations, and the best combined Gordon-Taylor/Isotherm model, which are also plotted on figure 3.5.

$$T_g = -530.66(a_w)^3 + 652.06(a_w)^2 - 366.33a_w + 99.458 \quad [0 < a_w < 0.575] \quad (3.1)$$

As discussed in section 3.3.2, water activity is a better measurement on which to base  $T_g$  predictions, as it is not affected by the other components present in a dairy powder. It can be simply measured with a calibrated RH probe.

### 3.4 CONCLUSIONS

Amorphous lactose desiccated over phosphorous pentoxide, a standard method for giving completely dry material, still contains 0.017gmoisture/glactose after 1 week of desiccation, which gradually reduces to 0.01g/g after 3 weeks. This has led to a great deal of scatter in the published glass transition temperature data for amorphous lactose. For example, the  $T_g$  of dry amorphous lactose, measured for samples desiccated over phosphorous pentoxide, has been accepted as being 101°C for a number of years (Roos and Karel 1990). However, the actual  $T_g$  for amorphous lactose, when there is no water present, has been measured as approximately 115°C by a number of independent authors.

It is uncertain why residual moisture remains in amorphous lactose after desiccation over phosphorous pentoxide. The amount of moisture left after 1 weeks desiccation indicates that the  $\alpha$ -lactose molecules may weakly bind one water molecule each, making this water difficult to remove. The low driving force for drying with phosphorous pentoxide at very low moisture contents may also play a part in residual moisture.

When the data affected by residual moisture is corrected by the amounts measured in this work, the literature data shows much better agreement. With such corrections made it is possible to predict the  $T_g$  of amorphous lactose given the moisture content, using the Gordon-Taylor equation (equation 2.2) with  $T_{g1}$  equal to 115°C and  $k$  equal to 6.9. In doing this, it is important that the total moisture content, including any residual moisture, is measured. Methods for this include weight change after oven drying, and Karl Fischer titration.

Combining the moisture sorption isotherm and the Gordon-Taylor equation to predict  $T_g$  based on water activity was unsuccessful. It was concluded that the best way to make predictions from water activity was to use a third order model fitted to the literature data (equation 3.1). This method of  $T_g$  prediction is preferable to using moisture content, as it is difficult to characterise the moisture content of amorphous lactose in commercial powders with other components present.

## CHAPTER 4

# CRYSTALLISATION OF AMORPHOUS LACTOSE

### 4.1 INTRODUCTION

As discussed in chapter 2, new crystallisation data has recently become available, which helped confirm the model of amorphous lactose crystallisation put forward by Bronlund (1997). To prove that crystallisation, like stickiness, depends only on the value of  $(T-T_g)$  and not the conditions required to achieve it, an experiment was performed at a high temperature and low humidity. The model of Bronlund (1997) was refitted to all the currently available data to improve the accuracy of its predictions.

### 4.2 METHOD

A gravimetric method was used to follow amorphous lactose crystallisation. A sample of amorphous lactose was equilibrated in a fluidised bed overnight. The moisture content was determined by oven drying and the water activity was measured at 20°C with a calibrated Hy-cal RH probe.

The QVF glass fitting, outlined in section 5.4.3.1.3 for the improved blow test apparatus, was used as a chamber in which an atmosphere of the desired humidity and temperature was maintained. The fitting was placed inverted on a bench top, without the distributor plate used in the stickiness experiments of chapter 6. A small aluminium weighing pan was hung into the centre of the chamber from a Sartorius M2P electronic microbalance, which was rested on an overhead stand. Approximately 100mg of amorphous lactose was placed on the pan, and its change in weight over time was recorded. The atmosphere inside the chamber was kept at a humidity to match the measured water activity of the sample. The amorphous lactose was loaded into the pan under dry air, to prevent moisture sorption from the atmosphere during transfer.

A  $(T-T_g)$  of 30°C was chosen for the experiment, which required a humidity of 26% and a temperature of 69°C. At these conditions, crystallisation was expected to be 90% complete after approximately 6 hours. At this low humidity the product of crystallisation was most likely beta lactose, and the rate of desorption was unlikely to be limiting. The solid state conversion of beta lactose to alpha lactose monohydrate was assumed negligible (Bronlund 1997). Moisture sorption was not limiting because the lactose was humidified before the experiment to a water activity of 0.26.

The open end of the glass fitting was partially sealed with aluminium tape to leave only an opening for the wire supporting the weighing pan, and for air to escape. The flow of hot air from this opening was diverted away from the microbalance, which was susceptible to heat and moisture damage. While air was flowing through the chamber the reading on the microbalance was unstable. In order to make a weight measurement the airflow had to be turned off, and after 10 seconds a stable reading could be recorded. Weight readings were taken at intervals of approximately 5 minutes until crystallisation was complete, as evidenced by a constant sample weight.

### 4.3 RESULTS AND DISCUSSION

Figure 4.1 shows the raw weight versus time data for the crystallisation experiment. The initial weight loss between the first and second readings was due to a small amount of amorphous lactose being blown off the weighing pan when the airflow was first turned on.

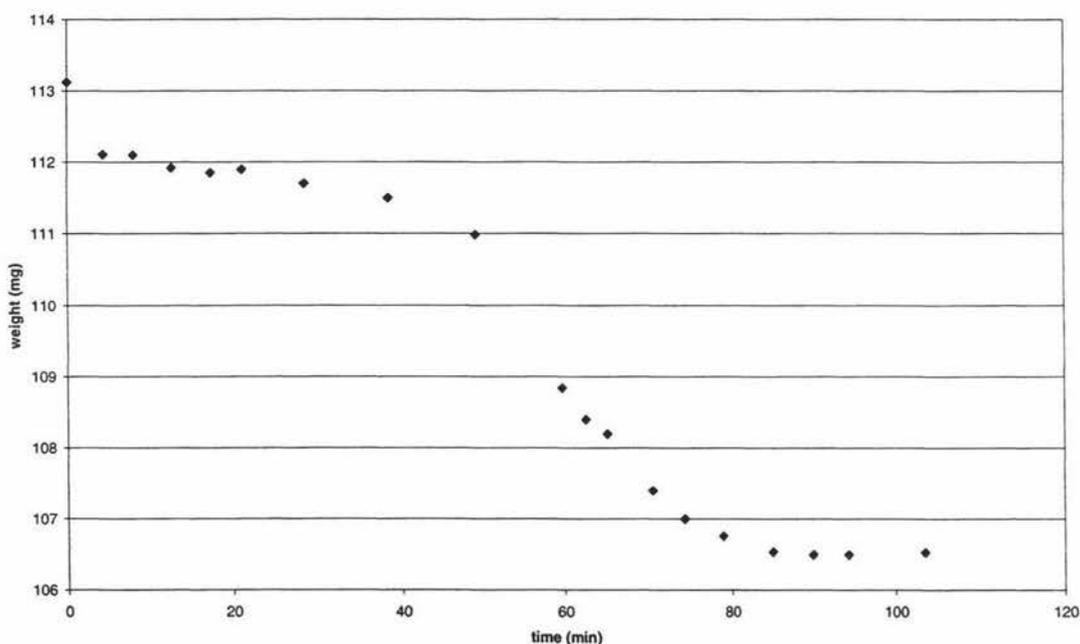


Figure 4.1 Weight change due to crystallisation of amorphous lactose at 26%RH and 69°C

It was noted that when the airflow to the apparatus was turned off in order to take a weight reading the RH probe registered an increase in relative humidity. The humidity was observed to increase to 31%, and took about 2 minutes to return to the desired value of 26% after the airflow was turned back on. This effect was thought to be due to heat loss from the glass chamber walls, and from ambient air entering the chamber while the

airflow was stopped. It is obvious that the amorphous lactose sample did not spend all the time at the correct experimental conditions. As such, the value of  $(T-T_g)$  was probably greater than  $30^\circ\text{C}$ , which means that crystallisation could be expected to occur in less than 6 hours. At a humidity of 31%,  $(T-T_g)$  is  $36^\circ\text{C}$ , and crystallisation is expected to take approximately 96 minutes to reach 90% of completion.

The data from figure 4.1 can be converted to a plot of crystallinity as a function of time, which is shown in figure 4.2. From this plot it can be seen that crystallisation was 90% complete after only 74 minutes.

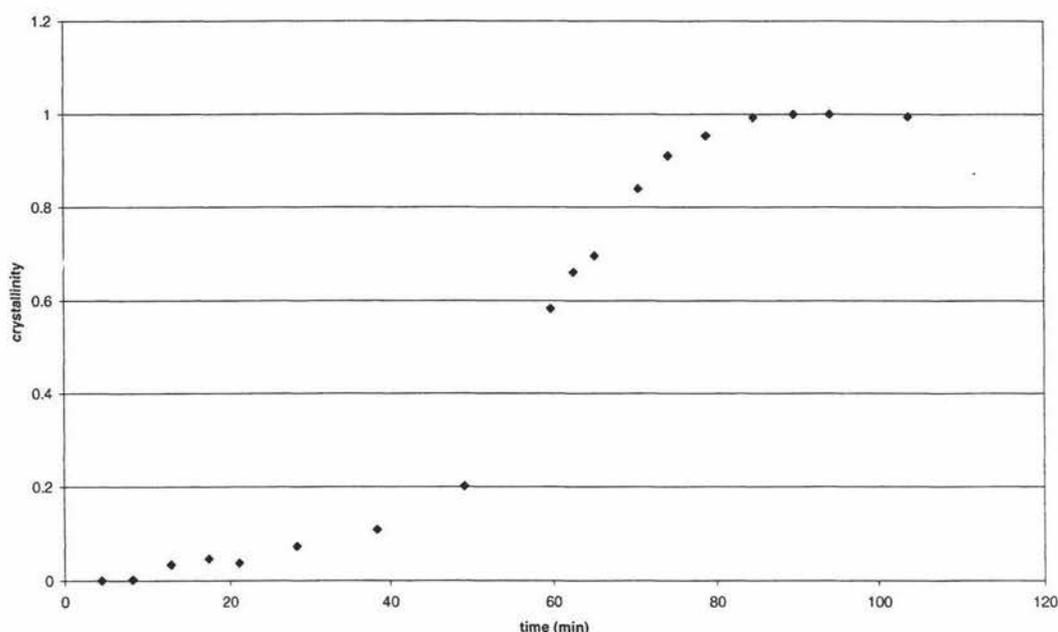


Figure 4.2 Crystallinity versus time for amorphous lactose crystallisation at 26%RH and  $69^\circ\text{C}$

Figure 4.3 shows an Avrami plot of the crystallisation experiment, which is a plot of  $\log[-\ln(\text{crystallinity})]$  versus  $\log(\text{time})$  from the linear form of the Avrami equation (equation 2.7). Both Bronlund (1997) and Schmitt *et al.* (1999) found  $n$ , the Avrami number, to be equal to 3, and drawing a best fit line through the data in figure 4.3 gives a value for  $n$  of 2.9. An Avrami number of 3 corresponds to linear growth in three dimensions under heterogenous nucleation conditions, where the number of nuclei is fixed (Bronlund 1997). The data in figure 4.3 does not form a very straight line, and there appears to be two distinct regions. In the early part of the graph the data gives a value for  $n$  of approximately 3, while in the later part  $n$  is closer to 4. This may indicate that the type of nucleation is changing from heterogenous to homogenous, where there is a fixed nucleation rate. Schmitt *et al.* (1999) used microscopy to observe that homogeneous nucleation did not occur at 57.5% RH and room temperature, at a  $(T-T_g)$  of approximately  $30^\circ\text{C}$ .

An alternative explanation is that there was insufficient time for complete desorption of the moisture released and the actual  $T_g$  of the sample was lowered. This would cause a runaway crystallisation reaction. It can be seen in figures 4.1 and 4.2 that at approximately 50 minutes the reaction appeared to suddenly speed up.

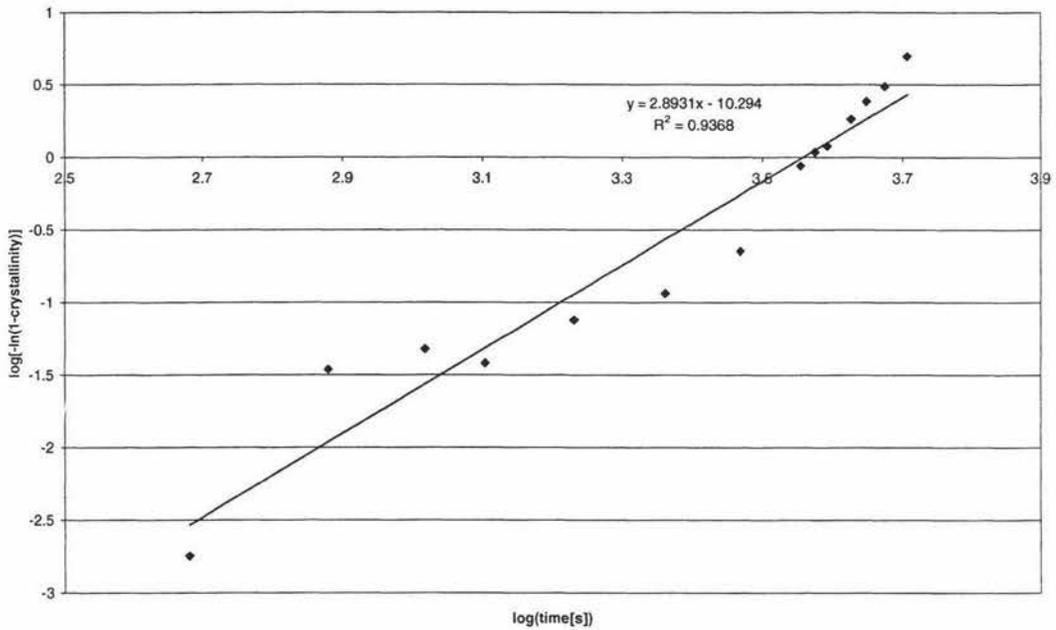


Figure 4.3 Avrami plot for amorphous lactose crystallisation

The size of the sample plays an important part in causing runaway crystallisation, as any moisture released needs to diffuse through the amorphous lactose sample. O'Donnell (1998) showed that diffusion of moisture through a packed bed is very slow. In an ideal crystallisation experiment the amorphous lactose sample should be very small and very thinly spread, so that moisture can readily escape into the air. Schmitt *et al.* (1999) used a sample size of only 15mg. The sample mass used in this experiment was 113mg, and on the small weighing pan it was heaped rather thickly, up to 4mm high in places. This made it possible that desorption from the sample was hindered, retaining moisture and leading to an increased rate of crystallisation, as  $T_g$  would be lowered and  $(T-T_g)$  increased. Desorption would be further hindered by collapse of the amorphous matrix. It was observed that the amorphous lactose sample collapsed to approximately half its original size in the first few minutes of the experiment, which could have had an effect on the rate that moisture was lost from the sample. With this in mind it is possible that the measured weight loss was in fact due only to drying of an already crystallised sample, and not to loss of moisture due to crystallisation.

