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MASSEY UNIVERSITY

**COLLEGE OF ENGINEERING
TE KUPENGA O TE MĀTAURANGA**

**CHARACTERISATION OF THE RHEOLOGICAL PROPERTIES
OF MOZZARELLA CHEESE**

**A THESIS PRESENTED IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF**

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ABSTRACT

An important usage of Mozzarella cheese is as an ingredient in pizza. For this reason, it is important to understand the functional properties of melting and flow behaviours of mozzarella cheeses. For instance, understanding the influence of temperature and moisture on the rheological properties of mozzarella cheese may help cheese the maker to optimise products.

A modified UW Meltmeter and rotational methods were used to characterise the rheological properties of mozzarella cheese. The temperature impact on the rheology was determined by measurement over the temperature range from 30 to 80 °C. To investigate the moisture content effect on the rheological properties, mozzarella cheese was dried over different salt solutions or by desiccation in a fridge prior to rheological measurement.

Modifications of the UW Meltmeter improved the sample preparation, temperature control during the testing and data analysis. The viscosity data obtained by the UW Meltmeter followed the Arrhenius law with an activation energy of $30.3 \pm 1.2 \text{ kJ} \cdot \text{mol}^{-1}$. In the rotational method (the shear rate ramp test), the data of viscosity versus shear rate followed the power law model, and the consistency index was fitted to the Arrhenius law and WLF model. The WLF model had a wider temperature range fit than the Arrhenius law. It was found that the viscosity determined from the UW Meltmeter and rotational rheometer was quite different. They are actually measuring different aspects of flow. In this study, the rotational experiment produced results that were more appropriate to explain flow behaviour in cheese in the conditions experienced in pizza baking. The methods to lower the moisture content of mozzarella cheese led to unexpected results where viscosity was not strongly dependent on moisture content. This may have been due to disruption of the structure of the mozzarella cheese during drying.

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1. BACKGROUND AND OBJECTIVES

1.1. Background

In the last 40 years, the production of cheese in New Zealand has increased to around 200,000 tonnes. New Zealand has become the third biggest producer and the second biggest exporter of cheese in the world (Hoogwegt Horizons, 2012; Index Mundi, 2012). The increase in cheese production indicates the growing demand for cheese from consumers. The prosperous cheese market prompts cheese makers to put more effort into improving the performance of their products. Therefore, characterising cheese behaviour has become important so that cheese can be made with desired quality and functional properties.

Mozzarella is used as an ingredient in some prepared foods and is a high volume cheese supporting food service industries. According to Wang (2002) and Rudan and Barbano (1998), the key functional properties of mozzarella include: the cheeses can be completely melted and fused together, but not too soupy after baking; some free oil can be released to the cheese surface to provide a shiny appearance but no oil pools are formed; a little browning and blistering can occur without an over-burnt appearance; a stretching behaviour should appear forming strings which are not brittle.

These functional properties of mozzarella are affected by both internal and external factors. The internal effects include cheese moisture content (Everett & Auty, 2008), fat content (Everett & Olson, 2003), calcium content (McMahon & Oberg, 2011). The external effects include temperature (Ko & Gunasekaran, 2008), and applied stress (Wang *et al.*, 1998). All these factors can affect the structure of the cheese. Example effects include the amount of protein-protein and calcium-protein interactions which have been shown to influence cheese melting properties (Lucey *et al.*, 2003).

Therefore, quantification of the link between the functional properties of cheese and the internal and external factors would be of great benefit by allowing improvement of the cheese performance and target desired properties. In the current study, the effects of temperature and moisture content on the melt and flow behaviour of mozzarella were investigated.

1.2. Objective of project

The major objectives of this project were:

- To identify and/or develop a methodology to measure flow properties (e.g. viscosity) for cheese samples under low shear conditions (gravity).
- To quantify the melt and flow behaviour of traditional mozzarella at different temperatures.
- To quantify the melt and flow behaviour of traditional mozzarella at different moisture contents using the developed method.
- To provide a relationship to predict the flow behaviour as a function of temperature and moisture content using the developed method.

2. LITERATURE REVIEW

2.1. Introduction

In order to develop the methods to estimate cheese flow properties under low shear conditions and establish how these change as a function of temperature and moisture content, it is important to first review the literature on cheese composition and structure, the mechanism for cheese melting, the factors effecting melting performance and the process of mozzarella cheese making. Also, understanding different types of rheological behaviour is necessary, which is helpful to select and adapt a model to describe the flow behaviour. Reviewing the methods to measure cheese flow during melting makes it possible to choose the most appropriate to use in this project and obtain more accurate data. What's more, the methods of modelling gravity driven flow should be well understood.

2.2. Melting cheeses

For melting cheeses, the textural and rheological properties play critical roles in its application. Cheese is considered as a viscoelastic material. When deformation is occurring, the mechanical energy is partly dissipated (regarded as viscous behaviour) and partly stored in the cheese (regarded as elastic behaviour) (Lucey *et al.*, 2003). Understanding the cheese composition, structure and melting mechanism is useful in realising the textural and rheological properties and its influence by diverse factors.

2.2.1. Cheese composition and structure

The composition of cheese mainly includes protein, fat, water, and minerals (notably calcium). These components play essential roles in affecting the texture and functionality of cheese. However, the texture and functionality of cheese are not simply affected by individual composition; in other words, each composition mutually influences the texture and functionality. Therefore, it is a good start to have the

understanding of the composition of cheese before researching the cheese functional behaviours.

It is well known that cheese is formed via the gelation of milk. In bovine milk, casein makes up around 80% of the total proteins. The families of casein include α_{s1} -, α_{s2} -, κ - and β -casein respectively accounting for 40%, 10%, 5% and 45% casein protein (Farrell Jr *et al.*, 2004). In cheese making processes, the κ -casein amino acid chain in milk is broken by renneting enzymes causing the instability of casein micelles. A coagulum is formed due to the casein micelle aggregation in the presence of enough calcium ions at a high enough temperature (Scott *et al.*, 1998). Therefore, α_{s1} - and β -casein are retained as the fundamental components of cheese.

Water in cheese exists in three states: free water, bound water and entrapped water (Everett & Auty, 2008). The free water is distributed in serum channels which can be easily extracted. The bound water, which is not able to act as a solvent, has structural bonding with casein as a constituent of the casein matrix. The entrapped water is restrained by the casein matrix but it can be released if cut (Everett & Auty, 2008; Vaclavik & Christian, 2008). It is found that the entrapped water increases during storage; this indicates the absorption of expressible water into protein matrix as entrapped water during storage (McMahon *et al.*, 1999).

Everett and Olson (2003) point out that the states of fat existing in cheese are not totally clear. It is considered that the emulsified state may exist or it may be filled in channels in the protein matrix appearing as pools or globules. The form of fat in cheese may affect the cheese properties by the fat globule size or the interaction between globules and protein matrix. Fox *et al.* (2000) hold a similar point of view. They state that the cheese properties like meltability, flowability or firmness are influenced by the fat globule distribution and size, while the size of fat globules depend on the processes and conditions used in cheese making like temperature, ingredients and aging time.

2.2.2. Functional properties of melting cheese

Some cheeses are used in cooking such as pizza, cheese sandwiches, pasta dishes, cheese burgers and sauces. Thus, it is essential to understand the properties of the cheese during its heating. In order to describe the behaviour of cheeses during cooking processes, a number of parameters are defined to express their functional properties. For instance, mozzarella as pizza topping baked in the oven will present the phenomenon of melting, flowing and stretching. The corresponding functional properties can be meltability, flowability and stretchability. Table 2-1 (Fox *et al.*, 2000) shows several conventional functional properties of melting cheese.

Table 2 - 1 Conventional functional properties of melting cheese (adapted from Fox *et al.*, 2000)

Property	Definition
Meltability	The capacity of cheese to soften to a molten cohesive mass on heating
Flowability	The capacity of melted cheese to flow
Stretchability	The capacity of melted cheese to create strings, cohesive fibres, or sheets during extension
Limited oiling off	The capacity of cheese to express free oil on heating

2.2.3. Mechanism for melting

A study by Park *et al.* (1984) shows that the cheese softening under 40°C is partly associated with the fat melting in cheese. They used a differential scanning calorimeter to observe the thermograms of cheeses in the range of 10 to 70°C. The results showed that melting enthalpy is required to heat the cheese only in the temperature range of 10 to 40 °C, reflecting the fat melting. In further heating, it is suggested that the interaction between proteins primarily governs the cheese melting. Bryant and McClements (1998) suggest that relaxation of the of casein-to-casein (CN-

CN) interactions plays a key part in the cheese melting. The bond strength of CN-CN is determined by the balance between electrostatic repulsion and hydrophobic interaction. With the temperature increasing, there are increases in both the electrostatic repulsion and hydrophobic interaction, however the balance shifts and favours more repulsion, and weakening of the casein matrix. This explanation is supported by Lucey *et al.* (2003). As temperature increases, the protein-protein bond becomes more relaxed and the behaviour becomes more liquid-like, thus cheese is able to flow.

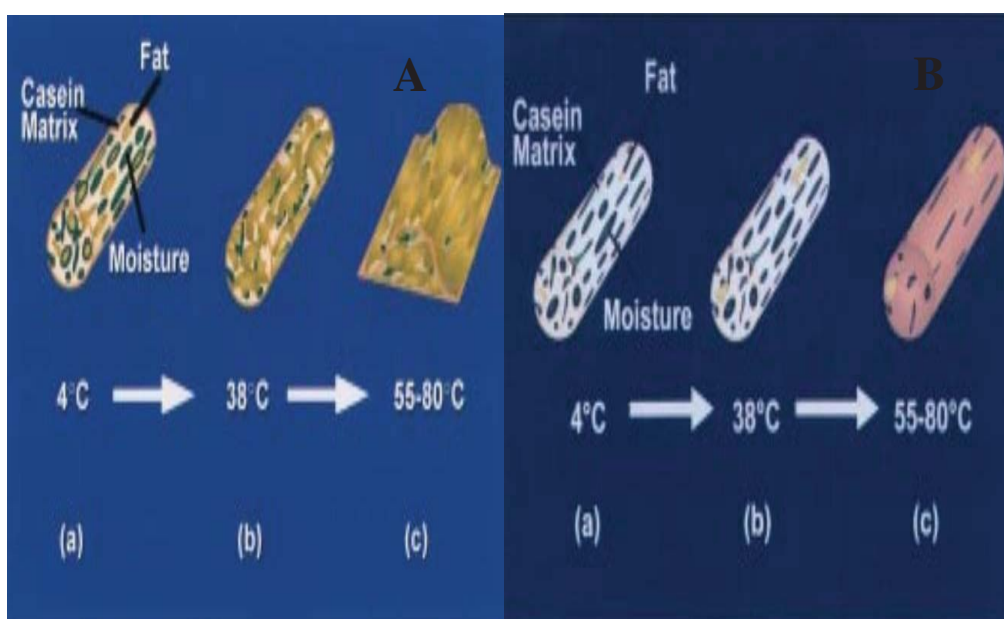


Figure 2 - 1 Schematic of cheese melting (Rudan & Barbano, 1998). A: Full fat cheese, B: Fat free cheese

Schematic diagrams (Figure 2-1) describing cheese melting with the changes occurring to fat, moisture and casein matrix were drawn by Rudan and Barbano (1998). For full-fat cheese (figure 2-1 A), the fat melts from 4 to 38 °C, and some fat is forced to the surface of cheese shred because the melted fat expansion is larger than the expansion of the protein matrix. The expelled fat coats the surface of the cheese shred, preventing moisture loss. As the temperature increases, the changes in the interactions between proteins, water-protein and calcium-protein and the decrease in the apparent viscosity bring about the shred collapse, thus the cheese starts to flow.

For fat-free cheese (figure 2-1B), the initial transport of fat to the cheese surface cannot occur causing the rapid dehydration on the cheese surface after heating. Therefore, cheese dries and weakening of the protein matrix do not occur, brown shell is formed and the cheese does not melt.

2.2.4. Factors effecting melting performance

The factors: milk composition, temperature, the extent of acidification, the Ca salt concentration, the extent of proteolysis, ripening reaction etc. have an effect on the rheological properties of cheese (Lucey *et al.*, 2003). Even sampling direction (Ak & Gunasekaran, 1997) and holding time before allowing sample to flow (Kuo, Wang, *et al.*, 2001) have been shown to have effects on the rheological properties of cheese. Several factors influencing the rheological properties of cheese are introduced below.

2.2.4.1. Temperature

It is well known that the cheese meltability increases with heating temperature within a range of temperatures regardless of the method utilised to assess meltability and regardless of the exact melting indicator used (Gunasekaran *et al.*, 2002; Lee *et al.*, 1978; Sutheerawattananonda & Bastian, 1998; Wang *et al.*, 1998). Viscosity denotes the resistance of cheese fluid to flow and is regarded as one indicator of meltability. Cheese with greater viscosity is more resistant to flow. Dimitreli and Thomareis (2004) studied the viscosity of processed cheese at 55 to 95 °C. Increasing the temperature resulted in a weaker shear rate dependence of the viscosity (figure 2-2). As can be seen from the figure 2-2, the change in viscosity becomes smaller when the temperature is higher. A similar phenomenon was obtained by Muthukumarappan *et al.* (1999a), the biaxial elongational viscosity of Cheddar cheese dropped rapidly before 50 °C, subsequently the drop became slower and slower.

Wang (2002) extended the temperature range in their research. They used a computer vision system to investigate the melting properties of cheddar and mozzarella cheese as indicated by melting degree (the ratio of area after and before

cooking) and melting rate (the increase in melting degree within the first minute) at the temperature range from 70 to 200 °C. The result was that the cheeses reached a maximum melting rate and melting degree at around 130-160 °C, while with the cooking temperature increase, there was a decrease in both of the two indicators. The moisture loss, oil evacuation and even evaporation at the high temperature may contribute to the decrease in the melting rate and melting degree.

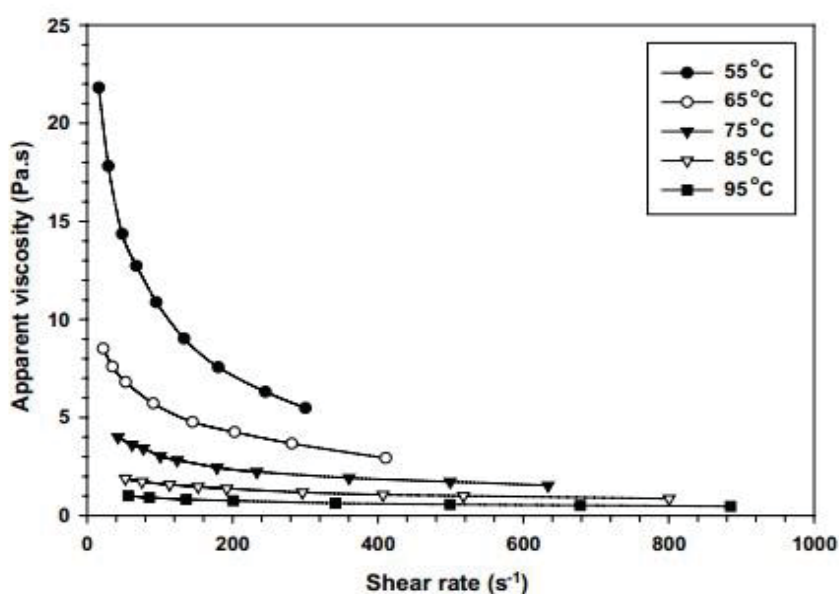


Figure 2 - 2 Flow curves of processed cheese at different temperature (Dimitreli & Thomareis, 2004)

2.2.4.2. Moisture

The relationships between compositional factors and melting properties are complex because of the interdependence between the compositional variables. Moreover, simple bivariate calculations of relationships between compositional factors and melting do not always illustrate actual correlations (Ruegg *et al.*, 1991). Probably for these reasons, Harvey *et al.* (1982) did not find that moisture always significantly affects melting properties.

Some studies prove the significance of moisture in impacting melting properties. The meltability correlated much better with fat on a wet matter basis than that for fat on a dry matter basis, demonstrating moisture also plays a major role in cheese meltability (Lefevre *et al.*, 2000). The complex viscosity of mozzarella cheese

decreased when moisture in the non-fat substance was increased, whereas the meltability was improved (Tunick *et al.*, 1993). The impact of the ratio of water to protein on cheese rheological properties of mozzarella cheese was investigated by Fife *et al.* (1996). They found that when the ratio of water to protein is increased in the mozzarella cheese, the meltability of cheese increases. McMahon *et al.* (1999) point out that making matrix proteins more hydrated can improve the meltability of cheese. That means that reducing the protein-to-protein interactions and increasing the interaction between entrapped water and protein enable improvements to the meltability of cheese. This view is supported by Taranto *et al.* (1979).

2.2.4.3. Fat

Tunick *et al.* (1993) in their study compared the properties between low fat cheese and high fat cheese. They found that the meltability was lower in the low fat cheese than in the high fat cheese, and low fat cheese was more elastic and viscous than high fat cheese. Other researchers (Kahyaoglu & Kaya, 2003; Wadhvani *et al.*, 2011) observed the same result in that reducing the fat content of cheese led to decrease in meltability. However, Fife *et al.* (1996) suggest that the meltability of cheese does not primarily depend on the content of fat in cheese. They measured meltability of five cheese samples all stored at 1 day with different fat content. The result was that the meltability of all those samples was not substantially different. In Rudan and Barbano (1998)'s opinion, the content of fat is not important but the amount of fat released on the surface of shred for mozzarella cheese during baking is important as it prevents moisture loss and browning.

2.2.4.4. Calcium

According to McMahon and Oberg (2011), if there is an extreme removal of calcium before cooking and stretching during cheese making, a lack of interaction between protein and protein occurs in the cheese, resulting in the cheese becoming overly soft and flowable when heated. Thus this kind of cheese can be readily melted but the stretch attribute will be unacceptable. As highlighted by Everett and Auty

(2008), as the ratio of the insoluble calcium to soluble calcium decreases, the cheese meltability increases.

2.3. Rheology

2.3.1. Types of rheological behaviour

2.3.1.1. Newtonian fluids

A Newtonian fluid is a fluid that has a viscosity independent of the shear strain-rate. In other words, for a given temperature the ratio of shear stress to shear strain-rate is constant. As in figure 2-3, the Newtonian fluid's flow curve plotting the shear stress vs. shear strain-rate is a straight line. The slope of the line is the viscosity. Materials such as water, mineral oil or vegetable oils are Newtonian fluids. Furthermore, in some cases, the liquids with low concentration like skim milk, can be regarded as Newtonian fluids (Bylund, 1995).

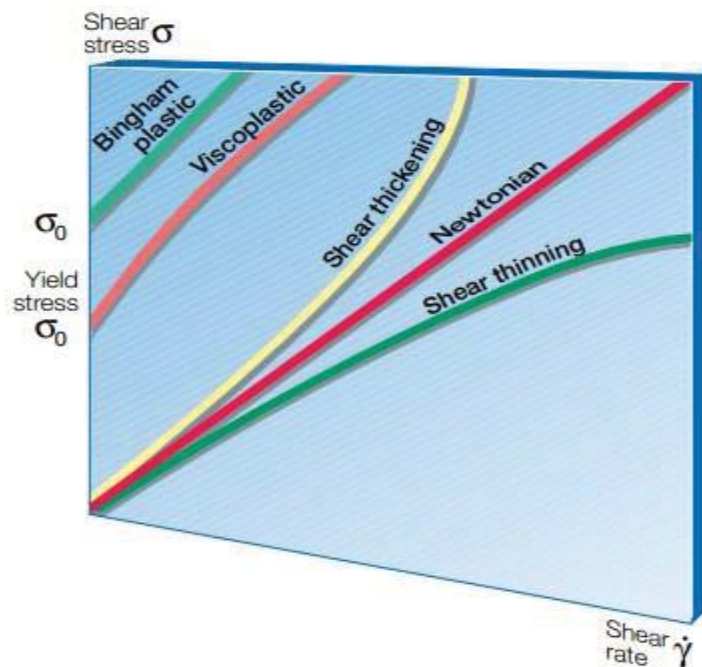


Figure 2 - 3 The types of rheological behaviours (Bylund, 1995)

The most appropriate model to represent the Newtonian fluid is the Newtonian fluid model:

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (2.1)$$

Where η is shear viscosity (Pa · s); τ is shear stress (Pa); $\dot{\gamma}$ is shear rate (s^{-1}).

For a great majority of liquids with low-molecular-weight, the model represents their behaviours perfectly in a wide shear strain-rate range. For some diluted emulsions, suspensions and long-chain molecules solutions, it may not be accurate but considered to be adequate for rough calculation (Whorlow, 1991).

2.3.1.2. Shear thinning flow behaviour

For a shear thinning liquid, the viscosity decreases with the shear strain-rate increase. Numerous liquid foods have this kind of behaviour. The dependence of viscosity on shear strain-rate can differ greatly between diverse products depending on the concentration and temperature. The cause of shear thinning behaviour is the deformation and rearrangement of particles as the shear strain-rate increases causing the flow resistance and viscosity to decrease. Cream, shampoo, salad dressings and juice concentrates are considered as typical shear-thinning fluids (Bylund, 1995).

Model: the power law fluid model (Whorlow, 1991):

$$\tau = k\dot{\gamma}^n \quad (2.2)$$

Or

$$\eta = \frac{\tau}{\dot{\gamma}} = k\dot{\gamma}^{n-1} \quad (2.3)$$

Where, τ is shear stress (Pa); $\dot{\gamma}$ is shear rate (s^{-1}); η is shear viscosity (Pa · s); k is the consistency index (Pa·sⁿ), which is related with the magnitude of the shear viscosity; n is the flow behaviour index. The main advantage for this model is the applicability of the power law fluid model to a large amount of non-Newtonian fluids

at wide-ranging shear strain-rates. The equation not only applies to shear thinning fluids but is also valid for shear thickening fluids introduced in the following section. When the stress is held a constant, equation (2.2) is the simpler equation to use. For shear thinning fluids, the viscosity of materials decreases with the rising shear strain-rate, the n in equation (2.2) is smaller than 1.

2.3.1.3. Shear thickening flow behaviour

For shear thickening fluids, the viscosities increase as the shear strain-rates increase. Generally, some high concentration suspensions represent this category of behaviour. In this type of fluid, the solvent at a low shear strain-rate plays the role of lubricant for suspended particles, while it is forced out as the shear strain-rate reaches a high level and the particles pack together densely. High concentration starch suspensions and wet sand are typical examples of shear thickening fluids (Bylund, 1995).

Model: the power law fluid model (Whorlow, 1991).

As introduced in section 2.3.1.2, the power law fluid model can be utilized for shear thickening fluid. On this occasion, the n in equation (2.2) is larger than 1.

2.3.1.4. Plastic flow behaviour (Bingham plastic and viscoplastic).

Fluids exhibiting yield stresses are regarded as plastic fluids. That means that a threshold force must be applied before the fluid is able to flow. If the force applied does not reach the material yield stress, deformation energy is stored in the material. In this phase, the material exhibits elastic properties. As soon as the force exceeds the material yield stress, the material starts to flow. At stresses above the yield stress such a fluid is labelled a Bingham plastic fluid, while the non-linear behaviour is called a viscoplastic liquid. Tomato paste, hand cream, toothpaste and greases are plastic fluids (Bylund, 1995).

1) The model for Bingham plastic flow behaviour: the Bingham model:

$$\tau = \tau_y + \eta\dot{\gamma} \quad (2.4)$$

In figure 2-3, the Bingham plastic fluid's flow curve plotting the shear stress vs. shear strain-rate is a line with a yield stress τ_y (Pa) on the stress-axis; the slope of the line η (Pa · s) is the material plastic viscosity.

2) The model for viscoplastic liquid: the Herschel-Bulkley model:

$$\tau = \tau_y + k\dot{\gamma}^n \quad (2.5)$$

The power law or Bingham models can both be considered as special status of Herschel-Bulkley model (i.e. with $\tau_y = 0$). This model can represent most flow behaviour in most materials (Whorlow, 1991).

2.3.2. Rheometry methods

With the intention of obtaining rheological properties of fluids, a variety of measurement techniques have been established. The techniques include capillary viscometers, rotational viscometers, oscillatory rheometers etc. which are all widely practical to food processing and polymer processing applications.