A further experiment was performed, in an attempt to rectify the problems with the experimental method. To eliminate or reduce the fluctuations in RH, the glass chamber was insulated inside and out with foam padding, and the opening for the wire supporting the weighing pan was made as small as possible. These modifications reduced the increase in humidity while a weight reading was taken to less than 1%RH. The sample size was decreased to approximately 25mg, and was spread over the weighing pan in a layer approximately 0.5mm thick, in an attempt to make sure desorption of water was not hindered. Also to help with water desorption, the conditions were altered to give a  $(T-T_g)$  value of only 25°C. At  $(T-T_g)=25^\circ\text{C}$ , using an RH of 17% and a temperature of 79°C, 90% of crystallisation was expected to have taken place after 18 hours.

Unfortunately, the second experiment failed to give useful results. Up to  $t=2$  hours, the weight readings from the balance were very stable, with an error of only 0.05mg. After 2 hours however, the microbalance became unreliable, and the weight readings varied by up to 0.5mg between successive measurements. Since the total weight loss due to crystallisation was expected to be in the order of only 1mg, it was obvious that due to the poor reliability of the balance reading this weight loss would be very hard to observe. The microbalance is susceptible to drafts, vibrations, heat and moisture, and it was exposed to all of these to some degree in this experiment. To avoid problems of this nature the balance should be further insulated from these factors. Alternatively, a  $(T-T_g)$  condition that gives crystallisation in less than 2 hours could be used, but care must be taken to ensure that moisture can be easily desorbed.

#### 4.3.1 FITTING MODEL TO AVAILABLE DATA

Figure 4.4 shows the available data for the time to reach 90% crystallisation. The data point from this work has been plotted at a  $(T-T_g)$  of 30°C, which was the planned  $(T-T_g)$  value. In reality, the  $(T-T_g)$  condition varied between 30 and 36°C throughout the experiment, and it is possible that it was much higher if desorption of moisture was hindered.

Figure 4.4 also shows the model for amorphous lactose crystallisation developed by Bronlund (1997). It has been refitted to include all the available data, to improve the accuracy of the constants. When first devised, these constants were found by fitting the model to the data of Roos and Karel (1990, 1992) and Bronlund (1997). Taking into account the data from Schmitt *et al.* (1999), the constants  $C_A$ ,  $C_B$  and  $C_C$  in equation 2.8 change slightly to become  $3.54 \times 10^4$ , 110.9 and  $2.66 \times 10^{27}$  respectively. Using these constants in equations 2.8 enables more accurate predictions of amorphous lactose crystallisation times to be made. At a  $(T-T_g)$  of 30°C the experimental data point from this work does not show good agreement with the model of crystallisation. This is due to the actual  $(T-T_g)$  conditions being higher than 30°C, and the strong possibility that

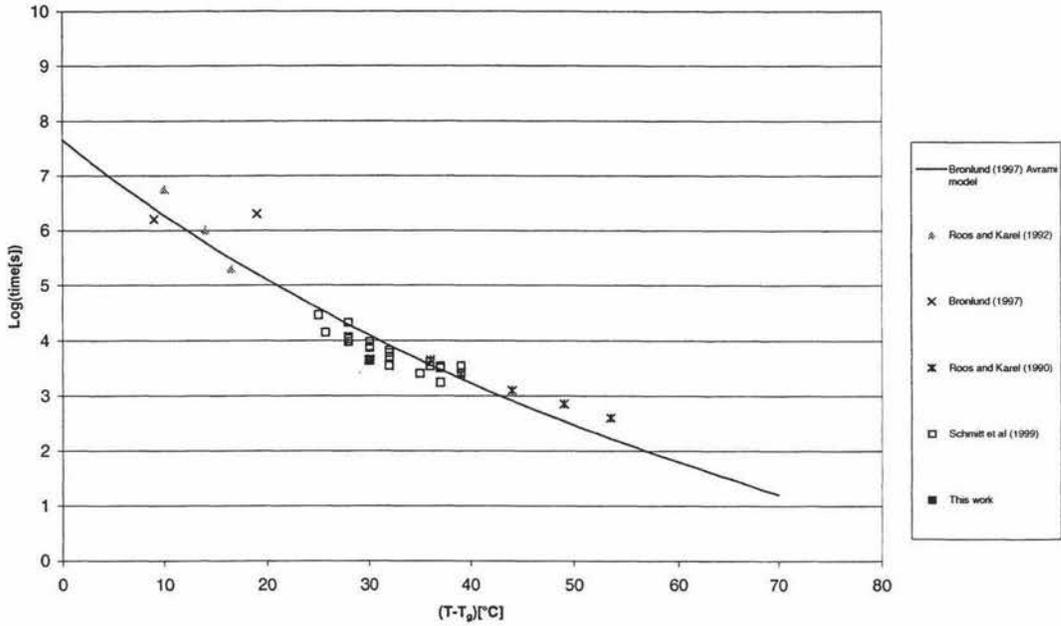


Figure 4.4 Time to 90% crystallisation for amorphous lactose

desorption of water was hindered and the crystallisation reaction became a runaway reaction.

#### 4.4 CONCLUSIONS

The gravimetric method, using a microbalance to follow weight loss, was applied to observe the crystallisation of amorphous lactose. Crystallisation occurred much faster than was predicted due to fluctuating RH conditions and the likelihood that moisture desorption was limiting. The balance used was very sensitive and the flow of air at the desired RH and temperature had to be stopped to allow a meaningful weight reading to be taken. This meant that the RH of the air around the sample fluctuated by up to 5%, causing the value of  $(T-T_g)$  to vary by 6°C. The sample was probably too large and too thickly spread, which limited the rate that moisture released by crystallisation could be desorbed into the air stream. Thus it is likely that  $T_g$  was lowered and the reaction took place at a faster rate.

The experiment was repeated, with modifications to eliminate the above problems. While these problems were solved, the microbalance used to follow the sample weight became unstable after 2 hours, and crystallisation could not be observed. Further stabilisation of the balance is required to make this experimental method a useful one.

The model of crystallisation developed by Bronlund (1997) has been shown to agree well with recent data from other workers. This model, with the improved constants calculated in this work, can be used to predict the time taken for amorphous lactose crystallisation as a function of  $(T-T_g)$ .

# CHAPTER 5

## STICKINESS TEST DEVELOPMENT

### 5.1 INTRODUCTION

As outlined in section 2.3.3, two methods were considered as being possibly useful to follow stickiness in amorphous lactose; the modified sticky point test and the blow test. This chapter deals with the development, evaluation and use of these tests to look at the conditions under which amorphous lactose becomes sticky. To be of use in this work, a stickiness test must:

- provide quantitative results as to the extent of sticking
- be able to observe the trend of stickiness over time
- give reasonably reproducible results

### 5.2 AIR SUPPLY

The tests mentioned above all required a supply of air with controlled temperature and humidity, either to humidify amorphous lactose samples through exposure to an airstream, or to control the environment in which a test sample was placed. A fluidised bed rig that is capable of providing such an air supply was developed by O'Donnell (1998). Because of the importance of this rig to the experiments in this work, the basic principles behind its operation and the modifications made to it are outlined here.

#### 5.2.1 PRINCIPLE OF OPERATION

The rig produces air at a constant relative humidity through what has been called the "two-pressure principle" (Wexler and Daniels 1952). This involves saturating a stream of air with water vapour at high pressure, then passing this stream through an expansion valve to a lower pressure. O'Donnell (1998) showed that the relative humidity of the low-pressure air stream is equal to the ratio of the low and high pressures (equation 4.1).

$$RH = \frac{P_2}{P_1} \times 100 \quad (4.1)$$

The rig operates by bubbling air through two 1.8m high steel columns of water at pressures up to about 6 bar. The bubble spargers and water level were designed to achieve saturation of the air, and the water is maintained at a constant temperature. The saturated air is then passed through an expansion valve, which brings the pressure close

to ambient, allowing the relative humidity to be set by changing the ratio of the two pressures. An in-line air heater is used to maintain a desired outlet air temperature, and the air is fed through a porous high-density polypropylene distributor plate to a fluidised bed. O'Donnell (1998) gives full details of the design of the rig.

## 5.2.2 MODIFICATIONS

The air supply rig was constructed for use in pilot scale trials for the conditioning of crystalline lactose, and so several modifications were needed before it could be used in this work.

### 5.2.2.1 Relative Humidity Output

Experiments to investigate the sticking of amorphous lactose require the relative humidity and temperature of the testing environment to be kept as constant as possible. The air heater in the rig keeps the temperature of the output air constant to within acceptable limits ( $\pm 0.4^\circ\text{C}$ , which is the accuracy of the thermocouple used). However, O'Donnell (1998) found that the relative humidity of the output air showed sinusoidal variations, with a period of about 90 minutes and an amplitude of 2%. While this was acceptable for conditioning crystalline lactose, it was deemed too variable for this work, as any amorphous lactose exposed to a fluctuation in RH of 2% could experience a change in  $T_g$  of up to  $8^\circ\text{C}$ .

The reasons for the RH fluctuation, and the steps taken to eliminate it are discussed in O'Donnell *et al.* (1999). These steps were implemented as part of this work. An extra pressure regulator was fitted to the incoming airline to eliminate pressure fluctuations from the air compressor. These small pressure fluctuations had caused small fluctuations in the output RH. A sensor used to control the water column temperature was relocated in order to measure the water temperature more directly. The previous control loop used an indirect measurement, causing the water temperature to fluctuate over a 90 minute period, affecting the output RH accordingly. These two modifications successfully reduced any unwanted fluctuation to below  $\pm 0.4\%$  RH.

### 5.2.2.2 Distributor Plate and Cone

The air supply rig was originally constructed with a fluidised bed, consisting of a 1.2m tall glass column, attached to the distributor plate. This was removed to allow for the use of smaller sized columns and other apparatus. In addition, a hose attachment was added to the steel cone below the distributor plate, to allow for the use of constant humidity air at locations remote from the rig. The two Hy-Cal RH probes used on the

rig were detached from their permanent positions, so they could be used in different pieces of equipment.

## **5.3 MODIFIED STICKY-POINT TEST**

### **5.3.1 INTRODUCTION**

The idea of a method similar to the sticky-point temperature test was raised, only using a fluidised bed to contain the sample powder, and a viscometer to measure stickiness. In a fluidised bed of amorphous lactose, moisture sorption onto the surface is very fast (O'Donnell 1998), and so any changes to the inlet air RH are transferred to the lactose particles quickly. As the particles gradually became stickier with increased RH and adhered to the viscometer spindle and each other, the viscometer indicated an increase in torque required to turn the spindle through the sample.

### **5.3.2 EXPERIMENTAL APPARATUS**

A small fluidised bed was constructed, consisting of a small plastic coated glass column, 10cm high and with an internal diameter of 5.2cm. This was attached to a polypropylene distributor plate, which was in turn fastened over the outlet of the air supply rig described in section 4.2. Amorphous lactose powder could then be placed in the bed and fluidised with air of controlled temperature and humidity.

A Brookfield DV-1 digital viscometer was positioned with its spindle in the centre of the bed. A Hy-Cal RH probe from the air supply rig was positioned in the bed at the same level as the head of the viscometer spindle. As a fluidised bed is a well-mixed environment, it was assumed that the reading from this probe was a good indication of the RH at the surface of the amorphous lactose particles. The RH probe was calibrated over saturated salt solutions, with standard RH values for the salts taken from Greenspan (1977) and Rockland (1960). A thermocouple was also installed in the bed, next to the RH probe.

### **5.3.3 METHOD**

Amorphous lactose produced at New Zealand Dairy Research Institute for the work of Lloyd *et al.* (1996) was used for these experiments. This amorphous lactose was easily fluidised due to its relatively large particle size. Other finer powders, such as the amorphous lactose produced for this work, were too difficult to fluidise and could not be used. Approximately 60g of amorphous lactose was added to the bed to reach a certain level. The airflow through the distributor plate was then turned up to about

15L/min to expand the bed to 7cm high. To maintain a small airflow through the fluid bed, yet have enough air passing through the air supply rig to maintain good temperature control, some air was allowed to bypass the bed. The incoming air was set to 26°C and a relative humidity below 30%. At a water activity of 0.3, the  $T_g$  of amorphous lactose is around 35°C, so this initial condition was below the glass transition point and the particles should not be sticky.

Both the #2 and #3 viscometer spindles were trialed, at speeds of 60 and 30 rpm. Once the viscometer and RH readings had levelled off, the RH was increased while maintaining a constant temperature. The RH could be increased rapidly, or it could be gradually increased in small steps. When changing RH, the air flow rate was kept as constant as possible. The outputs from the RH probe, thermocouple, and viscometer were logged on a Grant Squirrel 1000 data logger.

### 5.3.4 RESULTS AND DISCUSSION

The physical response of the fluidised bed to the increase in RH was very noticeable. As the RH increased, the bed maintained normal fluidisation until a point where, within a period of about 1 minute, the lactose particles slowed down, “rat holes” appeared in the bed, and fluidisation ceased. At this point the viscometer gave a high reading. Shaking or tapping the glass column would cause fluidisation to continue, but this would quickly cease once the outside disturbance was stopped. When the RH of the bed was decreased the bed would break up and re-fluidise.

Figure 5.1 shows the output from a typical experiment. As the RH begins to increase

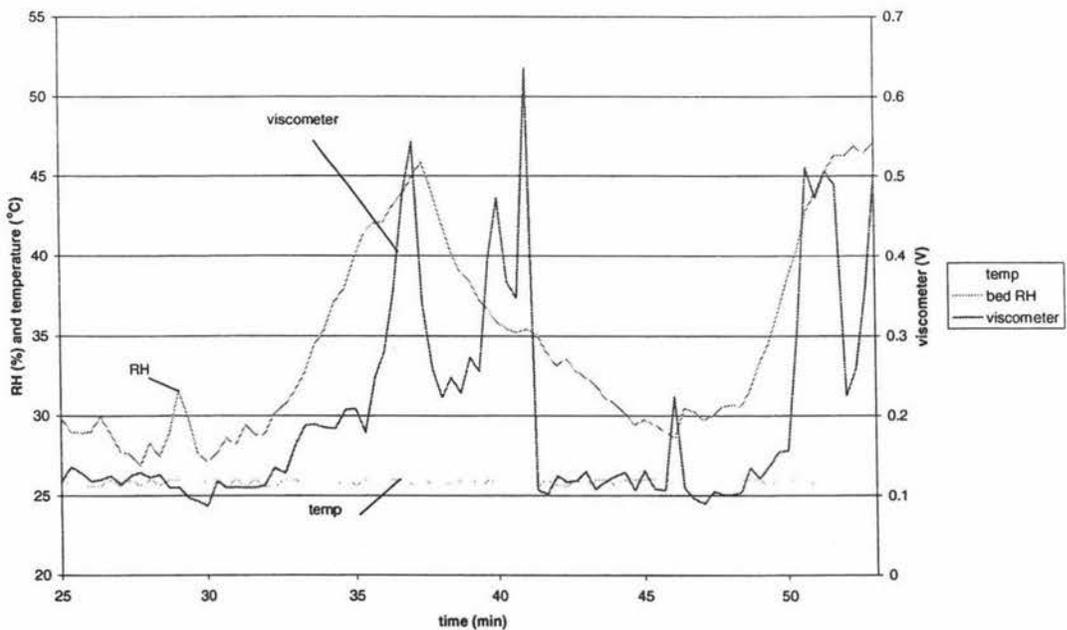


Figure 5.1 Modified sticky point test results

from below 30% the viscometer registers an increase also. This is because increasing the RH from the air supply rig causes a small decrease in flow rate. While care was taken to try to minimise this change in flow rate, by manually closing the air bypass valve, it was a difficult task. Some decrease in flow rate was inevitable. As the flow rate decreased the lactose bed became less fluidised and the viscometer spindle required more torque to turn. It was observed that even small changes in flow rate (1 or 2 L/min) were enough to increase the viscometer signal by 0.1V. In any case, the flow rate was stabilised within two minutes, which was observed in figure 5.1 as a plateau in the voltage reading. The viscometer signal showed a sharp increase when fluidisation ceased, reaching a maximum when the bed became packed. This sharp increase was observed when the RH of the bed reached 41.4%. Using the method for predicting  $T_g$  outlined in chapter 3, the glass transition temperature was estimated as 22°C, 4°C below the temperature of the bed. This would indicate that the amorphous lactose particles became sticky enough to stop fluidisation slightly above  $T_g$ . Although fluidisation ceased above  $T_g$ , the amorphous lactose particles showed no other signs of stickiness, such as lump formation, and did not appear noticeably sticky to touch.

After a peak was observed the RH in the bed was turned down to get fluidisation started again. The drop in the viscometer output at this point is due to the spindle forming a hole for itself in the packed bed. After 2 minutes this hole collapsed around the spindle and increased the measured voltage again. The bed was still packed at this stage, but shortly thereafter the glass surround of the bed was given a single sharp tap with a hammer, and the lactose instantly became fluidised again. At this stage the bed RH was about 35% and decreasing, while the air being supplied to the bed was at 20%, so drying was taking place. Drying was continued to below 30%RH before the RH was increased again. A small increase in viscometer output was noted again, due to diminished flow rate, before the sharp increase took place at 38.5%RH. This corresponds to a  $T_g$  of 25°C, which was higher than during the previous RH increase, but still lower than the bed temperature of 26°C. Again, it indicated that stickiness occurred when  $T_g$  was exceeded.

Taking into account the errors inherent in estimating  $T_g$ , the experiment shown in figure 5.1 indicated that amorphous lactose at or close to its glass transition temperature became too sticky to remain fluidised without vibrating or disturbing the bed. It was also apparent from experiments with this apparatus that the viscometer did not measure stickiness as such, but the effect that stickiness had on the fluidisation of the bed. As the bed became less fluidised it contracted and pressed in more on the viscometer, increasing the required torque. Evidence for this was the effect that the air flow rate had on the viscometer reading when the particles were far below  $T_g$ . Slightly lower flow

rates caused the bed to contract and increased the viscometer reading, even when  $T_g$  was higher than the ambient conditions.

### 5.3.5 CONCLUSIONS

Amorphous lactose particles became sticky at or just above the glass transition temperature, as evidenced by cessation of fluidisation in a fluidised bed of amorphous lactose when the bed conditions exceeded  $T_g$ .

While this knowledge is useful, and confirms that sticking begins at a temperature corresponding to  $T_g$ , the test does not show how amorphous lactose gets progressively more sticky over time, and it can not make any useful measurements once  $T_g$  has been exceeded and fluidisation has ceased.

## 5.4 BLOW TEST

The “blow test”, as developed by Paterson and Bronlund (1997), was discussed in section 2.3.4.4. It involves blowing a stream of air onto a bed of powder, and measuring the flow rate at which a channel is formed in the powder. This concept was used here in three different ways to try to develop a useful test for stickiness in amorphous lactose.

### 5.4.1 BLOW TEST IN MOISTURE DISHES

The simplest way to use the blow test was to follow the method originally used by Paterson and Bronlund (1997), and place the blow tester apparatus directly onto a sample of amorphous lactose in an individual moisture dish.

#### 5.4.1.1 Method

Spray-dried amorphous lactose powder, produced as described in section 3.2.3.1.1, was humidified in an expanded bed on the constant humidity air rig. Four different humidities were used, at approximately 10, 20, 30 and 40 % RH, and the moisture content at each humidity was measured and used to estimate  $T_g$ . Amorphous lactose was placed in 1cm deep plastic moisture dishes, levelled off with a straight edge, then sealed with aluminium tape.

While Paterson and Bronlund (1997) incubated samples over saturated salt solutions, samples here were placed in four ovens, set at different temperatures to give a  $(T-T_g)$  of 20°C for each set. Samples were removed at regular intervals and analysed with the

blow test. The blow test apparatus is shown in figure 5.2. Details of the dimensions of this apparatus are given in Paterson and Bronlund (1997).

#### 5.4.1.2 Results and Discussion

When the incubated samples were subjected to the blow test no results could be obtained, as the strength of the powder beds exceeded the capacity of the tester. To try to obtain some data the samples were then subjected to a test on an SMS TA-XT2 texture analyser, using a chisel probe and a maximum force of 25kg. While readings could be obtained from this, a plot of the data appeared scattered and random and nothing useful could be inferred from it.

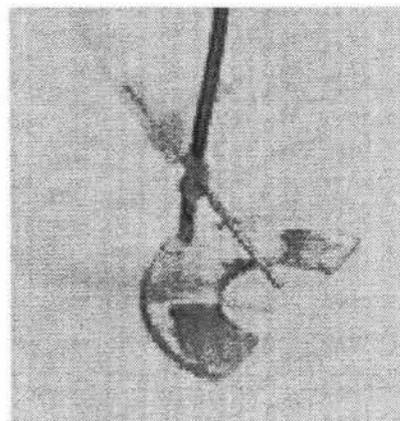


Figure 5.2 Blow test apparatus

There were several likely reasons for the failure of this test. The first is that the

( $T - T_g$ ) conditions were too high, and the amorphous lactose become highly sticky very quickly, too sticky for the blow tester. In the conditions used for the experiment, significant crystallisation was not expected to take place for several days. However, in the sealed dishes a small amount of crystallisation would release water and raise the humidity, increasing ( $T - T_g$ ) and causing sticking and crystallisation to occur faster. Further crystallisation leads to a further increase in ( $T - T_g$ ), and something akin to a chain reaction occurs, possibly fully crystallising the samples.

Probably the major reason for the failure of the test is that the powder beds collapsed markedly almost as soon as the experiment began. Consequently, the blow tester was too high above the bed for a meaningful test to be conducted. The higher the blow tester tube is from the powder bed then the more diffuse and slower the air jet becomes. Some shrinkage is expected when amorphous lactose changes from the glass to the rubber state and viscous flow occurs. However, the samples in the experiment were very loosely packed and this exaggerated the magnitude of the volume change upon heating above  $T_g$ . The moisture dishes used had steeply sloping sides and thus prevented the blow tester from being placed directly on top of the powder bed once it had shrunk.

#### 5.4.1.3 Conclusions

Several useful conclusions can be drawn from this experiment, even though it did not work as well as hoped. Firstly, the blow test tube needs to be kept at a small height above the powder bed to be tested. If it is too high then a higher flow rate is needed to

carve a channel. In this experiment, the shrinking of the powder caused the height above the bed to be so large that the blow test failed to register a result.

The conditions of the experiment need to be controlled so that the value of  $(T-T_g)$  remains constant throughout. The sealed dishes in this experiment meant that crystallisation caused  $(T-T_g)$  to increase uncontrollably. A more acceptable method is to expose the amorphous lactose samples to a constant flow of air at the correct humidity and temperature.

Finally, the amount of powder used in this experiment was very high. Even using the smallest dishes available, 400g of amorphous lactose powder was needed. Producing amorphous lactose was time consuming and difficult, so it was better to use as little powder for an experiment as possible.

#### 5.4.2 BLOW TEST ON A LARGE POWDER BED

After the failure of the blow test using moisture dishes, an experiment was devised to use the blow test on a larger bed of powder that was kept at a constant temperature and relative humidity.

##### 5.4.2.1 Experimental Apparatus and Method

The high-density polypropylene distributor plate (15cm diameter) was fastened on the rig with a metal retaining ring. The retaining ring formed a 3cm high wall around the plate, enabling it to be used as a very wide but shallow packed bed with forced air circulation, or as an expanded bed, depending on the flow rate.

A sample of amorphous lactose powder (approximately 60g) was humidified overnight with occasional mixing, then removed and stored in a sealed bag while its moisture content and water activity were determined. The empty bed was brought up to a temperature above the estimated  $T_g$ , but at a relative humidity equal to the water activity of the powder. Once both temperature and relative humidity were stable, the amorphous lactose sample was reintroduced to the bed and was levelled off as much as possible by tapping the metal wall. The airflow was reduced so that only a small amount of air was passing through the amorphous lactose powder and the bed was functioning as a packed bed with forced air circulation. A thermocouple and a Hy-Cal RH probe were positioned in the bed to monitor the conditions, and small adjustments were made with the air supply rig as necessary.

At regular time intervals the blow test apparatus was placed on the powder bed and a reading taken. Care was taken to ensure that areas of the powder disturbed by the blow tester were not used to make further measurements.

#### 5.4.2.2 Results and Discussion

Figure 5.3 shows a plot of the measured blow test flow-rates versus time for two different runs at the same  $(T-T_g)$  value of  $7^\circ\text{C}$ , one at  $27^\circ\text{C}$  and 43% humidity, and one at  $52^\circ\text{C}$  and 29% humidity. The data points represent the average of at least 2 measurements.

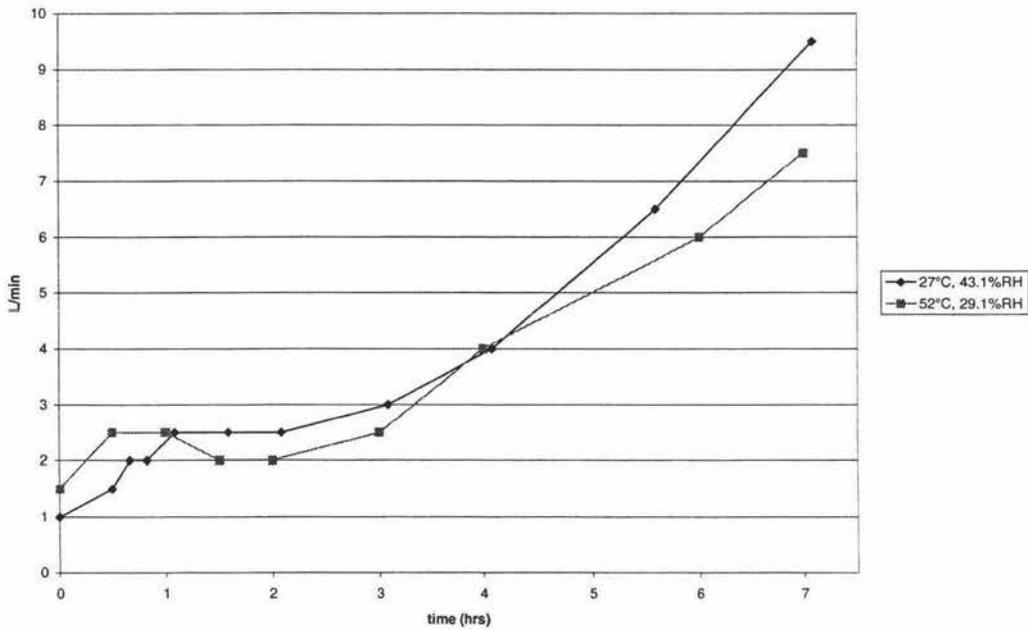


Figure 5.3 Blow test on distributor plate,  $(T-T_g) = 7^\circ\text{C}$

Figure 5.3 shows that both runs gave similar blow test profiles, even though different temperature and humidity conditions were used to obtain the  $(T-T_g)$  value of  $7^\circ\text{C}$ . However, the high temperature run started to diverge from the low temperature run at 4.5 hrs. A decrease of 1% in the relative humidity of the bed was observed at about this time and continued until the end of the experiment, despite attempts to bring it back to the correct value. This is the most likely cause of the observed divergence in the two data sets, as it would have caused the  $(T-T_g)$  value to drop by  $2^\circ\text{C}$ , leading to increased viscosity and slower interparticle bridge formation.