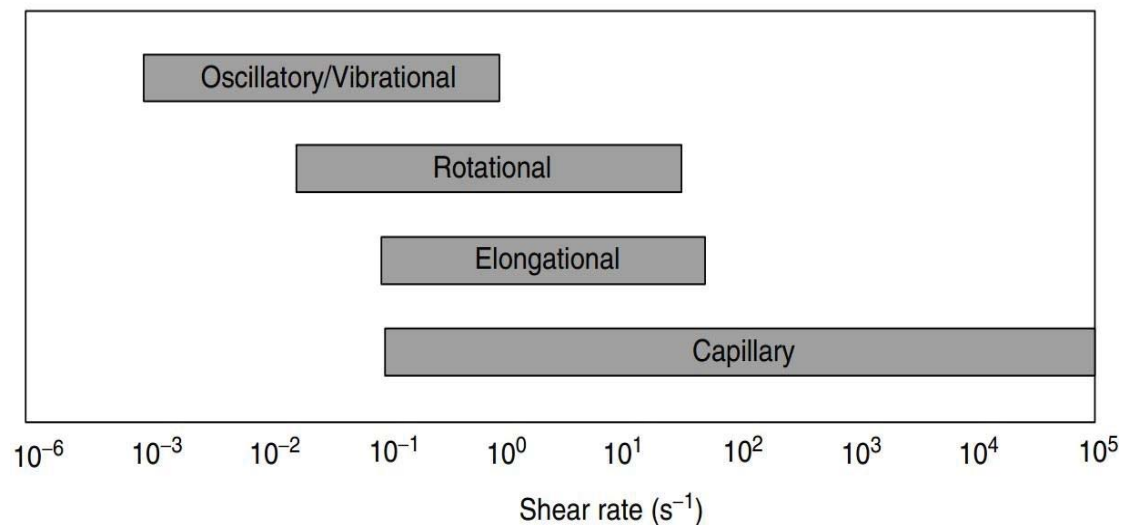


Figure 2 - 4 The strain-rate range for different rheological techniques (Gunasekaran & Ak, 2003)

In practice, whatever the material is, the selection of appropriate instrumentation for measuring its flow behaviours is important (Mao, 2007). The figure 2-4 shows the applicative ranges for several techniques.

2.3.2.1. *Capillary viscometers*

Capillary viscometry is a method where the time is measured for samples to flow through a pipe due to a certain pressure difference. It has been a method used extensively to measure viscosity because of the relative low-cost, simplicity and accuracy of the experimental instruments. However, the flow in the pipe is non-homogeneous from centre to wall of pipe. Therefore, mathematical corrections need be applied to obtain the true values. In some cases, it takes a long time due to the slow flow in pipe. Because of the similarity to a lot of process flows, it is widely applied to engineering applications (Chhabra & Richardson, 2008). Slippage may occur during the measurements of cheese due to fat separation especially at high temperature. The materials in the range of shear strain-rates from 10^{-2} to 10^4 s^{-1} are considered suitable for capillary viscometers. (Malkin & Isayev, 2012).

2.3.2.2. *Rotational viscometers*

The mechanism of a rotational viscometer is that the fluid viscosity corresponds to the required torque to turn the object within this fluid. Compared with other viscometers, the advantages of the rotational viscometer are that the continuous measurements at set of different shear strain-rates for one sample can be performed to analyse the shear dependent behaviour. Due to the constant shear strain-rate operation, it is able to test both non-Newtonian and Newtonian fluids. Disadvantages of rotational viscometers also exist including the high cost and that they are unable to achieve very high shear strain-rates (Singh, 2009). The shear strain-rate limits for rotational viscometers are 10^{-3} to 10^2 s^{-1} (Malkin & Isayev, 2012).

2.3.2.3. Oscillatory rheometer

For oscillatory rheometry, a sample is held between two collateral plates and subjected to a sinusoidal displacement or torque. The response of the specimen is then measured. The elastic and viscous aspects/characteristics of the shear modulus are calculated by the phase-lag of the material's response and amplitude. This rheometer covers an extensive range of frequencies and temperatures, so it is suited to measure curing and stable materials with viscosity in the 10^{-3} - 10^4 Pa·s range. The slippage could be an issue for this measurement as well.

2.3.2.4. Squeezing flow viscometry

For the traditional squeezing flow viscometry, the specimen is positioned between two parallel plates being compressed by one of the plates' vertical motion. Various modified geometries are available now (Corvalan & Campanella, 2005).

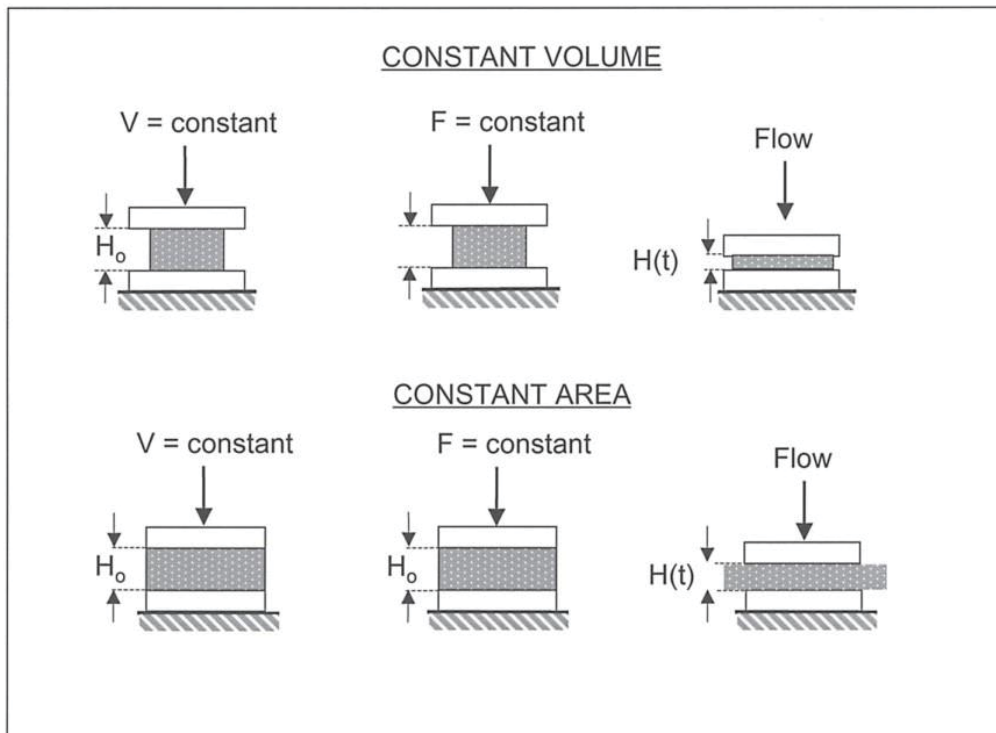


Figure 2 - 5 The basic test configurations of squeezing flow viscometry (Campanella & Peleg, 2002)

According to Campanella and Peleg (2002), the squeeze flow methods (figure 2-5) can be categorized to constant area and constant volume configurations by the

dimensions of specimen and plates. They are also classified to constant load and constant displacement rate applications. Due to different sample-plate contact scenarios, they are also divided to frictional squeezing flow and lubricated squeezing flow. Squeezing flow viscometry is usually applied for the determination of high-viscous materials' flow properties including polymer melts, semiliquid foods and semisolid foods (Gunasekaran & Ak, 2003). It is one of favourite methods, due to the simplicity of experimental set-up, overcoming the problem of slippage in comparison with other techniques and the similarity to processing flows in some manufacturing processes. However, issues with this non-standardised technique also exist, such as unknown or ill-defined boundary conditions (Engmann *et al.*, 2005).

2.4. Methods to measure flow during melting

In addition to methods for characterising rheology of products, other methods have been developed to characterise melting behaviour of products including cheese. These are discussed below.

2.4.1. UW Meltmeter

Wang *et al.* (1998) built a device called the UW Meltmeter shown in figure 2-6 for the purpose of exactly measuring the cheese melt/flow behaviour at different temperatures. At the bottom of the device, there is a stationary inner cylindrical ring equipped with an electric heater with a temperature controller. The inner ring engages with the outer annulus with a lever which is able to lift up or down. To start a test, first a sample well, 7-mm-deep and 30-mm-diameter, is formed by raising the outer annulus so as to place a cheese specimen molded to the same shape of the well. The top surface of the cheese is covered by a 66-mm-diameter circular plate equipped with a LVDT (linear variable differential transformer) which can avoid moisture loss in the surface of cheese and enable the continuous monitoring of the cheese sample height during the test. Once the set value of specimen temperature is reached, the outer annulus is lowered by the lever. The cheese specimen starts to flow forced by the LVDT

and circular plate's weight. Meanwhile, the height of cheese versus time is continuously collected by a computer data acquisition system via the LVDT.

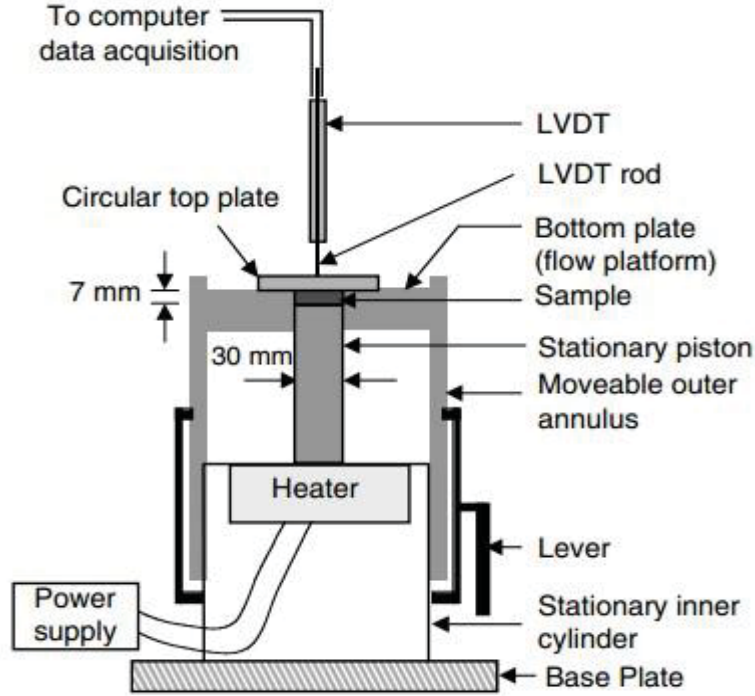


Figure 2 - 6 The UW Meltmeter (Gunasekaran & Ak, 2003)

The UW Meltmeter can be applied to both the constant force test and the constant deformation rate test. As the biaxial extensional flows under the assumption of constant sample volume, in constant force test, the biaxial stress growth coefficient (BSGC) η_B^+ can be calculated by the equation (2.6). In a constant deformation rate test, it can be calculated by the equation 2.7.

$$\eta_B^+ = \frac{\sigma_B}{\dot{\epsilon}_B} = \frac{F}{A(t)} / \frac{1}{2H} \left(-\frac{dH(t)}{dt} \right) = \frac{2FH^2(t)}{H_0 A_0 \left(-\frac{dH(t)}{dt} \right)} \quad (2.6)$$

$$\eta_B^+ = \frac{\sigma_B}{\dot{\epsilon}_B} = \frac{F}{A(t)} / \frac{1}{2} \frac{V_z}{H_0 - V_z t} = \frac{2F(t)(H_0 - V_z t)^2}{H_0 A_0 V_z} \quad (2.7)$$

Where: σ_B is the net stretching stress (Pa); $\dot{\epsilon}_B$ is the biaxial extensional strain rate (BESR) (s^{-1}); F is the squeezing force (N); A (t) is the real-time cross sectional area of sample (m^2); A_0 is the initial cross sectional area of sample (m^2); H(t) is the sample height (m), at the time t (s); H_0 is the initial height of sample (m); V_z is the deformation rate ($m \cdot s^{-1}$).

In the test (Wang *et al.*, 1998), the data of height versus time for mozzarella cheese under constant force were recorded (Figure 2-7), and further calculated and plotted as biaxial stress growth coefficient vs. biaxial extensional strain rate (Figure 2-8).

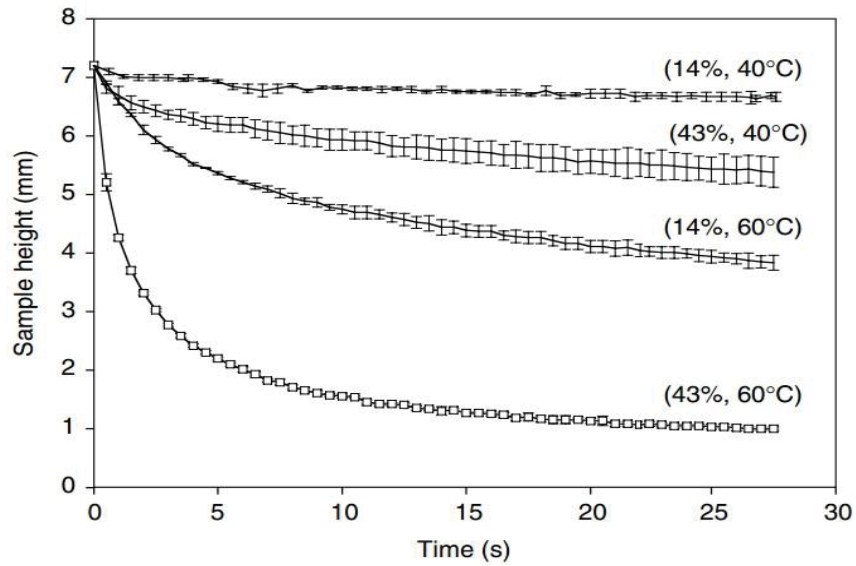


Figure 2 - 7 Mozzarella cheese sample height vs. time data obtained from the UW Meltmeter (Wang *et al.*, 1998)

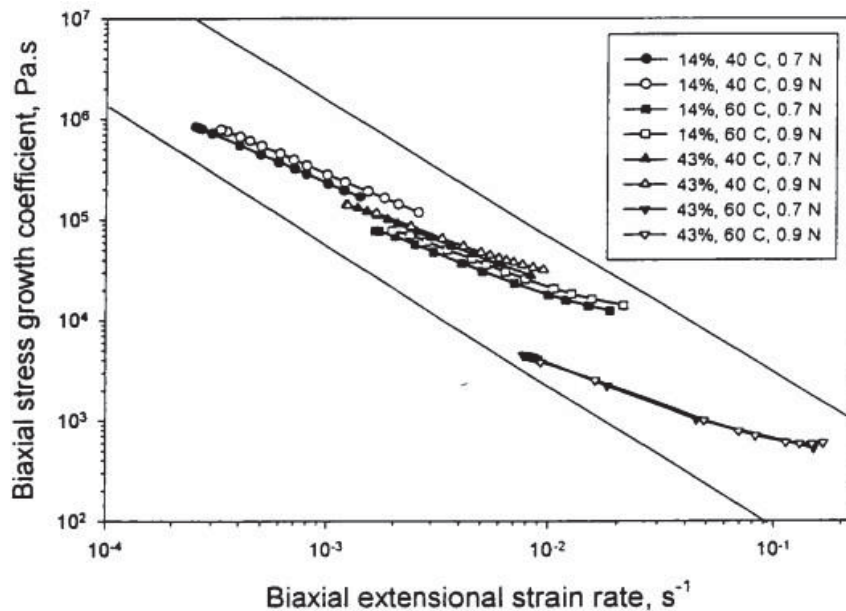


Figure 2 - 8 BSGC vs. BESR for mozzarella cheese (Wang *et al.*, 1998)

2.4.2. The Arnott test

Arnott *et al.* (1957) developed the cheese meltability measurement method subsequently called the Arnott test in order to measure the meltability of cheese and investigate the correlation between chemical components of Cheddar cheese and its meltability. The principle of this method is the comparison between the heights of cheese cylinder before and after a certain heat treatment. Firstly, the cheese cylinders are stored on a tray at 7.2 °C and measured to obtain their initial height. They are then positioned into an oven preheated at 100 °C for 15 minutes. Afterwards, the samples are taken out from the oven for room-temperature cooling for 15 minutes, and then placed into freezer at 7.2 °C for 30 minutes. After that, the heights at the samples' centres are measured. Finally, the percent difference between the heights of cheese cylinder before and after the heat treatment are used to express the meltability of the cheese.

2.4.3. The Schreiber test

One of the traditional tests to evaluate cheese meltability is the Schreiber test.

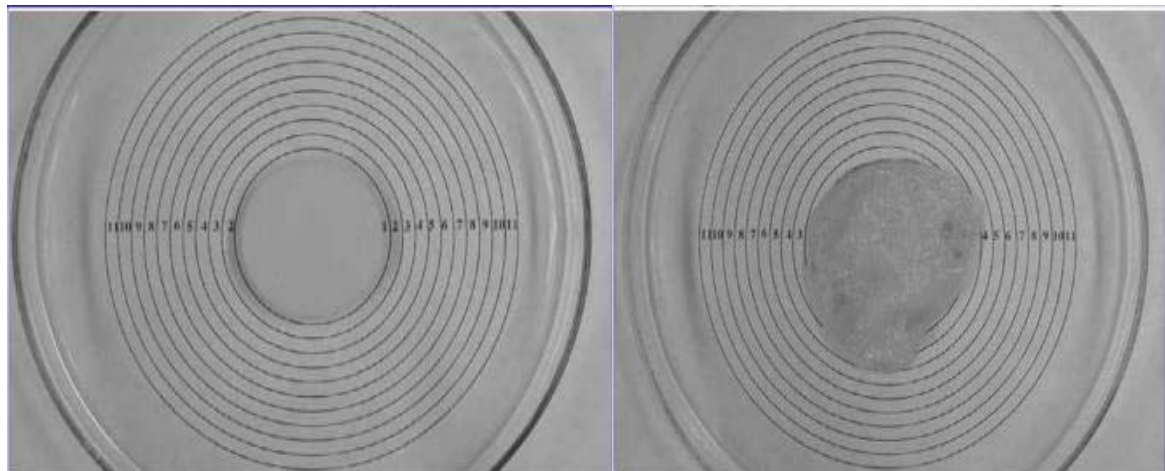


Figure 2 - 9 The Schreiber test (Gunasekaran & Ak, 2003)

To practice this test, the first stage is to prepare the specimen. A 0.5-cm-thick cheese sheet is stacked by two or three thin slices, and a copper cylinder with 41-mm inside diameter is inserted into the cheese sheet. Subsequently the specimen is

pushed out to the midpoint of a Petri dish marked with concentric circles with identification numbers (figure 2-9). Then, the dish is placed into an electric oven set temperature at 232 °C for 5 min. After that, it is taken out to a horizontal surface to cool for 30 min. Then the flow's outer edge radius is read numerically. If the collected number is equal or greater than 4, it is acceptable, otherwise the test is invalid. As the number increases, the cheese melts more easily (Gunasekaran & Ak, 2003).

2.5. Mozzarella cheese making

The process of mozzarella cheese making is stated by the following stages, based on the descriptions given by Arcangelo *et al.* (2005)

2.5.1. Milk quality

Originally, the milk used to make mozzarella cheese was water buffalo's milk. In practice, most recent cheese makers prefer to use cow's milk because obtaining cow's milk is easier. As the material of cheese making, the milk generally should be of good quality. The counts of somatic cells and bacteria should be low. High counts of somatic cell will influence the milk constituents' state and concentrations. Subsequently it deteriorates the properties of rennet coagulation and curd syneresis resulting in bad quality and a reduced yield of cheese. The appropriate pH of milk is required. If the pH of raw milk is alkaline, it may indicate the udder disease of cows.

2.5.2. 2.5.2 Thermal treatment

Generally, milk should have an adequate pasteurization treatment for the mozzarella manufacture. The aim for this step is to kill the harmful or unwanted bacteria and enzymes. The typical pasteurization is heating milk at about 72-74 °C for 17 to 20 sec, which can adequately inactivate the enzyme system, reduce spoilage and eliminate pathogens. However, over heat treatment gives rise to the denaturation of whey protein, curdling to weak texture and curd with high moisture.

2.5.3. Curd formation

2.5.3.1. Calcium addition

In order to make sure the gel strength is sufficient, the direct adding calcium salt can be carried out. A proper calcium level improves the clotting activity of milk. The target calcium level is controlled at 0.3 gram of CaCl_2 per litre of milk. It is found that the gel time can be reduced because of the improvement of rennet property by calcium.

2.5.3.2. Acid development

The lactic fermentation is a traditional method to acidify the cheese milk. After starter culture is added into milk, the lactose in milk is converted to corresponding lactic acid resulting in the decrease in milk pH in favour of moisture loss in the curd forming and changing the protein structure. Acid will continue developing until cultures are killed during the heating/stretching step.

2.5.3.3. Rennet-Catalyzed coagulation

Rennet can be obtained from newly-born calves or bacteria and fungi. It is added to coagulate the cheese milk, while whey is the remaining liquid. The coagulation is considered to happen in two stages. The primary stage is that the κ -casein amino acid chain is broken by the enzyme while glycomacropeptide and para- κ -casein are produced. In the secondary stage, coagulum is formed due to the aggregation of the casein micelles. Adhesion fusion is mediated via calcium ions and heating.

2.5.4. Cutting

When the coagulum reaches a suitable gel strength, it is cut into small curds. After about 5 min rest, the curds are mildly stirred preventing clumping. This stirring encourages the curd to lose water, lactose and whey proteins. Once curds reach the

desired pH, the whey is drained and the curds adhere to one another to form a mass which is then stretched.

2.5.5. Stretching

An important property for mozzarella cheese is its stretching behaviour specially when used as pizza topping. Therefore, the stretching stage is important for mozzarella making. Generally, the curds are put into hot water at around 70 °C. In this stage, an auger system is used to knead the curds physically, and then the aligned protein fibres are formed. The temperature of stretching is essential because of its subsequent effect on mozzarella ripening, hence influencing the functional properties of mozzarella.

2.5.6. Molding

After the curds reach the desired stretching property, they are shaped and cooled to certain by immersing into cold brine solution containing 22-44 % NaCl and 0.1% CaCl₂ able to prevent the loss of net calcium. The residence time is dependent on the size of the cheese block and the strength of the salt solution. The salt level finally achieve, 1.2-2.0 %. Ultimately, the mozzarella cheese is vacuum packaged to ripen.

2.6. Conclusion

As can be seen from the literature review, the factors affecting the rheological properties of cheese are various including protein, moisture, fat, and calcium. For pasta filata cheeses, the protein fibre direction also influences the melting properties. All these factors are widely investigated by diverse methods. But most of the studies only pay attention to the rough trend in rheological properties associated with or induced by these factors. Few articles focus on the accurate rheological property relationship to factors accounting for variability induced by temperature and moisture. However in order to characterise mozzarella functionality property, these rheological

property relationships are required. The effects of moisture content and temperature on viscosity during cheese melting is the primary focus in this study.

For investigating melting behaviour of cheeses, a number of methods are available. For the methods like Schreiber test and Arnott test, the test results cannot be further calculated to viscosity and do not appear to have good reproducibility. By contrast, UW Meltmeter and rotational viscometer are more appropriate for acquisition of comparatively reliable data and calculation of viscosity. But uneven temperature distribution and moisture loss potentially exist during the tests using these methods. This may have an impact on the precision of test result. Unfortunately, there are few articles addressing these questions. Therefore, it is necessary to identify probable problems with the techniques. Depending on the problems identified, some modifications may be made to accurately measure the required viscosity data of cheese.

3. UW MELTMETER METHOD DEVELOPMENT

3.1. Introduction

As discussed in the literature review, the flow conditions of cheese in the UW Meltmeter test are similar to real cheese flow during pizza baking. Also, the method includes careful temperature control and attempts to prevent moisture loss during measurement. Hence, the UW Meltmeter was considered as a suitable method for this study. This chapter focuses on validation of key characteristics of the UW Meltmeter test and modification of the procedure including cheese sample preparation, temperature control and data analysis.

3.2. Estimation of key process conditions during pizza baking

The strain rate under gravity flow conditions can be estimated using equation 3.1:

$$\dot{\epsilon} = \frac{1}{2h_0} \cdot \frac{\Delta h}{\Delta t} \quad (3.1)$$

Where $\dot{\epsilon}$ is biaxial strain rate (s^{-1}); h_0 is initial height (m); Δh is deformation (m) during a unit time Δt (s).

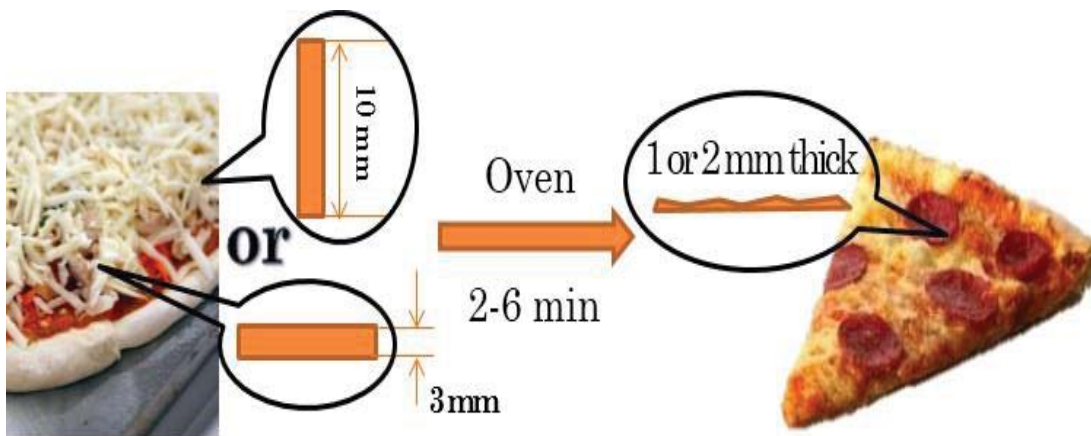


Figure 3 - 1 Mozzarella cheese melting during pizza baking

The length and thickness of mozzarella shreds are approximately 10 and 3 mm respectively as shown in figure 3-1. The maximum biaxial extensional strain rate (BESR) should be at the situation that the shreds are standing, having 10 mm initial height and then melt into a 1 mm thick cheese layer in a short time (2 min). Similarly, for the minimum value, the initial height is the thickness of mozzarella shred (3 mm) but in the maximum cooking time (6 min). By calculation, the strain rate range of interest is about $0.001 - 0.004 \text{ s}^{-1}$. The maximum stress to cause flow in pizza cooking will be due to gravity with an initial height of 3-10 mm. This corresponds to about 25-100 Pa (the mozzarella cheese density is about 1100 kg/m^3 according to Ferrari *et al.* (2003)). Therefore, data collection in this project is focussed in or around these stresses and strain rates.