Figure 5.3 shows an initial sharp increase in the first half-hour of the experiment. The very first reading at time=0 was after the powder had just been placed in the bed and

had no time to come to the correct temperature – essentially a reading of the powder below its  $T_g$ . After half an hour, the powder had time to reach the conditions of the experiment and had started to become more cohesive. After this time there appears a plateau in the readings for the next 1.5 hours. The reason for this is unknown.

This experimental technique provided more promising results, but was still unsatisfactory. The major problem was limiting disturbances to other sections of the powder before they were used for testing. The mere act of placing the blow tester on the bed disturbed an area with the base of the tester, which could then no longer be used. In addition, using the blow test apparatus, especially at higher airflows, disturbed another part of the bed. When the powder had become reasonably cohesive the air jet from the tester often lifted up large areas of the bed and rendered them useless for further tests. Occasional vibrations from the air supply rig also caused disturbances.

Maintaining the proper height of the blow tester tube above the powder was problematic, as the apparatus tended to sink into the powder, and the surface of the powder was not perfectly level.

The method for controlling humidity and temperature was not ideal, as to prevent any lifting of the packed bed the air flow-rate had to be very low. As such, the bed takes a long time (at least half an hour, as mentioned above) to come to the correct conditions. The air supply rig had trouble controlling the temperature and humidity accurately at such low flows, and the response to control inputs was very sluggish.

#### 5.4.2.3 Conclusions

Although this experiment gave evidence that  $(T-T_g)$  determines sticking behaviour, irrespective of the moisture and temperature conditions, it still had a number of problems. To take this idea further it was necessary to:

- Prevent testing in one portion of the powder bed from disturbing other parts of it, by using physical barriers to divide the bed into individual parts.
- Stop the base plate of the tester from contacting the surface of the bed, by suspending the tester above the area to be tested rather than resting it on the powder.
- Increase the airflow through the bed so that the desired conditions in the powder were achieved more rapidly, yet without breaking up the bed in the process. This was accomplished by reversing the airflow through the bed.

### 5.4.3 IMPROVED BLOW TEST

The conclusions of the previous section were used to design an improved blow test apparatus, with reverse airflow through a segmented packed bed, and the blow tester suspended from above the bed rather than resting on it.

#### 5.4.3.1 Experimental Apparatus

##### 5.4.3.1.1 Distributor Plate

The high-density polypropylene distributor plate from the air supply rig was used as the basis for a reverse flow packed bed. A thin plastic ring, 108mm in diameter and 5mm high was glued onto the distributor plate to form a retaining wall. A smaller 25mm diameter, 5mm high ring was glued in the centre of the plate, and 18 plastic strips, each 3mm high, were used to join the inner and outer rings, with  $20^\circ$  of arc between each strip. This divided the plate up into 18 equal sized segments, much like the segments of a grapefruit half, so that the blow test could be performed on each segment, with the walls protecting the other segments from damage. Figure 5.4 shows the segmented distributor plate.

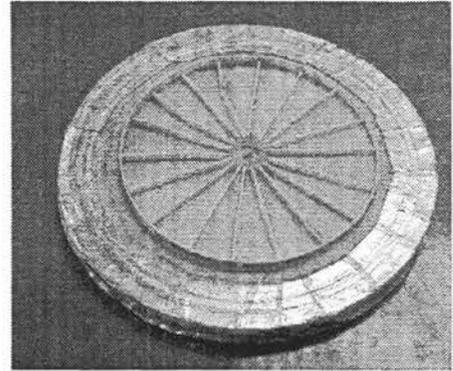


Figure 5.4 Segmented distributor plate

##### 5.4.3.1.2 Blow Tester

A modified blow tester was designed in order to suspend the tube of the tester over the powder bed without disturbing it. This consisted of a vertically orientated stainless steel pipe, 9mm in diameter, with a short brass arm attached at right angles close to the bottom. A 40mm length of 1.3mm internal diameter stainless steel tube functioned as the blow test air delivery tube. This was placed in the brass arm at a  $45^\circ$  angle, and was positioned to be 1mm above the top surface of the powder bed in the assembled apparatus. A rubber airline was connected to the blow test tube through a hole in the vertical pipe wall, and then passed up the

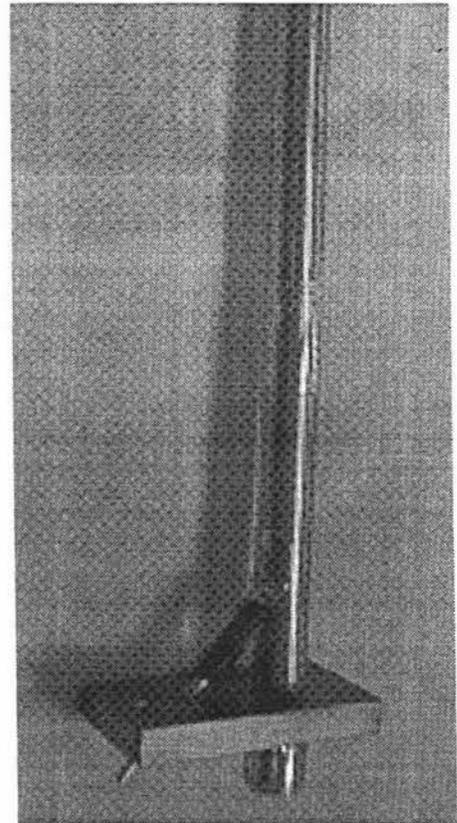


Figure 5.5 Modified blow tester

centre of the pipe. Figure 5.5 shows the modified blow tester, which was manufactured at the Institute of Technology and Engineering workshop, Massey University. All holes in the blow tester were sealed off, other than the small diameter blow tube. Metal tape was wrapped around the bottom of the vertical pipe so that it would fit snugly into the inner plastic ring on the distributor plate. In this way, the blow test tube could be positioned above a segment on the plate, approximately 2mm above the surface of the powder bed, and easily rotated around to the other segments when required. The compressed air for the blow tester passed through a pressure regulator, a rotameter and then to the blow tube by way of a needle valve. A ball valve was installed in the line so that the flow of air could be quickly shut off once the end point of a measurement had been reached.

#### 5.4.3.1.3 Glass Enclosure

For the improved blow test to work, air had to be directed down through the sample and the distributor plate. In addition, the vertical shaft of the blow tester had to be supported, and temperature and RH probes had to be included. A QVF glass fitting was used to accomplish all this. It rested on the distributor plate, and fit tightly around the packed powder bed. A rubber bung with several holes bored through it was placed in the narrow end of the fitting. A hole in the centre of the bung allowed for the vertical shaft of the blow tester and the blow test air line to pass through. Two other holes, offset from the centre, gave spaces for a Hy-Cal dew point RH probe, and a fitting to attach an air hose from the air supply rig. A small diameter hole allowed a type-K thermocouple to be inserted in the powder bed. All the items fitted tightly into their respective holes, and no air could escape past them.

The QVF fitting was attached to the distributor plate by means of two QVF metal retaining rings and four bolts. This arrangement gave an air tight seal – hence all air entering the testing chamber had to pass through the powder sample and out the bottom of the distributor plate. The pressure drop across this helped to ensure plug flow conditions, so that all parts of the bed experienced the same humidity and temperature. Figure 5.6 shows the assembled apparatus (the retaining rings have been left out for clarity).

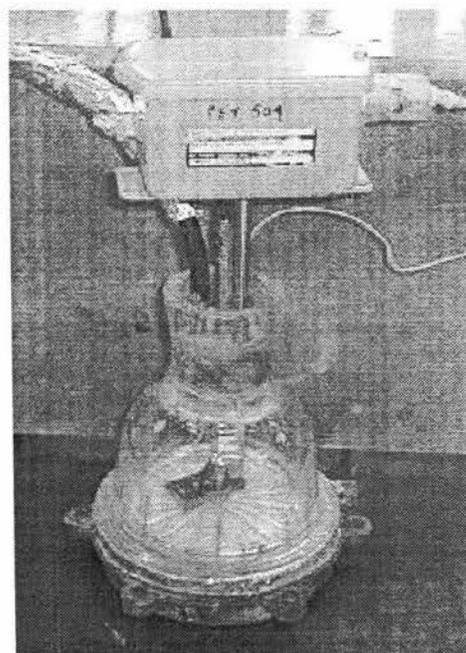


Figure 5.6 Improved blow test apparatus

#### 5.4.3.2 Experimental Method

A sample of amorphous lactose was first humidified in an expanded bed on the air supply rig. This took place for at least 24 hours, and the bed was agitated at regular intervals. The sample was then removed and sealed in an airtight container – any headspace in the container was purged with the same air used to humidify the sample. The container was sealed in a plastic bag purged with the same air, to further reduce the possibility of exposing the sample to ambient air.

The moisture content of the amorphous lactose was determined, and the water activity measured. The  $T_g$  of the powder was estimated from these measurements, and a  $(T - T_g)$  condition of  $7^\circ\text{C}$  was chosen for the first trial. The air supply rig was used to produce air with a relative humidity equal to the water activity of the amorphous lactose, at a temperature  $7^\circ\text{C}$  above the estimated  $T_g$ . For the first trial the conditions were  $36.4^\circ\text{C}$  and 34.4% RH. Air at this temperature and humidity was allowed to pass through the empty test chamber until the conditions were stable. The distributor plate was filled with approximately 40g of pre-humidified amorphous lactose powder, then tapped on a hard surface to ensure the lactose filled the bed properly. The surface of the bed was levelled off with a straight edge. Care was taken to ensure the small centre ring was clear of powder so the vertical shaft of the blow tester could slot into place. The bed was filled in a dry atmosphere, to prevent any moisture sorption from the atmosphere. It was assumed that moisture desorption was negligible, and that once the sample was introduced to the testing chamber any moisture loss would quickly be made up as it was exposed to the humid air stream.

With the air flow turned off, the plate with the powder bed was attached to the glass fitting and the retaining rings were positioned and then bolted into place, forming a sealed environment for the test. The positioning of the plate and retaining rings was a tricky manoeuvre, requiring some care to get the thermocouple and blow tester aligned in the correct positions without knocking the bed and spoiling the level surface. Alignment marks were made around the outside of the glass fitting and the distributor plate to aid correct positioning, and with some practice it was found this operation could be accomplished in about 30 seconds. Once the powder bed was sealed in the test chamber the airflow was turned back on, forcing air through the powder.

Taking a reading involved positioning the blow tester over the segment to be tested and making sure that the tube was aligned in the centre of the segment. As the walls of the segment were under the powder, marks indicating their positions were made on the glass enclosure to facilitate the correct positioning of the tester. Using the needle valve, the airflow to the tester was turned up at a constant rate. The endpoint was observed when a channel was carved into the bed. When the endpoint occurred at low flow rates a large broad hole was usually formed. As the powder got stickier, and higher flow rates

were required, the channel in the bed tended to become narrower and shallower. The order that the bed segments were used was determined randomly, to eliminate any possible error that could result from performing measurements in a continuous clockwise or anticlockwise sequence.

Once an endpoint was observed, the ball valve in the air line was turned off, immediately cutting off the supply of air. The flow meter and a stopwatch were recorded on video, as it was too difficult to observe the endpoint of the experiment, the exact time of the measurement, and the flow rate at the endpoint simultaneously. The recording of the experiment was viewed later, and the maximum flow rate before the airflow was cut off was recorded, along with the time. Flow rates were measured to 0.5 L/min, and time to the nearest second. The experiment lasted for approximately 7.5 hours, and most readings were taken as two replicates.

### 5.4.3.3 Results and Discussion

Figure 5.7 shows the graph of flow rate versus time for the first trial at  $(T-T_g)=7^\circ\text{C}$ . It shows a similar shape to the graph of figure 5.3, although because the blow tubes used in the two experiments had different diameters the results cannot be quantitatively compared.