3.3. Sample preparation



Figure 3 - 2 Cork borer and wire cutter

A cork borer (see in figure 3-2) was used to cut cheese blocks to obtain 30 mm diameter cheese cylinders. The cheese cylinders were cut into 7 mm thick slices with a wire cutter and template. The boring and cutting was done immediately after the cheese blocks are removed from 4 °C fridge because samples cut at low temperatures ($\sim 4^\circ\text{C}$) are more uniform than those cut at room temperature (Casiraghi *et al.*, 1985; Luyten, 1988). The samples containing the original surface of the cheese blocks were

discarded due to the irregularity of their surface shape and texture. The 7 mm thickness and 30 mm diameter samples were wrapped with Saran wrap to prevent surface drying. Samples were then stored for at least 1 hour at 4 °C until testing to ensure a uniform temperature was maintained throughout each cheese sample.

3.3.1. Current cheese sample template

The success of a squeeze flow test largely depends on the accuracy and quality of test specimens. Therefore, it is crucial to keep perfectly parallel end faces and a truly cylindrical shape for samples (Gunasekaran & Ak, 2003).

In the existing method of cheese sample preparation, cheese cylinder was placed in a template, and then the cheese cylinder was pushed by operator's finger. The uncertain contact between finger and cheese sample may lead to uneven force on the cylinder. This may have an impact on the shape of the sample and may further affect the accuracy of the test. As can be seen in figure 3-3, the height of the template is smaller than the diameter of cheese cylinder. During the cheese cutting, the wire cutter moves through the cheese before reaching the template. It is difficult to ensure the cutting direction is parallel with the gaps on the two sides of template.

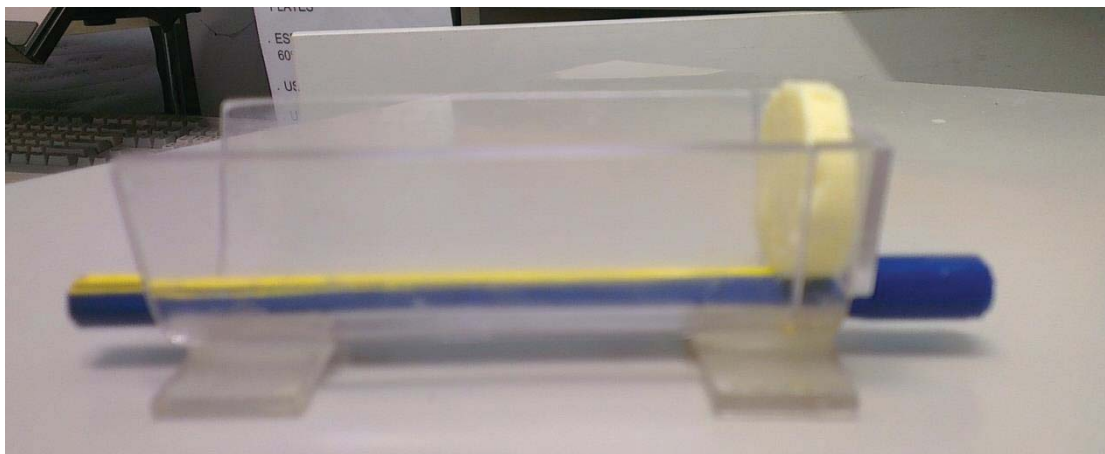


Figure 3 - 3 Existing cheese sample template

3.3.1.1. *Cut quality for the current sample template*

Because of these potential issues in the preparation of cheese samples, and the likely impact on the result of the UW Meltmeter test, an analysis of the cut quality

of traditional mozzarella sample was necessary.

Observation of the shape of cheese samples from cutting is a direct way to test the potential issues in the preparation of cheese samples. Weight control of sample is another indicator of shape quality of samples. Therefore, traditional mozzarella cheese was used to prepare samples. 9 samples (3 samples can be obtained from each cheese cylinder) were cut. The weights of specimens were measured after the cutting.

3.3.1.2. *Results for sample variation in standard template*

The weight average of 9 samples was 5.25 g, and its coefficient of variation was 2.2%. The small coefficient of variation might not reflect the negative cut quality of cheese sample for the template. It was found that the end faces of specimens cut with the existing sample template were not always parallel and flat (show in figure 3-4). This confirms the hypothesis that the design defect of the current sample template led to bad quality cheese samples.



Figure 3 - 4 The shape of sample cut by the current original template

3.3.2. **New cheese sample template design**

Initial experiments suggested that the sample preparation method using the existing sample template was not as good as expected (i.e. the cheese samples did not have a uniform cylindrical shape). To avoid the issues outlined above, a new cheese sample template was built. The new template included two major design aspects: 1) a pusher with 30 mm diameter end faces, 2) taller walls with 40.6 mm groove depth;

30.0 mm groove base diameter; 37.5 mm groove width (figure 3-5). The pusher, ensures a balanced force applied to the end face of sample and controlled force direction. The taller walls ensured that the entire cheese cylinder can be contained in the groove of the template, which guarantees the cutting direction without changing during cheese cutting.

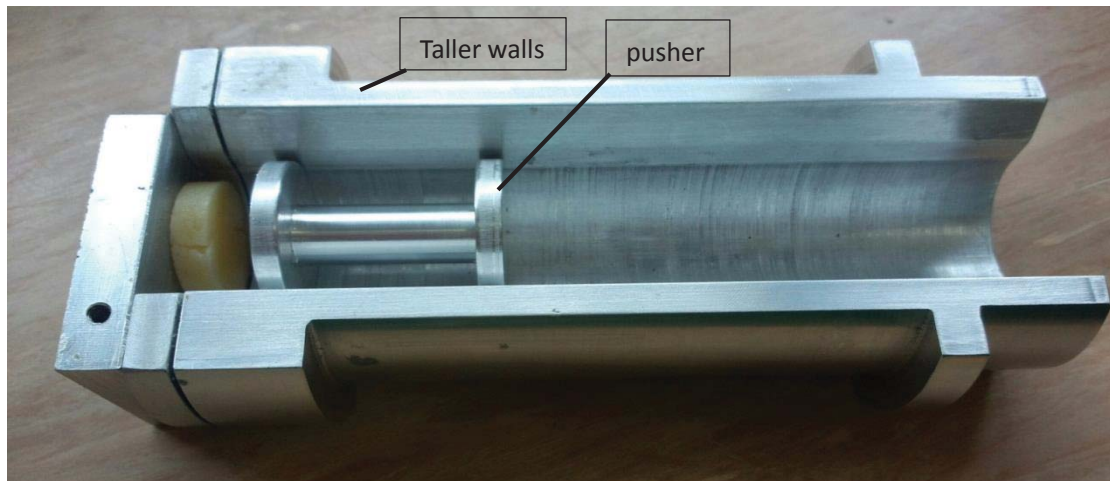


Figure 3 - 5 New cheese sample template

3.3.2.1. *Cut quality for the new sample template*

The method to test the cut quality of sample using new sample template is the same as the method outlined in section 3.3.1.1. The same mozzarella cheese was used.

3.3.2.2. *Results and comparison with the old template*

A sample cut using the new sample template is shown in figure 3-6. All samples from this new preparation method had more flat end faces when compared to samples prepared with the original cutting template (see figure 3-4).



Figure 3 - 6 The shape of a sample cut by new template.

As given in table 3-1, the weight coefficient of variation of samples cut by new template are smaller than those cut by original template. The lower coefficient of variation indicates that the differences of cheese weight using new method are less spread out than those using original method.

Table 3 - 1 Weight of samples cut by two templates

Template	Original	New
Mean weight/g	5.25	5.17
CV	2.2%	1.5%

3.3.3. Procedures for UW Meltmeter test

The UW Meltmeter was introduced in the literature review. The UW Meltmeter used in this study is shown in figure 3-7. In this study, 3 duplicates were run at different temperatures. Before each test, silicone grease is spread around the apparatus to reduce friction between the moving parts.



Figure 3 - 7 UW Meltmeter

The UW Meltmeter bottom plate is moved to start position forming a well, then silicone oil is sprayed in the well and under the top plate, and heavy paraffin oil is painted on the well and about a 10 mm ring on the top surface above the well to supply a lubricated condition for the test.

The first sample of a day was a dummy run, without cheese, which is used for height data calibration. The dummy run may be beneficial as it allows lubricants to soak into the instrument parts. A cheese sample is then placed in the well and covered with top plate for 8 minutes pre-heating.

The test starts by quickly moving the Meltmeter lever from the START to RUN position. At the same time, the UW Meltmeter software is set to record the sample height as a function of time. When 1800 data points (6 min at 5 points per second data acquisition rate) or slightly longer is achieved, the test data acquisition is stopped and the final cheese height at this point is recorded.

The old cheese sample is scraped off and the bottom and top plates are cleaned with paper in preparation for the next test. Between each test, thermal equilibration of Meltmeter is re-established by waiting at least 5 minutes. When the temperature setting is changed, the new test should be started after the Meltmeter has been on for at least 30 minutes.

3.4. Temperature distribution in the UW Meltmeter

It is important to accurately control the temperature of the samples during testing because temperature influences the rheological properties of mozzarella cheese (Gunasekaran & Ak, 2003). While the UW Meltmeter is said to be an isothermal test, there is no literature evidence to support this. As a result, there was a need to test the method to determine if the test was truly isothermal.

3.4.1. Choice of mozzarella analogue

The challenge to identify the temperature distribution of cheese sample is to keep thermocouples in appointed locations because mozzarella cheese changes shape (i.e. flows) during testing. In order to overcome this issue, a material that does not melt at testing temperatures was identified. The main properties that needed to be considered are the thermal conductivity and volumetric heat capacity that should closely match mozzarella cheese for the test to be relevant.

The thermal conductivity and heat capacity of a material are determined by its structure and composition including protein, water and fat. According to Stroshine (2004), the moisture content is the major factor which determines the thermal conductivity and heat capacity. The moisture content of halloumi cheese is close to mozzarella. What's more, they have a similar fibrous and layered texture (Papademas & Robinson, 1998). Thus, it was assumed that the thermal conductivity and heat capacity of halloumi cheese were close to those of mozzarella cheese, and that it would be used to investigate the potential for temperature gradients in the sample. Because halloumi does not melt, experimental measurement is possible.

3.4.2. Temperature of cheese sample during testing

To investigate the temperature control of the bottom plate of UW Meltmeter, a thermocouple with surface probe was placed into the well of UW Meltmeter before cheese samples were placed into it. Halloumi cheese samples were tested at 40 and 70°C (across the temperature range of interest in this study) using the methods outlined in section 3.3.3. The temperature time history was recorded by a data logger in one second intervals.

In order to place thermocouples into the testing points in the cheese sample without changing the heat transfer and test mechanism of the UW Meltmeter, a new top plate was created (figure 3-8). The modified top plate was made with the same dimensions as the UW Meltmeter's (2.2 mm thickness and 66 mm diameter). Two

thermocouples were placed through the plate. One was for monitoring the temperature of the top surface, and the other was to measure the centre temperature of the cheese (figure 3-9). Another thermocouple was attached to the top surface of the modified plate to monitor its temperature.