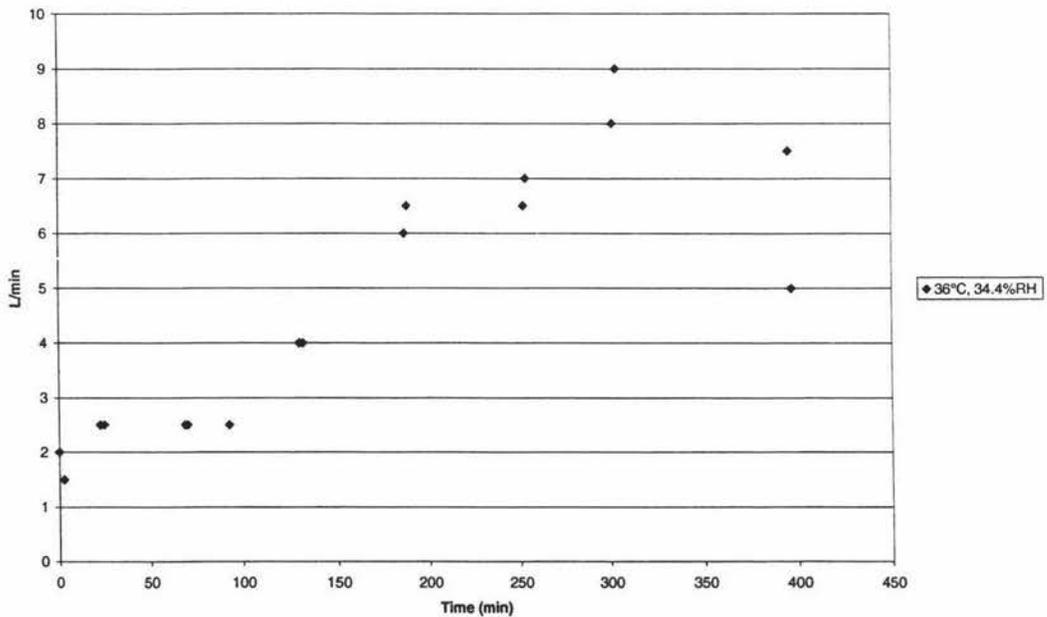


Figure 5.7 Initial improved blow test experiment,  $(T-T_g)=7^\circ\text{C}$

The first point to note about the graph is that the readings at time=0 are much lower than the next readings taken 20 minutes later. This was due to the fact that the first readings were taken just after the airflow through the bed was turned on, and the amorphous lactose had not yet come up to the desired temperature of 36°C.

Approximately 3 minutes were required before the bed reached this temperature. Hence, when the first readings were taken the value of  $(T-T_g)$  was not 7°C, and may not have even been a positive value. To keep the readings in a run consistent with each other, the first reading should not be taken until the correct conditions for the desired  $(T-T_g)$  value are reached. With a thermocouple in the bed this is simple enough to monitor.

The plateau in the readings up until 100 minutes is puzzling, and was similar to that observed in figure 5.3. It is possible that interparticle bridges of a certain size need to form before sticking is observed, and that this 100 minute period may be the time required to build these bridges. The Frenkel equation (equation 2.4) can be used to calculate that the ratio of interparticle bridge radius to initial particle radius ( $x/a$ ) after 100 minutes at a  $(T-T_g)$  of 7°C is 0.08. Wallack and King (1998) used scanning electron microscopy to measure interparticle bridges and obtained 0.1 as a good approximation of the value of  $x/a$  at the end point of the sticky point temperature test. These two values are reasonably close. It is possible to calculate that at a  $(T-T_g)$  of 10°C it would take 10 minutes of contact for a bridge with  $x/a=0.08$  to be built, and at a  $(T-T_g)$  of 15°C 1 minute would be required. If 0.08 is the value of  $x/a$  required before sticking is observed, then at these conditions a plateau would not be observed using the improved blow test, as the first reading after time=0 is taken at 30 minutes.

After 100 minutes of the experiment, the graph forms a reasonably straight line up until the final readings at about 400 minutes. The straight-line portion of the graph is encouraging, as it gives a simple relationship between time and the extent of stickiness, ie: the longer the amorphous lactose spends at a condition above its  $T_g$ , the stickier it becomes. The two replicates at 400 minutes disagree by a large amount, and both are lower than the general trend until that point. After the measurements at 300 minutes were taken the apparatus accidentally received a small jolt. It was found in later experiments that any cracks or irregularities in the powder leads to lower flow rates at the endpoint, compared to a powder with a regular surface. In particular, the powder fails easily if any cracks are present. The jolt to the apparatus could have caused some movement and weakening of the powder, leading to the low final readings. This source of error can only be eliminated by taking extra care during the experiment to avoid any disturbances.

Shrinkage of the bed is another possible problem. Amorphous lactose powder tends to shrink when above its  $T_g$ , meaning the blow test tube is further away from the bed surface. Short experiments to look at the extent of shrinking showed that this effect was

not important. The bed was very thin (5mm) and reasonably densely packed, and shrinkage was not significant. At a  $(T-T_g)$  of  $25^\circ\text{C}$  the vertical shrinkage of the bed was measured as 0.5mm, and at  $(T-T_g)$  values of 10 and  $15^\circ\text{C}$  it was not possible to measure any shrinkage of the bed at all.

During the experiment, the RH and temperature conditions in the test chamber were generally very stable, to within  $\pm 0.2^\circ\text{C}$  and  $\pm 0.3\%$  RH. However, these conditions were affected to some extent by ambient conditions outside the apparatus. The ambient temperature in the lab could affect both the temperature and humidity in the testing chamber due to heat losses through the glass wall. A decrease in temperature in the laboratory caused the temperature and humidity in the chamber to drop, while an increase in ambient temperature caused the opposite effect. This could be quite noticeable if a window was opened in the lab and a cold draught came through, and could happen in a short space of time. While the conditions of the experiment were monitored at least every 15 minutes, a change could occur in this time which would occasionally be in the order of 1% RH and  $2^\circ\text{C}$ . A return to the desired conditions could usually be affected within 30 seconds using the controls on the air supply rig. As a result, while conditions in the test chamber were generally kept stable, they could fluctuate, lowering or raising the  $(T-T_g)$  value accordingly.

Apart from the final two readings, the replicates in the experiment were close to each other, generally agreeing within 0.5L/min. Some disagreement was to be expected, as there were several variables, outlined above, which can affect the final reading that is taken. Despite all these, figure 5.7 shows that the improved blow test can be used to give a good indication of how amorphous lactose powder becomes progressively stickier as it spends longer time periods above its glass transition temperature.

## 5.5 ANALYSIS OF BLOW TEST FORCES

The flow rate readings from the blow tester give good qualitative indications of how sticky the powder bed is at a given time. However, it should be possible to relate a flow rate reading to the actual force on a lactose particle in the bed through the use of Bernoulli's equation, and thus gain an understanding of the magnitude of the forces involved.

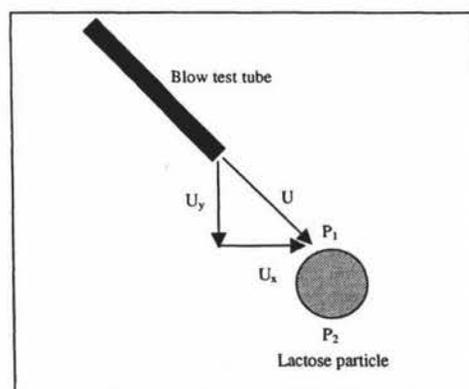


Figure 5.8 Blow test

### 5.5.1 PHYSICAL BASIS FOR MODEL

Figure 5.8 shows the situation under consideration. The impinging air jet, with velocity 'U', gives rise to a pressure differential across the lactose particle, which tends to force the particle out of the bed. This can be calculated from equation 5.1, where ' $\rho_a$ ' is the density of air. The tendency to force the particle out is opposed by the normal component of the air jet, with velocity ' $U_y$ ', which tends to push the particle into the bed. This can also be calculated from equation 5.1, with 'U' replaced by ' $U_y$ '.

$$P_2 - P_1 = \frac{1}{2} \rho_a U^2 \quad (5.1)$$

The forces exerted on the particle by these pressure differentials can be found using equation 5.2, where ' $A_p$ ' is the cross-sectional area of the lactose particle.

$$F = (P_2 - P_1) A_p \quad (5.2)$$

At the endpoint of the test the particle is blown out of the bed, and the upward force from the air jet must equal the sum of the weight force of the particle plus the normal force introduced by ' $U_y$ ', and any force due to stickiness ( $F_s$ ).

$$\frac{1}{2} \rho_a U^2 A_p = mg + F_s + \frac{1}{2} \rho_a U_y^2 A_p \quad (5.3)$$

The velocity of the air jet, 'U', and its vertical component, ' $U_y$ ', can be found using equations 5.4 and 5.5, where 'x' is the flow rate in L/min, and 'A' is the cross-sectional area of the blow tube. The constant  $1.67 \times 10^{-5}$  is a conversion factor from L/min to  $m^3/s$ .

$$U = \frac{Q}{A} = \frac{1.67 \times 10^{-5} x}{A} = 12.58x \quad (5.4)$$

$$U_y = U \cos \theta = 8.88x \quad (5.5)$$

Combining equations 5.3, 5.4 and 5.5, and substituting for the mass of the lactose particle gives equation 5.6, an expression for the stickiness force due to rubber bridging, where k is a combined constant equal to 79.4.

$$F_s = \frac{1}{2} \rho_a k(x)^2 A_p - \rho_p V_p g \quad (5.6)$$

In the case where the amorphous lactose is below its  $T_g$ , if  $F_s=0$  equation 5.6 can be solved for 'x' to give the flow rate in L/min expected when there is no stickiness. Performing this calculation gives a value of 0.05 L/min, compared with the observed value of approximately 3.5 L/min for amorphous lactose powder in conditions below  $T_g$ .

Obviously, there is some force other than the stickiness due to amorphous lactose rubber bridging acting between the lactose molecules to give rise to this extra strength. This force is most likely to be interparticle adhesion due to van der Waals forces, which was found to be significant in settled beds of fine powders by Baerns (1966). These forces are effective over the distances that exist between two particles in a bed, and are more important than electrostatic interactions (Baerns 1966). A complete expression for the stickiness force, including ' $F_o$ ', the attractive force due to van der Waals forces, is:

$$F_s = \frac{1}{2} \rho_a k(x)^2 A_p - \rho_p V_p g - F_o \quad (5.7)$$

From equation 5.7, where  $x=3.5$  L/min and  $F_s=0$  (amorphous lactose powder below  $T_g$ ), the magnitude of ' $F_o$ ' can be calculated as  $8.2 \times 10^{-8}$  N. ' $F_o$ ' can be determined experimentally from a sliding plate experiment, using equation 5.8, where ' $\phi$ ' is the angle of slide, ' $\mu_f$ ' is the interparticle friction coefficient, ' $m_t$ ' is the total mass of the sample used and ' $N$ ' is the number of particles in the sample (Baerns 1966).

$$F_o = \frac{m_t g \sin \phi - \mu_f m_t g \cos \phi}{N} \quad (5.8)$$

A sliding plate experiment was not carried out as part of this work, however, Baerns (1966) used this method to determine the value of ' $F_o$ ' for several different types of particles. It was found that for alumina particles with the same diameter as the amorphous lactose used in this work ( $27 \times 10^{-6}$  m), the value of  $F_o$  was  $3.1 \times 10^{-8}$  N. This is of the same order of magnitude as the value calculated above for amorphous lactose. Values for other types of particles with varying sizes ranged from  $2.5 \times 10^{-10}$  N to  $3 \times 10^{-6}$  N.

It can be concluded that while the forces involved in the blow test are complex, the blow test can be simplified to the force from the air jet overcoming the weight of the particle, plus any additional forces. These additional forces are due to van der Waals attractive forces and the force that comes from the amorphous lactose particles sticking together. Since the weight force and van der Waals forces are constant, the blow test measures the change in the sticking force.

## **5.6 CONCLUSIONS**

The modified sticky point test showed that amorphous lactose becomes sticky above its glass transition temperature. However, this test does not show the progression of stickiness with time, or show to what extent the amorphous lactose had become sticky. As such, it was concluded that this test was of limited further use in this work.

The improved blow test was evaluated as a good test for investigating the rate and the extent of amorphous lactose stickiness. This test measures the flow rate from an air jet required to carve a channel in a bed of amorphous lactose. The temperature and RH conditions were controlled with reasonable accuracy, and stickiness was measured after a precisely defined contact time, during which viscous flow could occur. The results were reasonably reproducible, however, care must be taken to ensure a meaningful test by avoiding sharp impacts near the apparatus and avoiding large ambient temperature changes. This test will be used in chapter 6 to investigate the sticking behaviour of amorphous lactose in more detail.

# CHAPTER 6

## STICKING OF AMORPHOUS LACTOSE

### 6.1 INTRODUCTION

According to the viscous flow models outlined in chapter 2, amorphous lactose becomes sticky when conditions exceed its glass transition temperature and rubber bridges are formed between particles. The longer the contact time of the particles, the larger and stronger these bridges become. These models of viscous flow depend only on the difference between the temperature of the amorphous lactose and its glass transition temperature, irrespective of the temperature and humidity combination required to achieve this. However, this dependence on  $(T-T_g)$  had never been adequately verified by experiment.

The previous chapter developed a reliable method for following how amorphous lactose becomes sticky over time. This was applied to investigate the sticking behaviour of amorphous lactose. The specific aims of this section of work were:

- To prove or disprove that amorphous lactose stickiness depends only on the value of  $(T-T_g)$ , and not on the temperature and humidity combination required to achieve this.
- To investigate to what extent amorphous lactose becomes sticky under different conditions, and the rate at which it becomes sticky.
- To recommend what conditions should be avoided to prevent stickiness of amorphous lactose from becoming a problem.

### 6.2 METHOD

The improved blow test procedure outlined in chapter 5 was used to investigate the relationship between stickiness and time at different  $(T-T_g)$  values.  $T_g$  was estimated, using the methods discussed in chapter 3, from the measured moisture content and/or water activity of the amorphous lactose powder. Moisture contents were measured using the oven drying technique, while water activities were measured at 20°C with a calibrated Hy-Cal RH probe.

## 6.3 RESULTS

### 6.3.1 $(T-T_g) \approx 10^\circ\text{C}$

Figure 6.1 shows the raw results for several different experiments at a  $(T-T_g)$  of approximately  $10^\circ\text{C}$ .

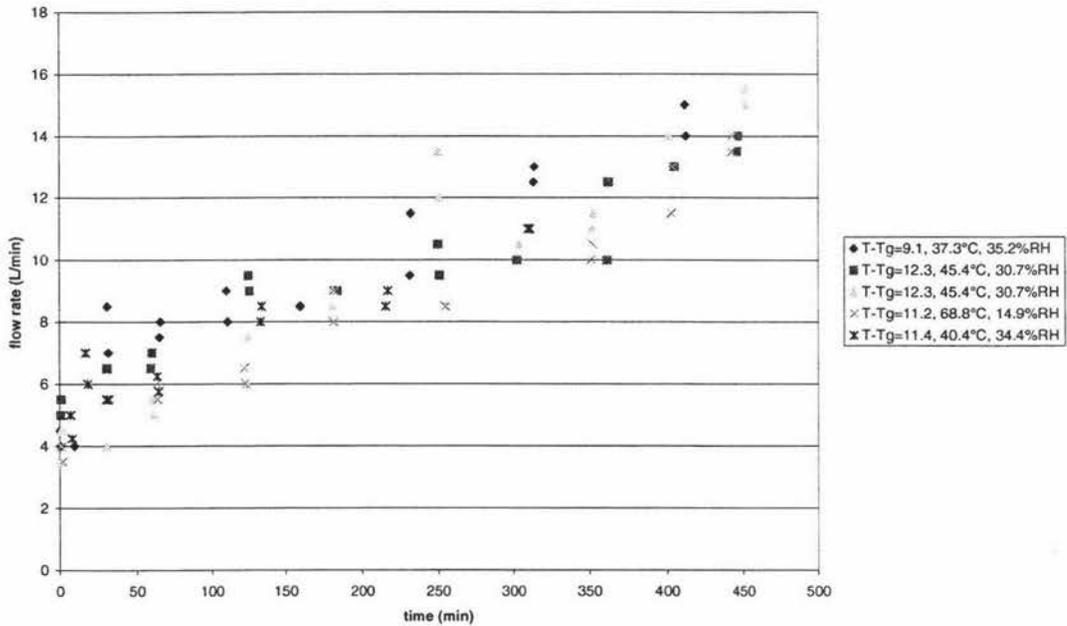


Figure 6.1 Blow test results for  $(T-T_g) \approx 10^\circ\text{C}$

While there is a degree of scatter amongst the data, the results from the different runs show remarkable agreement, when the nature of the blow test and the method of estimating  $T_g$  are considered.

Figure 6.2 shows a comparison of two runs done at exactly the same conditions, in order to gain an idea of the error inherent in the method. The figure shows that while the results are very similar, there is still some variation in the observed stickiness curves. Possible reasons for these discrepancies include imperfections in the bed surface and fluctuations in the conditions of the experiment, as discussed in chapter 5.

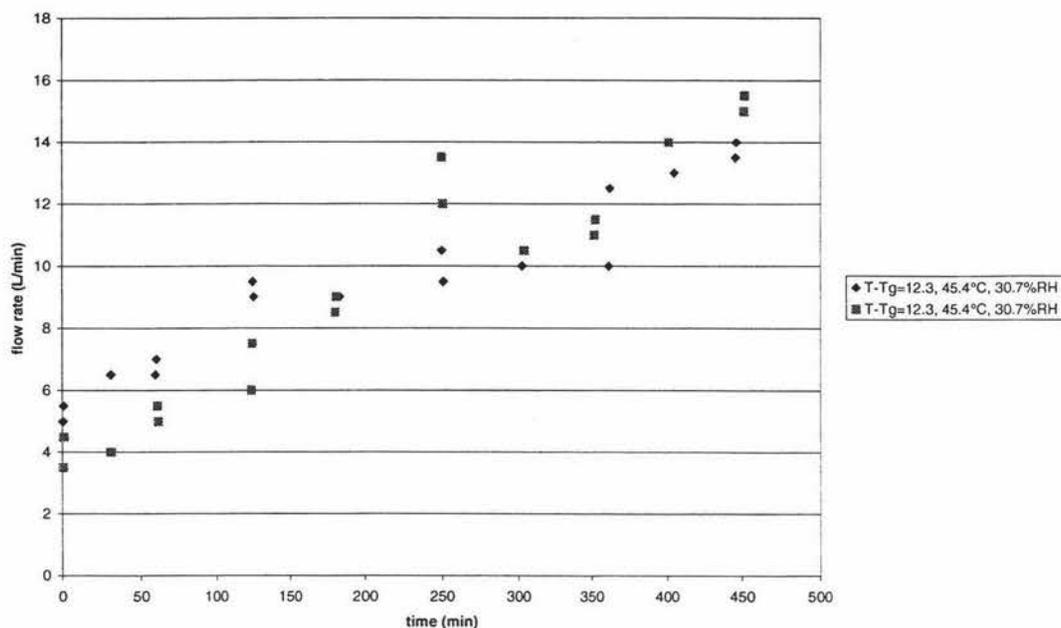


Figure 6.2 Comparison of two runs at the same temperature and humidity conditions

At a time of about 250 minutes in figure 6.2, one of the runs showed unusually high readings. This can be traced back to when the two measurements were made. The tester was not aligned properly and the jet of air was directed at the plastic walls that divided the bed into segments. Later experimentation to see what affect the dividing walls had on the endpoint showed that positioning the tester over a wall increased the flow rate reading at the endpoint by about 3-4 L/min compared to positioning over the middle of a segment. Overall, the two runs at the same conditions show that the improved blow test is subject to some variations, but that it is reproducible in terms of general stickiness trends.

### 6.3.2 $(T-T_g) \approx 0^\circ\text{C}$

Figure 6.3 shows the results obtained at  $(T-T_g) \approx 0^\circ\text{C}$ , from experiments performed at  $59^\circ\text{C}$ ,  $49^\circ\text{C}$  and  $31^\circ\text{C}$ . Inspection of this graph shows that at a temperature very close to  $T_g$ , little stickiness was observed by the blow tester. The initial flow rate values of 3-3.5 L/min correspond to free flowing powder, as measured with amorphous lactose powder held below its  $T_g$ . Towards the later stages of the runs the experiments at  $59^\circ\text{C}$  and  $31^\circ\text{C}$  showed small increases in flow rate to 5-6 L/min, which was due to the fact that  $(T-T_g)$  was slightly greater than  $0^\circ\text{C}$  for these two runs.

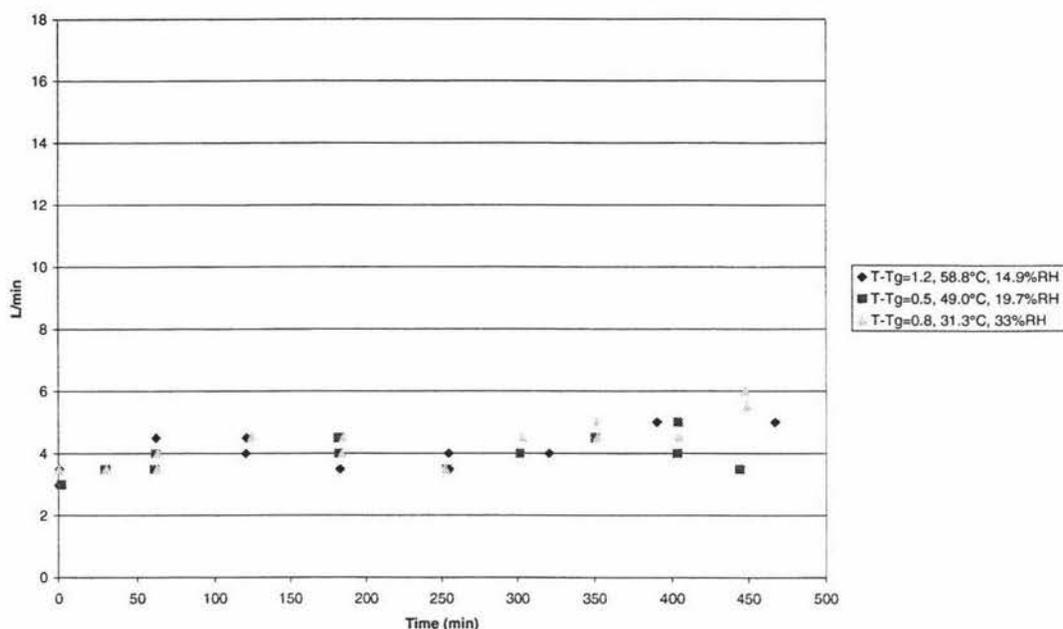


Figure 6.3 Blow test results for  $(T-T_g)=0^\circ\text{C}$

The variation and scatter amongst the data shown in figure 6.3 is another indication that the improved blow test gives a good indication of the general trends, but is still subject to some uncontrollable error.

### 6.3.3 $(T-T_g) \approx 20^\circ\text{C}$

Figure 6.4 shows the results of an experiment performed at a  $(T-T_g)$  of  $21.9^\circ\text{C}$ , at  $70^\circ\text{C}$  and  $20\%RH$ . Compared with the experiments at  $(T-T_g) \approx 10^\circ\text{C}$ , this experiment started at a higher blow test reading of about  $7\text{ L/min}$  after the  $(T-T_g)$  condition had been reached, and it became sticky at a faster rate.

The second replicate at 350 minutes showed a very large drop of  $5.5\text{ L/min}$  compared with the preceding measurement taken only seconds before. The explanation for this is that, between these two measurements, the bed accidentally received a relatively large jolt from a dislodged piece of ancillary equipment. Disturbances like this were identified as a possible problem during the method development, as they weaken the powder bed and cause lower readings. All the measurements taken after this accident are lower than would be expected, and have been ignored for data analysis purposes.

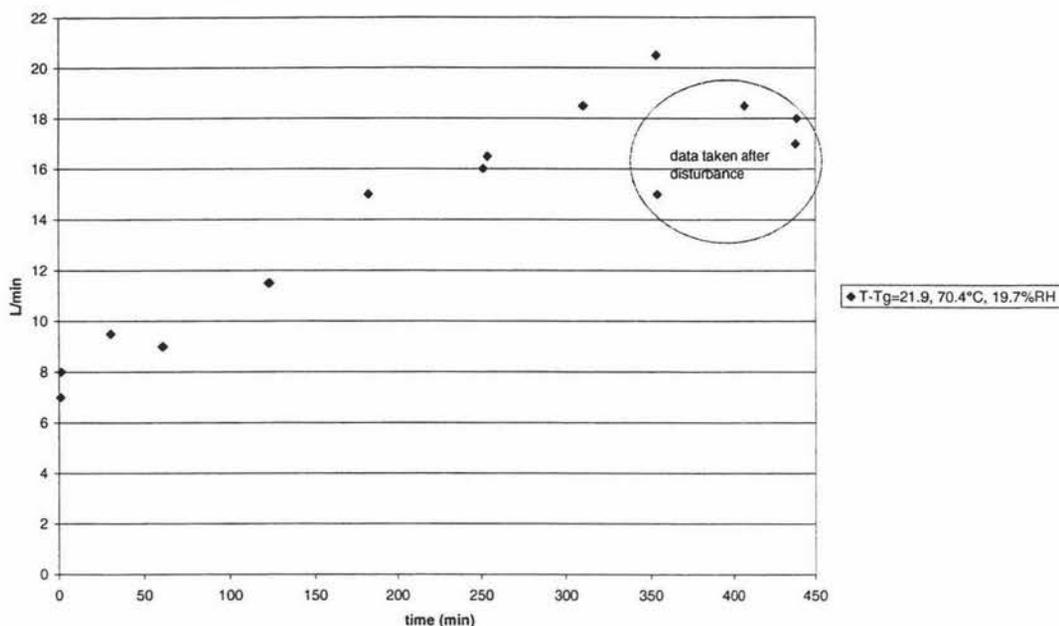


Figure 6.4 Blow test results for  $(T-T_g)=20^\circ\text{C}$

### 6.3.4 EXPERIMENTS AT DIFFERENT CONDITIONS

Figures 6.1 and 6.3 show experiments at the same approximate  $(T-T_g)$  values ( $10^\circ\text{C}$  and  $0^\circ\text{C}$  respectively). These  $(T-T_g)$  values were obtained using a variety of different temperature and RH conditions. At low  $(T-T_g)$  values, data obtained at  $59^\circ\text{C}$  and 15% RH [ $(T-T_g)=1.2^\circ\text{C}$ ] closely follows data obtained at  $31^\circ\text{C}$  and 33% RH [ $(T-T_g)=0.8^\circ\text{C}$ ]. At higher  $(T-T_g)$  values data obtained at  $69^\circ\text{C}$  and 15% RH [ $(T-T_g)=11.2^\circ\text{C}$ ] shows reasonable agreement with the rest of the data, obtained at temperatures from  $37^\circ\text{C}$  to  $45^\circ\text{C}$  and 31% to 35% RH.

The agreement of the experiments at different temperature and humidity conditions, but the same  $(T-T_g)$ , is evidence for the assertion that only the amount that the temperature exceeds  $T_g$  determines the sticking behaviour of amorphous substances.

### 6.3.5 HIGHER $(T-T_g)$ VALUES

Experiments were attempted at  $(T-T_g)$  values of  $25$  and  $28^\circ\text{C}$ . No measurements were obtained, as the stickiness of the bed exceeded the capacity of the blow tester to carve a channel in it, in a time frame shorter than it took to assemble the apparatus and take a reading (30 seconds). When the apparatus was dismantled after these aborted runs, the powder was in a very sticky, semi-fluid state. The amorphous lactose, in this advanced sticky state, was practically one continuous phase, and could be peeled off the distributor plate in whole sections and moulded into balls or other shapes.

This was similar to how a dairy factory staff member described a high lactose milk powder that was experiencing processing problems, as mentioned in section 1.1. This powder reached a state like chewing gum, where it could be moulded and formed into shapes in the same way as described above. The staff member involved attributed this behaviour to the amorphous lactose in the powder being in the rubber state.

While the high  $(T-T_g)$  experiments did not give any results as such, they were useful from the point of view that they showed the conditions under which amorphous lactose becomes very sticky in a very short space of time. In all other experiments below  $(T-T_g)=25^\circ\text{C}$  the stickiness measured by the blow test increased gradually over time, but above this value the stickiness increased from nothing to too large to measure almost instantaneously. The suddenness of this change suggests that it is similar to the sticky-point measured by Downton *et al.* (1982) and Wallack and King (1988), where the force required to turn a stirrer in an amorphous powder increased rapidly in the space of 1 or 2 seconds. Using the WLF equation, it can be calculated that the critical viscosity range reported by these workers at the sticky-point corresponds to  $(T-T_g)$  values of  $15\text{-}35^\circ\text{C}$ .