Figure 3 - 8 The modified top plate

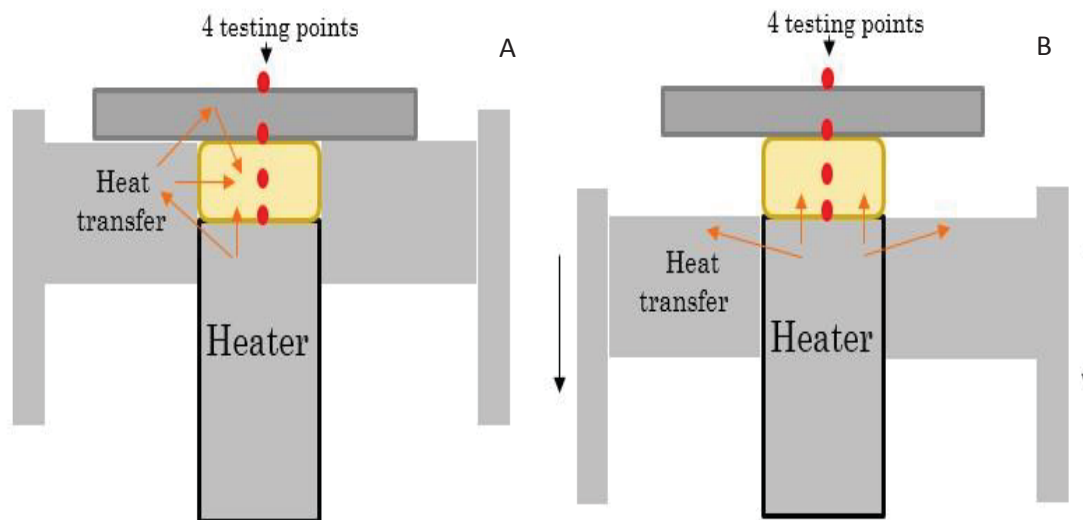


Figure 3 - 9 The mechanism of heat transfer during UW Meltmeter test. A: during the pre-heating; B: mechanical testing

3.4.3. Results

3.4.3.1. Halloumi deformation during the test

The halloumi cheese kept its shape during all tests. They did not melt but instead softened. Mozzarella cheese melted and flowed under the same conditions.

Table 3-2 shows the final height of halloumi samples were much higher than those of mozzarella at both 40 °C and 70 °C test temperatures.

Table 3 - 2 The final height of samples

Temperature	40 °C		70 °C	
Cheese	Halloumi	Mozzarella	Halloumi	Mozzarella
Initial height (mm)	7.08	7.10	7.08	7.10
Mean final height (mm)	6.54	2.87	4.09	0.72

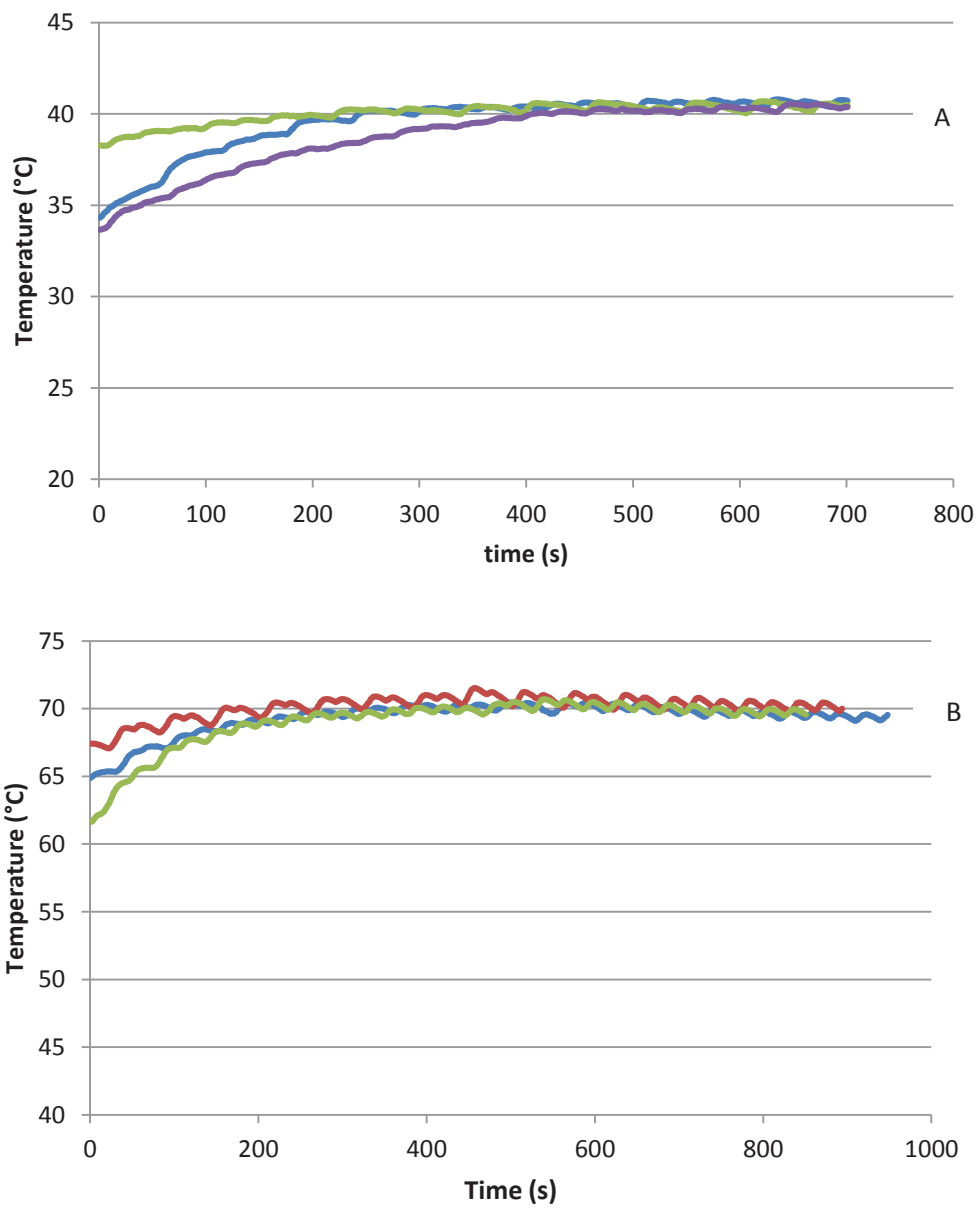


Figure 3 - 10 The temperature of cheese base. A: three samples tested at 40 °C; B: three samples tested at 70 °C

It took approximately 8 minutes for the temperature at the bottom to become constant during the initial heating period of the UW Meltmeter test (figure 3-10). After 8 minutes pre-heating, the temperature of cheese bottom already struck a balance around the set point temperature although it kept fluctuating due to the mechanism of the temperature controller—PID (proportional integral derivative) control. The fluctuation was around 0.5 °C, and the temperature was better controlled at low temperature than at high temperature (see table 3-3). Table 3-3 gives the average temperature of the bottom of sample after reaching equilibrium. The difference between the set point temperature and the temperature detected was small. Therefore, it was concluded that the temperature of cheese base was well controlled.

Table 3 - 3 The base temperature of cheese during testing

Set Temp.	40			70		
Run	1	2	3	1	2	3
Mean (°C)	40.41	40.61	40.30	69.84	70.46	70.07
STDEV (°C)	0.168	0.131	0.129	0.353	0.354	0.305

The results of the temperature investigation in the cheese were repeatable, as can be seen from figure 3-11. The time when the temperature of a sample reaches the set-point of 70 °C is much shorter than at 40 °C. The temperature fluctuations at the top surface of cheese and top plate, as observed on the bottom of sample, were evident, but this was not observed at the centre of the cheese. The reason for this is that the thermal conductivity of aluminium is much larger than the thermal conductivity of cheese. The aluminium quickly conducts the heat from the stage, while the lower thermal conductivity of cheese subdues the small and frequent change in the heating, making the temperature more stable.

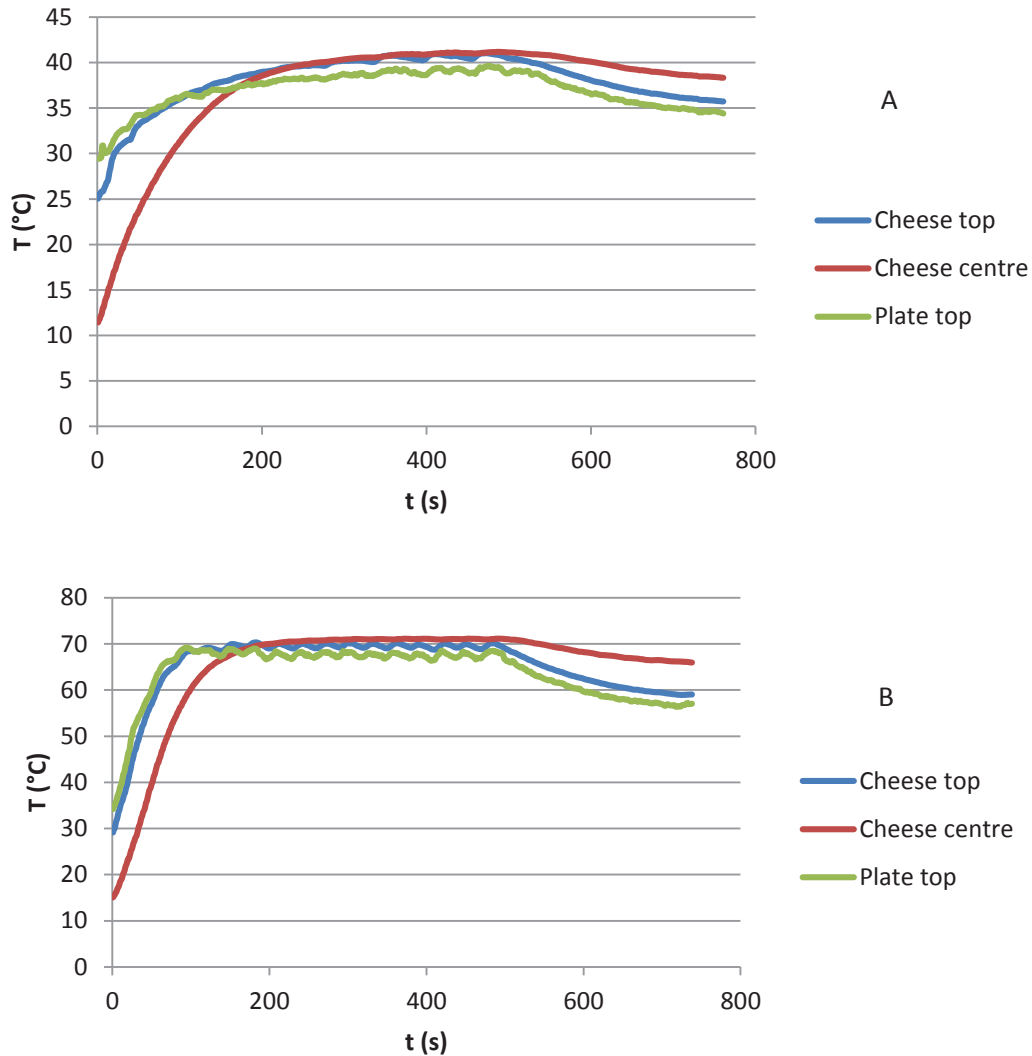


Figure 3 - 11 Temperatures of cheese centre, cheese top and plate top. A: three samples tested at 40 °C; B: three samples tested at 70 °C

After 8 minutes pre-heating, the temperature difference between the centre and top of the samples was very small. For 40 °C the samples temperatures were almost the same (less than 0.5 °C difference). Thus, it can be considered that samples were approximately isothermal after 8 min pre-heating. When mechanical testing started (after 480 s), all temperatures began to drop. The rate that the cheese top temperature dropped was greater than that of the cheese centre. In the 4 minute mechanical test, the temperatures of the cheese top surface and centre dropped about 4 and 2 °C respectively for the 40 °C tests, and about 10 and 5 °C respectively for the 70 °C tests. This indicated that the top plate acted as a heat sink for the cheese sample. As shown in the mechanism of heat transfer demonstrated in figure 3-9,

during the pre-heating period, the top plate and bottom plate remain in contact. Heat is directly transferred from the bottom plate to the top plate and this is why samples were almost isothermal after pre-heating. When mechanical testing started, the bottom plate was brought down, breaking thermal conduction, allowing the top plate to be quickly cooled by the surrounding air. This lost thermal contact explains the drop in the temperature of the cheese centre, cheese top and plate top. It is clear that the temperature of the upper surface of the top plate was the coldest throughout the tests, followed by the temperature of cheese top with about 2 °C higher. The drop in temperature of the cheese centre is slower compared with the other two temperatures due to heat transfer from the bottom plate.