It is impossible to conclude that amorphous lactose at a  $(T-T_g)$  of  $25^\circ\text{C}$  is at its sticky-point without performing a sticky-point temperature test. However, it can be concluded that at this condition it is at a point where stickiness increases very quickly, and that  $(T-T_g)$  values of this magnitude should be avoided when processing and storing powders containing amorphous lactose.

## 6.4 DATA ANALYSIS

### 6.4.1 THE RATE OF STICKINESS ONSET

The data obtained with the improved blow test was linear and could be approximated with straight lines as a zero order process. Figure 6.5 shows the best-fit lines for the raw data presented above. The data points were not included to avoid cluttering the graph, but the  $R^2$  values were all above 90%. It is immediately noticeable that the different lines do not all originate at the same point. The higher the  $(T-T_g)$  value, the higher the initial reading at  $\text{time}=0$  was. It should be noted that  $\text{time}=0$  was the time at which the amorphous lactose sample had reached the desired temperature condition, measured by a thermocouple buried in the bed. Thus, before this point was reached, the sample had spent a short time above its  $T_g$ . This time varied depending on the individual experiment, and ranged from 2 to 7 minutes.

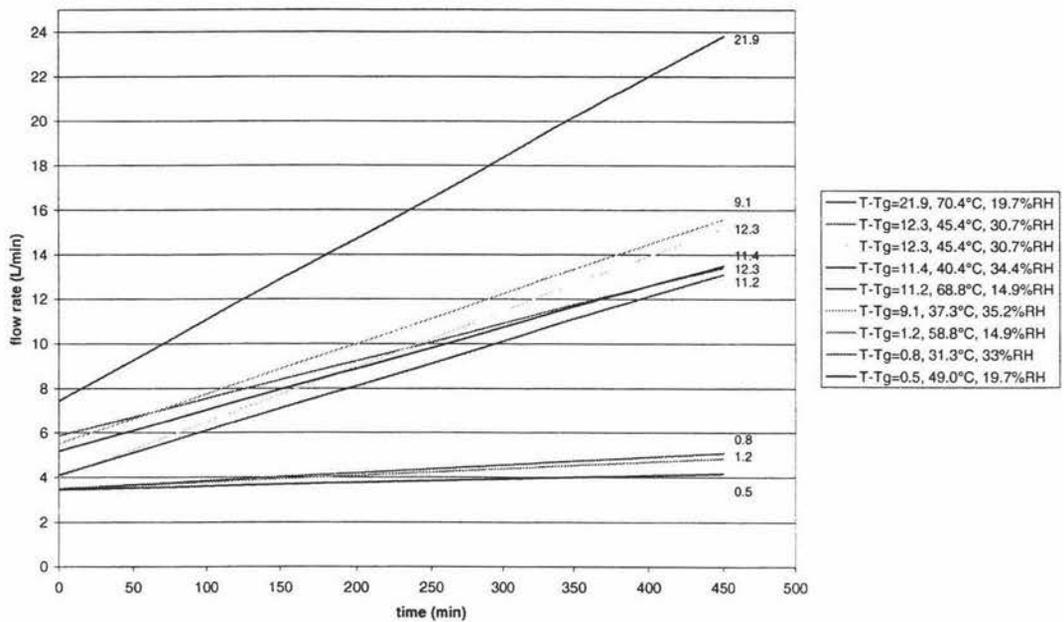
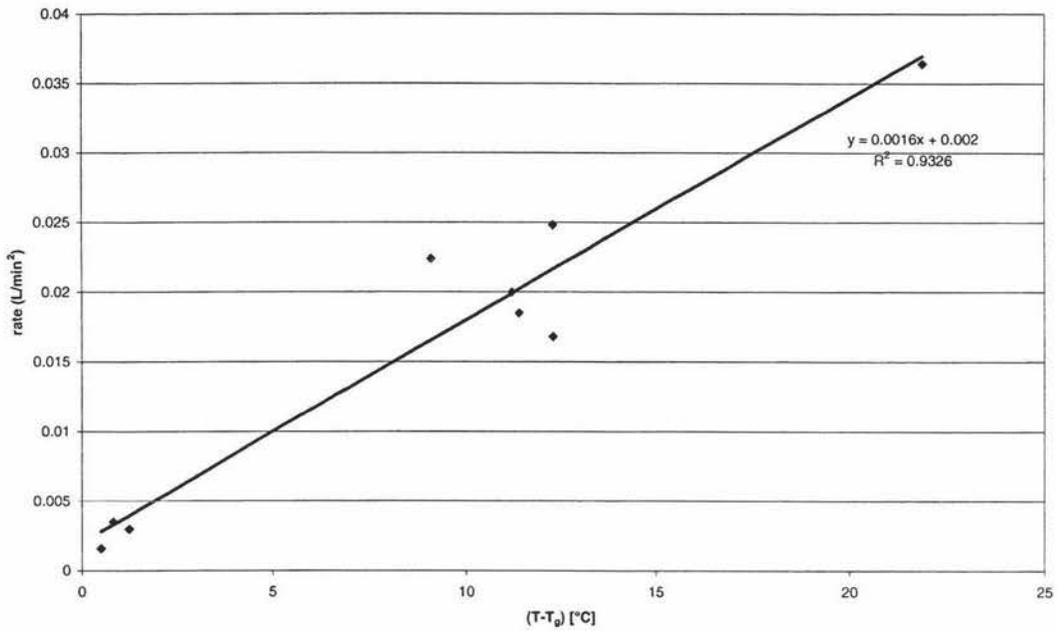


Figure 6.5 Best fit lines for all experiments

It is obvious then, that from the time the airflow was turned on, until the time the first reading was taken, a very fast initial increase in the cohesiveness of the powder occurred for the experiments at  $(T - T_g) > 0$ . This was not consistent with the linear stickiness/time relationship observed over the next 7.5 hours. The flow rate for free flowing amorphous lactose powder was measured as 3.5 L/min, and this is the value recorded for the  $(T - T_g) = 0^\circ\text{C}$  experiments at time=0.

It is not known why this fast initial response is observed. It is possibly due to the amount of time that each experiment spent above  $T_g$  before conditions reached the desired  $(T - T_g)$  value. Some small amount of viscous flow would occur in this time and lend some cohesiveness to the particles. However, this amount of time was only 2-7 minutes, which is negligible when compared to the remainder of the experiment. It is more likely that this initial stickiness occurs when the points where particles are already touching enter the rubber state. A lower viscosity would mean that these contact points would be stickier, so one would expect to see the initial stickiness increase with increasing  $(T - T_g)$ , as was observed.

The slopes of the best-fit lines in figure 6.5 are a measure of the rate at which amorphous lactose became sticky. Figure 6.6 shows the slope of the lines in figure 6.5 plotted against the  $(T - T_g)$  value they were obtained at.



**Figure 6.6** Rate of sticking at different  $(T-T_g)$  values

These rates form a linear relationship with  $(T-T_g)$ . However, there is a lot of scatter around the  $(T-T_g)=10^\circ\text{C}$  point, which was most likely due to the error and uncertainties inherent in the experimental procedure, and in estimating  $T_g$ . Figure 6.6 shows that the rate that amorphous lactose becomes sticky over time depends on the magnitude of  $(T-T_g)$ .

#### 6.4.2 FLOW RATE CORRELATIONS

Throughout the process of performing experiments with the improved blow test, observations were made on the condition of the powder at certain flow rate values. This involved dismantling the apparatus at the completion of the run, and probing the bed of powder with a spatula. It was noted how easily the bed could be disturbed, what form it took after it was disturbed (lumps or powder), and how easily any lumps could be crushed. In some cases where there was little or no data for certain flow rates, a bed of powder was specifically made sticky so that observations could be made for these flow rates. Table 6.1 shows a summary of the observations made for various flow rates required to carve a channel into the powder bed.

**Table 6.1 Observations of powder condition at endpoint of the blow test**

Flow rate (L/min)	Observations
0-3.5	Free flowing powder
4-6.5	Some caking strength, but easily disturbed. When disturbed forms powder with no lumps.
7-9.5	When disturbed forms lumps which are fragile and easy to break up into powder.
10-12.5	More difficult to disturb. Forms larger lumps with more strength.
13-15.5	Hard to break up bed, lumps have significant strength.
16-18.5	Lumps are larger (whole segment sized) and difficult to crush.
19-22	Limit of tester. Very difficult to break up bed. Forms very hard large lumps.

Although the blow test readings can be related to physical phenomena through table 6.1, the question arises of how to further relate these results to a level of stickiness that will cause a problem during powder manufacture. This is practically impossible to do, as it would be hard to perform the blow test on caked powder inside process equipment. In addition, the effect of compression is unknown. Amorphous lactose would reach a higher caking strength if it were compressed under the same  $(T-T_g)$  and time conditions, for example, when hitting the wall of a cyclone at high speed, or being moved in a screw auger.

The best that could be done under the circumstances was to define a caking strength that may lead to problems of sticking in process equipment. The value chosen was 8 L/min, where amorphous lactose powder is in an early stage of stickiness. It was still easy to disturb or move around at this strength level, and any lumps formed were easily dispersed by only light pressure.

### 6.4.3 PREDICTION OF STICKINESS WITH TIME

Using the best fit lines of figure 6.5, the time taken for amorphous lactose to reach a caking strength of 8 L/min can be calculated at the different  $(T-T_g)$  conditions. Figure 6.7 shows the log of these times plotted against  $\log(\text{viscosity})$ , which is a function of  $(T-T_g)$ . The times are plotted against viscosity as this is the physical property that determines sticking behaviour. It should be noted that the three data points at high viscosities [ $(T-T_g)=0^\circ\text{C}$ ] are only extrapolations from experimental data, while the other data points were measured experimentally.

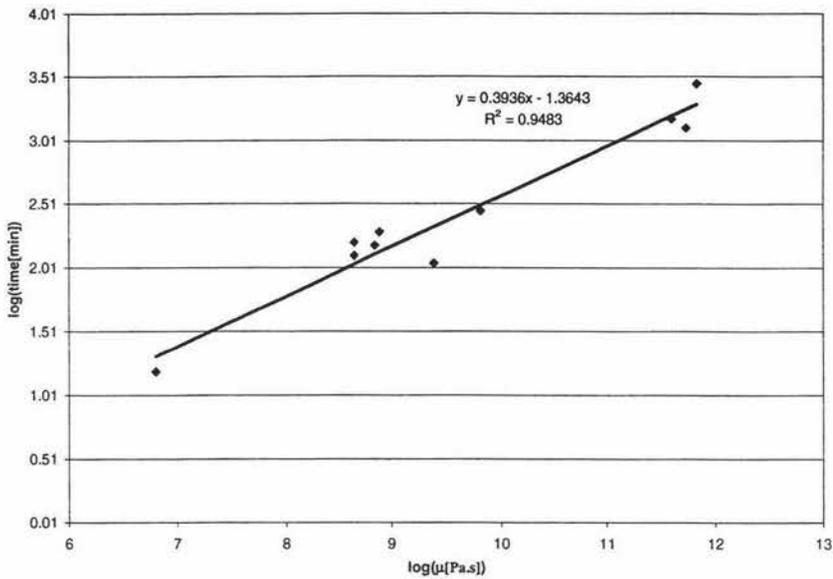


Figure 6.7 Contact time required to reach a strength of 8 L/min

A linear fit can be applied to the data of figure 6.7. A prediction can be made as to how long amorphous lactose will take to reach a level of stickiness of 8 L/min, by relating the temperature and water activity to a  $(T-T_g)$  value and hence a viscosity, and using this best fit line to determine the required time.

Figure 6.8 shows predicted contact times required to reach a strength indicated by a flow rate of 8 L/min on the blow tester, for various water activities and temperatures.

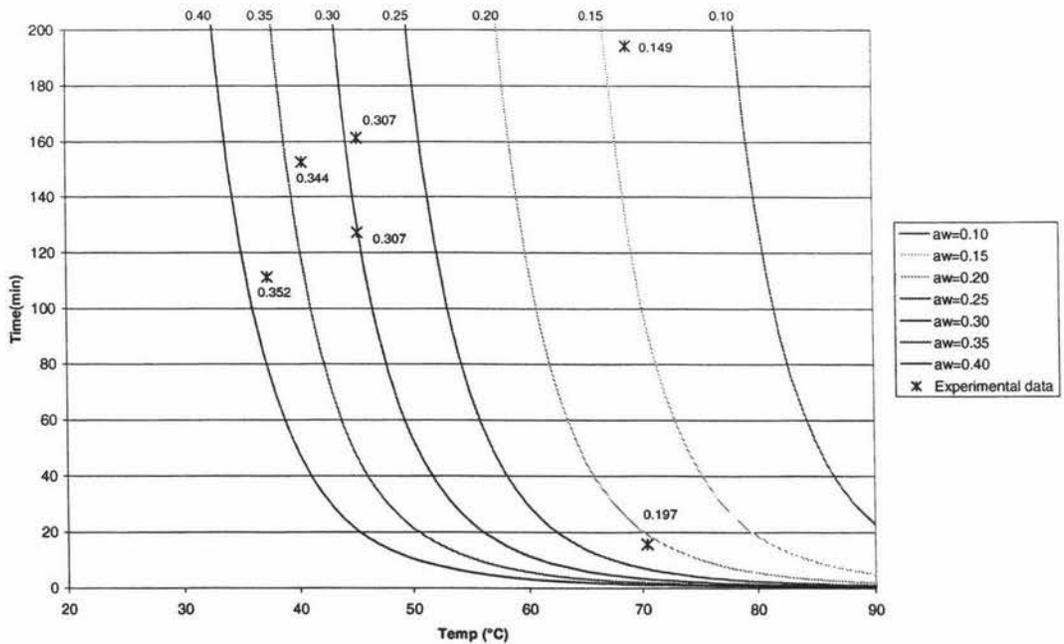


Figure 6.8 Predicted contact time to reach 8 L/min

Also plotted on figure 6.8 is the data shown in figure 6.7, plotted as a function of the experimental temperature instead of viscosity. The data points are labelled with the water activity that they were obtained at. These points show good agreement with the predictions.