3.5. UW Melimeter modification

Modifications to the UW Melimeter were undertaken in order to reduce the thermal gradients that can occur during testing as identified above.

3.5.1. Top plate modification

It was identified in the previous section, heat is quickly lost from the top plate during testing. Temperature is an important factor that has a significant effect on viscosity. Temperature gradients within a sample of cheese will reduce the accuracy of viscosity data acquired. Therefore, it was necessary to modify the device to reduce the thermal gradients within the cheese samples.

To insulate the top plate, a 10 mm thick, 70 mm diameter layer of expanded polystyrene (EPS) was glued to the top of the plate seen in Figure 3-12. EPS was obtained from Lanwood Plastics Industries (Palmerston North, New Zealand). Its conductivity was approximately 0.036 W/m·K, and the density was 16 kg/m³ (data provided by Lanwood Plastics Industries).

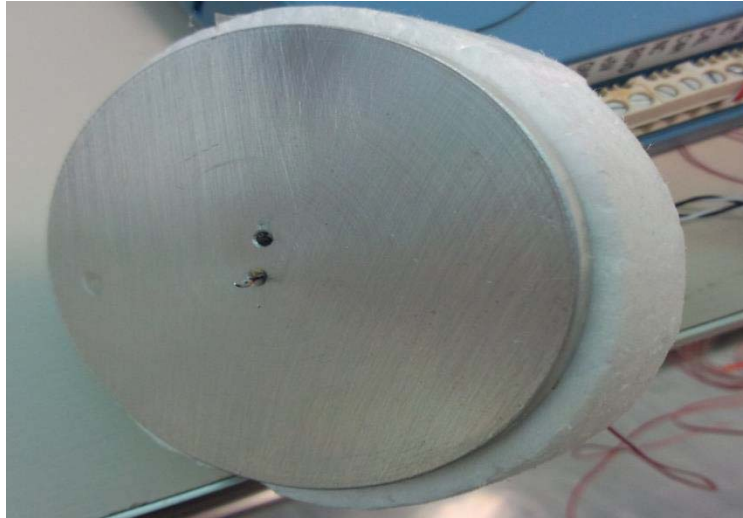


Figure 3 - 12 The modified top plate attached with EPS

3.5.2. Testing effects of insulation

Three thermocouples were placed in or around the modified annulus plate. Two thermocouples were placed through the plate to measure the plate surface temperature and cheese sample temperature while the third thermocouple was placed between the interfaces of the top plate and EPS plate to measure the heat flux through the plate.

Triplicate halloumi cheese samples at 40 and 70°C respectively were tested using the method outlined in section 3.3.3. The data of temperature versus time were recorded by the data logger with a 5 points per second data acquisition rate.

3.5.3. Results

With the added insulation, the temperature of cheese top and upper surface of the top plate were almost the same during the whole experiment, which indicated the EPS plate prevented heat loss from the top plate, shown in figure 3-13. During the 8-minute pre-heating, both the cheese centre and top reached the same temperature. During the 4-minute test, all temperatures decreased, however the difference between them was not large. In other words, the test can be considered practically isothermal. The results show that the modification with EPS reduced the thermal gradients that were noted in the original test. Because the halloumi sample did not

flow, these tests represent a worst case scenario when compared with testing of mozzarella samples.

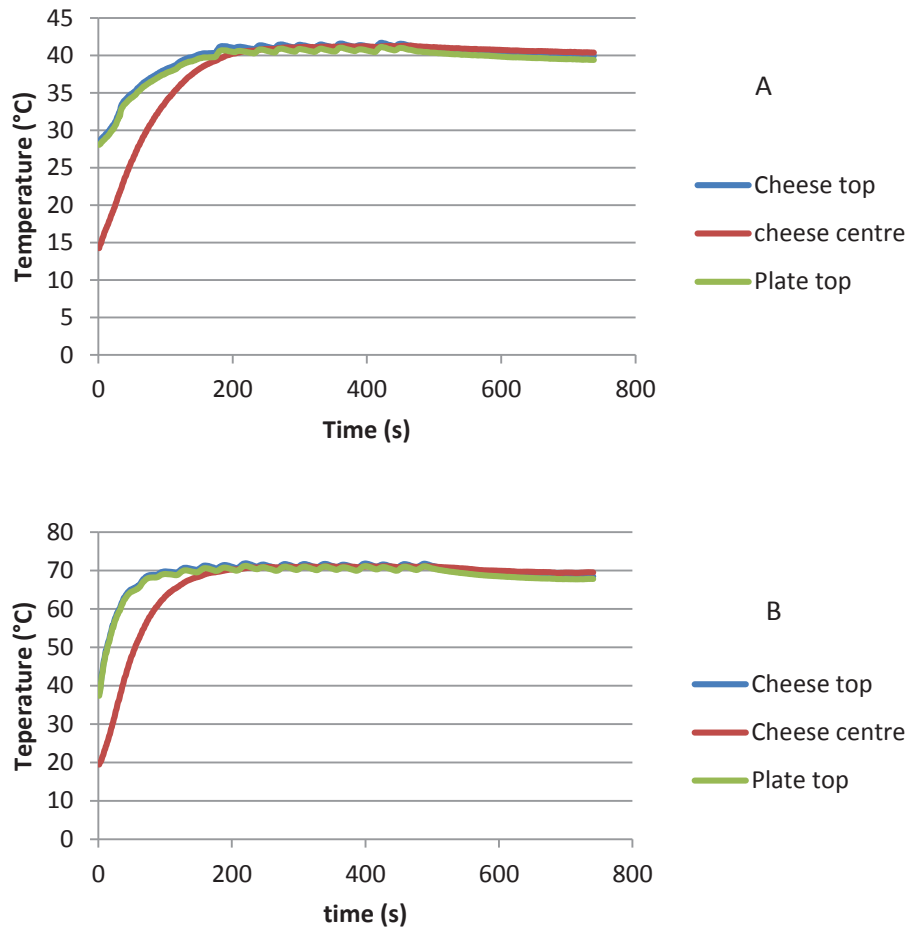


Figure 3 - 13 The temperatures of cheese centre, cheese top and upper surface of top plate. A: three samples tested at 40 °C; B: three samples tested at 70 °C

3.6. Data analysis method

3.6.1. Biaxial stress growth coefficient calculation

Due to the design of the device, when the Meltmeter lever is moved from the START to RUN position, the level transducer is moved up first then put down leading to some data values at the beginning being higher than the initial height (figure 3-14). Therefore, this data was removed during data analysis. The raw data from the test method was calibrated using the final height of dummy samples, which are the tests run without sample carried out at the beginning and end of the day.

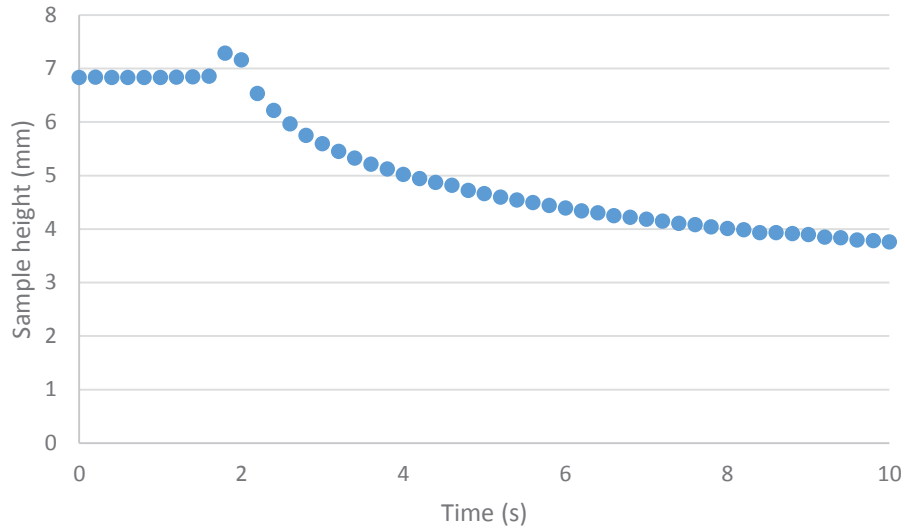


Figure 3 - 14 The raw data record at the beginning of the UW Meltmeter test

3.6.2. Regression model for height vs. time

Wang *et al.* (1998) used a double exponential decay model (Eq. 3.1) to fit experimental sample height versus time.

$$H(t) = a \cdot e^{-b \cdot t} + c \cdot e^{-d \cdot t} \quad (3.1)$$

Where a, b, c and d are constants. The equation represented their original data for constant force tests with an R-squared value between 0.90-0.98. However, in this study, it was found that this function did not fit data very well at small times for some samples (see figure 3-15 for an example of such data). This poor fit could create some errors in analysis as some researchers (Nair *et al.*, 2000; Oommen *et al.*, 2002; Wadhwani *et al.*, 2011), use the percentage change in height of sample at 10 or 16 s as an indicator of cheese meltability because of the most sensitive apart of the entire testing. Therefore, improvement in the regression curve function may result in more accurate outcomes.

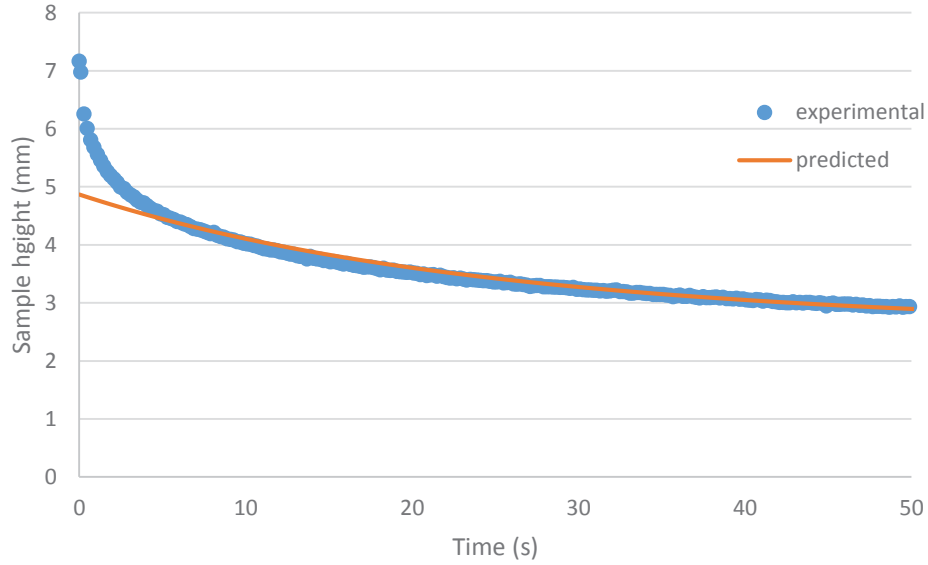


Figure 3 - 15 Compare between experimental data and predicted data by double exponential decay model at 60 °C

In this study, the Morgan- Mercer-Flodin (MMF) model (equation 3.2) was used to describe experimental height versus time data.

A curve of sample height versus time is plotted using the calibrated data. Eq. 3.2 is fitted to the data using the Solver function in the Microsoft Excel 2010.

$$H(t) = \frac{ab + c \cdot t^d}{b + t^d} \quad (3.2)$$

Where, $H(t)$ is sample height (m) at time t (s); a , b , c and d are constants; The net stretching stress σ_B is from the squeezing force, F , divided by momentary cross-sectional area of the sample, $A(t)$. Assuming that specimen volume is constant during the testing, the σ_B can be expressed as:

$$\sigma_B = \frac{F}{A(t)} = \frac{F}{H_0 A_0} \cdot H(t) \quad (3.3)$$

Where, H_0 : height at time zero (m); $A_0 = \pi R_0^2$ is the cross-sectional area of sample at time zero (m^2); R_0 : radius of sample at time zero (m).

The biaxial extensional strain rate $\dot{\epsilon}_B$ can be calculated with Eq. 3.4.

$$\dot{\epsilon}_B = -\frac{1}{2H(t)} \cdot \frac{dH(t)}{dt} \quad (3.4)$$

Therefore, the biaxial stress growth coefficient is obtained as:

$$\eta_B^+ = \frac{\sigma_B}{\dot{\epsilon}_B} \quad (3.5)$$

Samples of the plot of BSGC against BESR can be seen in figure 2-8.

The parameters in the MMF model have relative physical significance. For example, when time is equal to 0, the height is equal to 'a', so the value of 'a' indicates the initial height. When time is infinity, the height approaches 'c'. The value of 'c' indicates the final height of sample. 'b' and 'd' are related to the flow speed and /or mechanism.