It can be seen from figure 6.8 that the time taken to reach a strength indicated by a flow rate of 8 L/min is strongly dependent on the temperature at a given water activity – a small change in temperature causes a large change in the required contact time. The effect of water activity is also large. For example, at a temperature of 70°C, increasing the water activity from 0.15 to 0.20 lowers the required contact time from 100 minutes to about 20 minutes.

The curves in figures 6.8 bend sharply to the right below contact times of 20 minutes. In this region conditions are above  $(T-T_g)=25^\circ\text{C}$ , and the predicted times are approaching zero. It was found experimentally (section 5.3.5) that at  $(T-T_g)>25^\circ\text{C}$  amorphous lactose powder became very sticky in less than 30 seconds, and no measurements could be made in this region using the blow test. The time predictions at such high  $(T-T_g)$  values are therefore unreliable, as contact time tends to zero above  $(T-T_g)=25^\circ\text{C}$ , much faster than predicted.

#### 6.4.4 CONDITIONS TO AVOID

While figure 6.8 could be used to show what conditions to avoid to eliminate stickiness problems from amorphous lactose, it involves picking a contact time and working backwards to obtain the temperature and water activity conditions. This is not very intuitive, and the contact time is difficult to attach meaning to. Since the contact time to reach a certain level of stickiness depends on the value of  $(T-T_g)$ , it is possible to re-plot figure 6.8 in terms of the water activity and temperature of the powder, and the amount that  $T_g$  is exceeded by (figure 6.9).

Figure 6.9 essentially shows a plot of the temperature of amorphous lactose at different water activities, and indicates what  $(T-T_g)$  will be at these conditions. From the experimental work reported in this chapter it is known how much contact time is required to reach the given level of stickiness of 8 L/min at the different values of  $(T-T_g)$ . At a  $(T-T_g)$  of  $10^\circ\text{C}$  3 hours is required, so sticking is occurring only slowly. At  $25^\circ\text{C}$  above  $T_g$ , amorphous lactose is instantly very sticky, so sticking is occurring much faster. At  $T_g$ , sticking is occurring very slowly and theoretically below  $T_g$  no stickiness should be observed. It should be noted that if a different level of stickiness was chosen, figure 6.9 would remain the same, but the contact times required to reach this stickiness would change.

From these observations, the conditions to avoid can be inferred. At  $(T-T_g)$  conditions of 25°C and above, amorphous lactose is sticky even with very short contact times. This condition should be avoided, even in process equipment where contact times are short, such as cyclones and fluidised beds. At the other end of the scale, powders containing amorphous lactose should be stored at conditions below  $T_g$ , to avoid any sticking and caking over long periods. It is possible to work with amorphous lactose in the region between  $T_g$  and  $(T-T_g)=25^\circ\text{C}$ , but not for indefinite periods. This region applies to areas

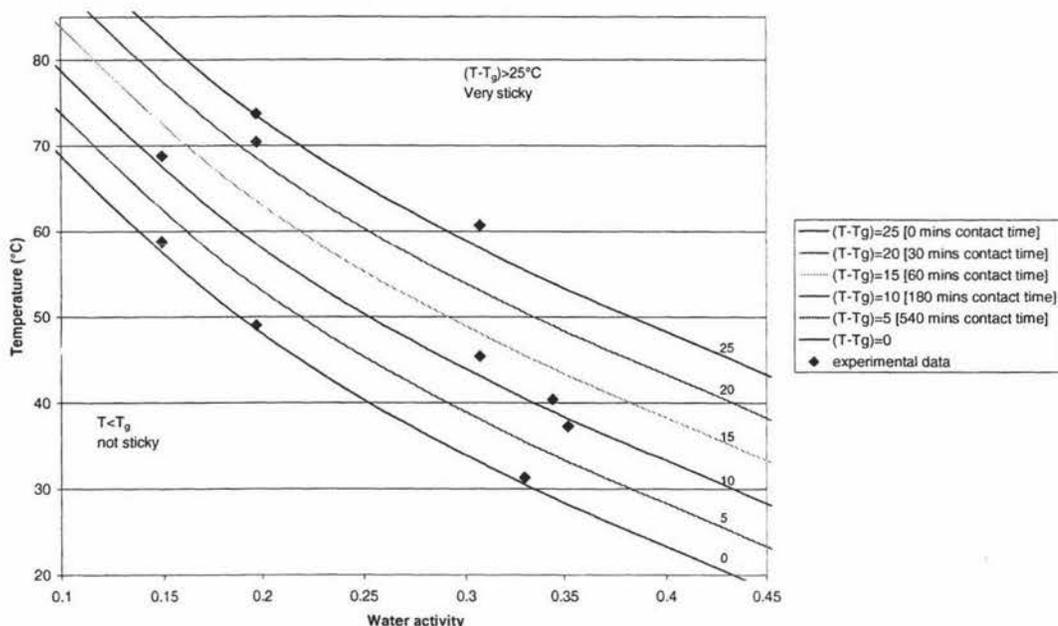


Figure 6.9 The different regions of stickiness

of processing where contact times are of intermediate length, such as short-term storage in a silo, or conveying along an auger. As a conservative estimate, it is recommended that for operations like this  $(T-T_g)$  should be less than 10°C.

Figure 6.9 can be used to show some important ideas. At a constant temperature, it shows what water activity amorphous lactose needs to be dried to, in order to avoid stickiness problems at the drier outlet. Powder particles at a temperature of 70°C need to be dried to a water activity of 0.22 to avoid the danger region. An important point to note is that since stickiness is a surface phenomenon, it is the water activity of the surface that needs to be below this value. This is also important when considering the mixing of two streams. If a stream of powder meets a stream of air at a higher humidity then the surface of the powder particles will absorb moisture and could possibly become sticky. In one factory, a staff member indicated that stickiness problems were often encountered where a stream of fines from the drier met a stream of cooler air.

At a constant water activity, the effect of increasing temperature can be seen in figure 6.9. At a water activity of 0.20 and a temperature of 65°C, amorphous lactose is at a  $(T-T_g)$  of 17°C, and will probably be safe to dry further in a fluidised bed without being too sticky. If the outlet temperature is increased, perhaps in order to push more product through the drier, then the  $(T-T_g)$  value increases. At 73°C, only 8°C higher than previously, the conditions exceed  $T_g$  by 25°C and the region of instant stickiness is reached. This explains why it was noted by some factory staff that sticking problems often began when the outlet temperature from the spray drier was increased to try and dry more product.

## 6.5 CONCLUSIONS

This chapter has shown that the sticking behaviour of amorphous lactose is determined only by the amount that the glass transition temperature is exceeded by, or  $(T-T_g)$ . Amorphous lactose at the same value of  $(T-T_g)$ , but at different temperatures and water activities, showed the same relationship of caking strength with time.

Amorphous lactose is stickier at higher values of  $(T-T_g)$ , and becomes sticky at a faster rate at higher  $(T-T_g)$ . The extent of stickiness and the rate of sticking can be estimated from the results in this chapter.

It was found that at conditions higher than  $(T-T_g)=25^\circ\text{C}$ , amorphous lactose became very sticky almost instantaneously. Because of this, conditions giving  $(T-T_g)>25^\circ\text{C}$  should be avoided in all areas of processing. Even very short contact times, such as those in a fluidised bed, are sufficient to lead to particles sticking together under these conditions.

Between  $T_g$  and  $(T-T_g)=25^\circ\text{C}$  amorphous lactose takes time to build interparticle bridges and stick together. Processing in this region is possible, but to be safe the value of  $(T-T_g)$  should be minimised. It is suggested that a  $(T-T_g)$  of 10°C would be a good limit to remain below. At this condition, amorphous lactose takes longer than 3 hours of contact time to reach a moderate level of stickiness.

For long term storage of powders, it is recommended that conditions be below the glass transition temperature of amorphous lactose. Theoretically, no stickiness should be observed below  $T_g$ , but the experiments in this work dealt with time periods of up to 8 hours, so storage trials for longer periods may be needed to verify this.

## CHAPTER 7

### CONCLUSIONS AND RECOMMENDATIONS

The sticking behaviour of amorphous lactose is determined by the amount that the glass transition temperature is exceeded by. Amorphous lactose at the same value of  $(T-T_g)$ , but at different temperature and humidity conditions, showed the same relationship of stickiness versus time.

The values of  $(T-T_g)$  that could cause problems in different areas of powder manufacture were identified. It was found that at a  $(T-T_g)$  of  $25^\circ\text{C}$ , amorphous lactose becomes very sticky in a very short space of time. Conditions leading to a  $(T-T_g)$  of  $25^\circ\text{C}$  or greater should therefore be avoided. Even in fluidised beds or cyclones, where particle to particle contact times are very short, amorphous lactose  $25^\circ\text{C}$  above its  $T_g$  will almost certainly cause sticking and caking problems.

At lower  $(T-T_g)$  values amorphous lactose was found to be less sticky – at  $(T-T_g)=10^\circ\text{C}$  it took approximately 3 hours for amorphous lactose powder to reach an early level of stickiness. Processing operations where contact times are longer than a few seconds, for example short-term storage in hoppers, or screw auger conveying, could cope with amorphous lactose in this state without problems. Keeping amorphous lactose below a  $(T-T_g)$  of  $10^\circ\text{C}$  is suggested as a conservative practical limit to help avoid sticking and caking problems in these situations.

It was found that at  $T_g$ , amorphous lactose needs a very long time to show any evidence of stickiness. Theoretically, keeping a powder below its  $T_g$  for long-term storage should avoid caking problems due to amorphous lactose. Trials may be necessary to confirm this.

Implementing the results of this work should be relatively simple. Knowing what  $(T-T_g)$  should be avoided means that the temperature and moisture conditions to be avoided are also known. If temperature and relative humidity were monitored at key locations, such as at the spray drier outlet, in cyclones and in fluidised beds, then the plant could be operated in such a way as to avoid the critical  $(T-T_g)$  conditions. However, the instrumentation to monitor temperature and humidity is not often in place in commercial installations.

In order to know what the value of  $(T-T_g)$  is, it is important to know what  $T_g$  will be at different moisture contents and water activities.  $T_g$  can be estimated as a function of moisture content from the Gordon-Taylor equation. Much scatter and disagreement

exists in the available  $T_g$ /moisture content data, due to the presence of residual moisture in amorphous lactose that had been dried over phosphorous pentoxide. This method of desiccation has been accepted to give completely dry samples, but it was shown that for amorphous lactose some residual moisture was left even after 3 weeks of desiccation. The possibility of residual moisture needs to be considered when measuring the moisture content of amorphous lactose.

It was found that the best way to estimate  $T_g$  as a function of water activity was through a cubic function that had been fitted to the available data (equation 3.1). The mechanistic approach of combining the moisture sorption isotherm for amorphous lactose with the Gordon-Taylor equation did not give good predictions due to the combined effect of small errors in the two equations. It is preferable to predict  $T_g$  from water activity. In commercially produced powders, the presence of other components such as fat and protein makes it difficult to know the moisture content associated with the amorphous lactose portion.

Attempts to follow amorphous lactose crystallisation with time were unsuccessful, due to fluctuating experimental conditions, hindered moisture desorption and the sensitivity of the microbalance. However, new data from other sources has helped confirm the model for amorphous lactose crystallisation. This model was fitted to all the currently available data to improve the accuracy of the constants in it, and can be used to predict the time for crystallisation of amorphous lactose. More work is needed to confirm that crystallisation, like stickiness, depends only on the value of  $(T-T_g)$ .

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## NOMENCLATURE

a	Initial particle radius	m
A	Cross sectional area	m <sup>2</sup>
A <sub>p</sub>	Particle cross sectional area	m <sup>2</sup>
a <sub>w</sub>	Water activity	
c	GAB constant	
C <sub>A,B,C</sub>	Avrami model constants	
C <sub>1,2</sub>	WLF constants	
D	Particle diameter	m
f	GAB constant	
F	Force	N
F <sub>o</sub>	Van der Waals cohesive force	N
F <sub>s</sub>	Force due to sticking	N
G	Acceleration due to gravity	m/s <sup>2</sup>
k	Gordon-Taylor equation constant	
k	Avrami rate constant	s <sup>-3</sup>
k	Combined constant	
K	Viscous flow constant	
M	Moisture content	kg water/kg dry solids
M <sub>o</sub>	Monolayer moisture content	kg water/kg dry solids
m	mass	kg
m <sub>t</sub>	total sample mass	kg
n	Avrami index	
P	Pressure	Pa
Q	Flow rate	m <sup>3</sup> /s
R	Universal gas constant	J/K <sup>-1</sup> mol <sup>-1</sup>
t	Time	s
T	Temperature	°C
T <sub>g</sub>	Glass transition temperature	°C
U	Air velocity	m/s
V <sub>p</sub>	Particle volume	
w	Mass fraction	kg/kg
x	interparticle bridge radius	m
x	flow rate	L/min
Y	Crystallinity	

## Greek Letters

$\mu$	Viscosity	Pa.s
$\mu_g$	Viscosity at the glass transition	Pa.s
$\mu_f$	interparticle friction coefficient	
$\sigma$	Surface tension	N/m
$\rho_a$	Air density	kg/m <sup>3</sup>
$\rho$	Amorphous lactose density	kg/m <sup>3</sup>
$\theta$	Blow tester angle	°
$\phi$	angle of slide	°