By comparing the two models, it can be seen that the MMF model fitted the experimental data better than the double exponential decay model (figure 3-16, 3-17, 3-18). The raw data was evenly scattered around the regression curves of the MMF model. The residuals for the MMF model were much smaller and more balanced than those for the double exponential decay model, especially for the beginning area (close to the axis) where the density of data points is low but the change in value is relatively large.

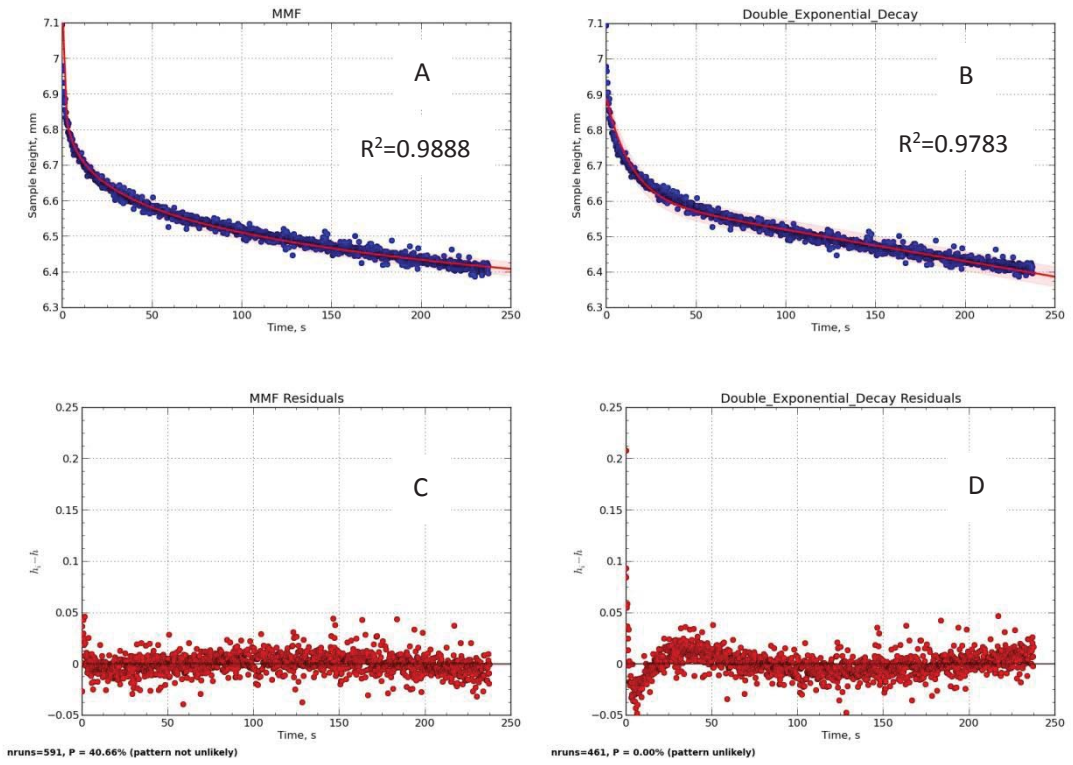


Figure 3 - 16 The regression of sample height vs. time at 30 °C by two models and its residuals. A: raw data and the MMF model; B: raw data and the double exponential decay model; C: the residuals for the MMF model; D: the residuals for the double exponential decay model.

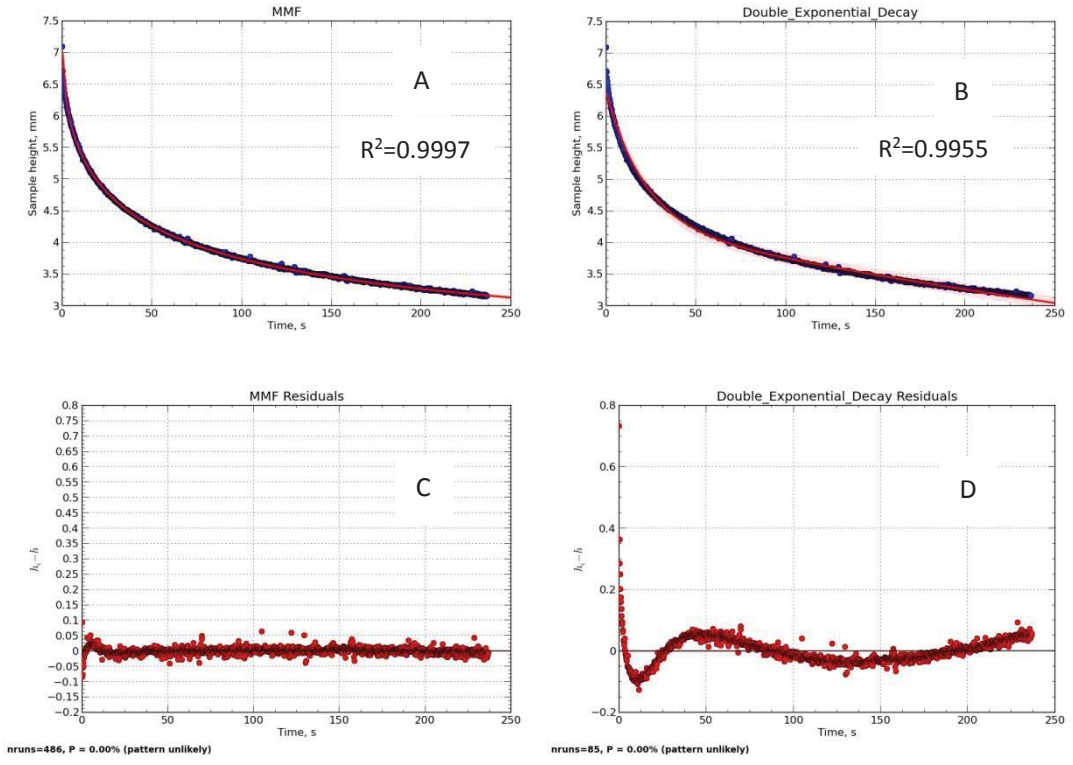


Figure 3 - 17 The regression of sample height vs. time at 45 °C by two models and its residuals. A: raw data and the MMF model; B: raw data and the double exponential decay model; C: the residuals for the MMF model; D: the residuals for the double exponential decay model.

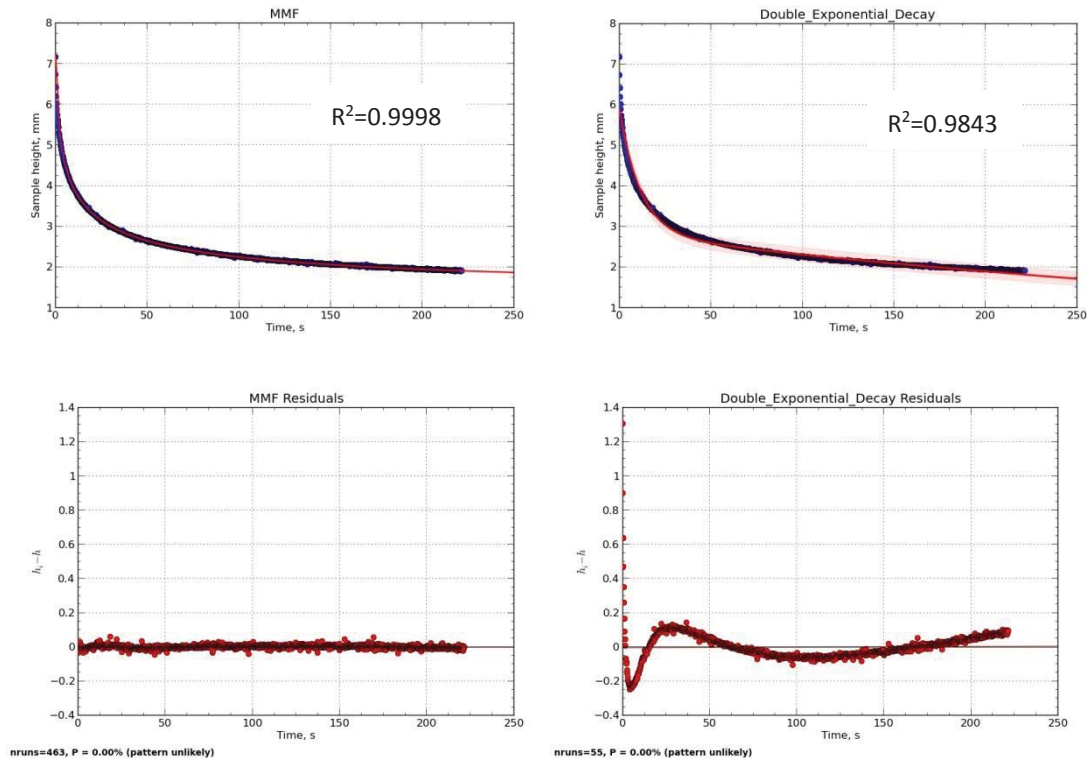


Figure 3 - 18 The regression of sample height vs. time at 60 °C by two models and its residuals. A: raw data and the MMF model; B: raw data and the double exponential decay model; C: the residuals for the MMF model; D: the residuals for the double exponential decay model.

3.7. Mozzarella anisotropy and the impact of cheese sampling

It was introduced in the literature review that traditional mozzarella production includes curd stretching and kneading for mozzarella which aligns cheese proteins and creates anisotropy within the cheese structure. Anisotropic materials with oriented structure are likely to exhibit anisotropic physical properties. The effects of sampling direction (parallel or perpendicular to protein fibre orientation) on the fracture properties of mozzarella cheese was seen in tensile tests by Ak and Gunasekaran (1997). They found that the fracture toughness, stress and strain in the parallel direction were greater than those in the perpendicular direction. This anisotropy forms the basis for a hypothesis that anisotropy and cheese sample selection has an effect on the results gained from the UW Meltmeter. If this is true, there will be a need to sample cheese according to the direction of the cheese proteins/fibres.

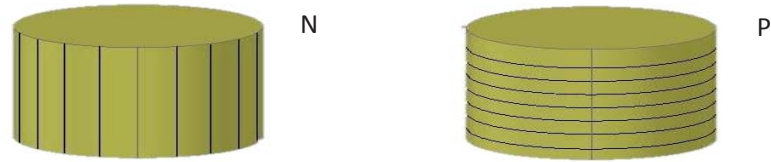


Figure 3 - 19 The fibre direction of samples. N: normal direction; P: parallel direction

The fibre direction being perpendicular with the end faces of sample is called normal direction in this study; the fibre direction in parallel with the end faces of sample is called parallel direction (Figure 3-19). Samples of traditional mozzarella (Fonterra, New Zealand) were taken from a large block of cheese according to the method outlined in section 3.3. A total of nine cheese cylinders were sampled in the normal direction and nine were sampled parallel to the fibre direction in the cheese block. Triplicate UW Meltmeter tests were carried out at 30, 40 and 60 °C for both the parallel and normal samples using the method outlined in section 3.3.3.

Table 3 - 4 Mean BSGC at 3 BESRs for two fibre direction sample at 30 °C

Shear rate s^{-1}	Normal			Parallel		
	Mean, Pa.s	STDEV	CV, %	Mean, Pa.s	STDEV	CV, %
1.0E-03	503822	11378	2.3	509844	12022	2.4
1.0E-02	52093	862	1.7	52633	683	1.3
1.0E-01	5355	50	0.9	5341	66	1.2

Table 3 - 5 Mean BSGC at 3 BESRs for two fibre direction sample at 45 °C

Shear rate s^{-1}	Normal			Parallel		
	Mean, Pa.s	STDEV	CV, %	Mean, Pa.s	STDEV	CV, %
5.0E-03	54545	2513	4.6	49840	2814	5.6
1.0E-02	30746	1147	3.7	28373	1426	5.0
1.0E-01	4557	93	2.0	4396	161	3.7

Table 3 - 6 Mean BSGC at 3 BESRs for two fibre direction sample at 60 °C

Shear rate s^{-1}	Normal			Parallel		
	Mean, Pa.s	STDEV	CV, %	Mean, Pa.s	STDEV	CV, %
1.0E-02	20256	336	1.7	20109	948	4.7
1.0E-01	3268	149	4.6	3263	155	4.8
1.0E+00	458	16	3.5	455	22	4.8

The mean viscosities, standard deviation and coefficient of variation are given in table 3-4, 3-5 and 3-6. The mean viscosities and expected errors at three different BESR are plotted in figure 3-20. The tables and figure show the results were repeatable and the BSGC of the mozzarella cheese was not affected by the difference in fibre direction in the UW Meltmeter measurements. The insensitivity of an isotropic structure on the rheological properties of mozzarella cheese was also reported by Muliawan and Hatzikiriakos (2007).

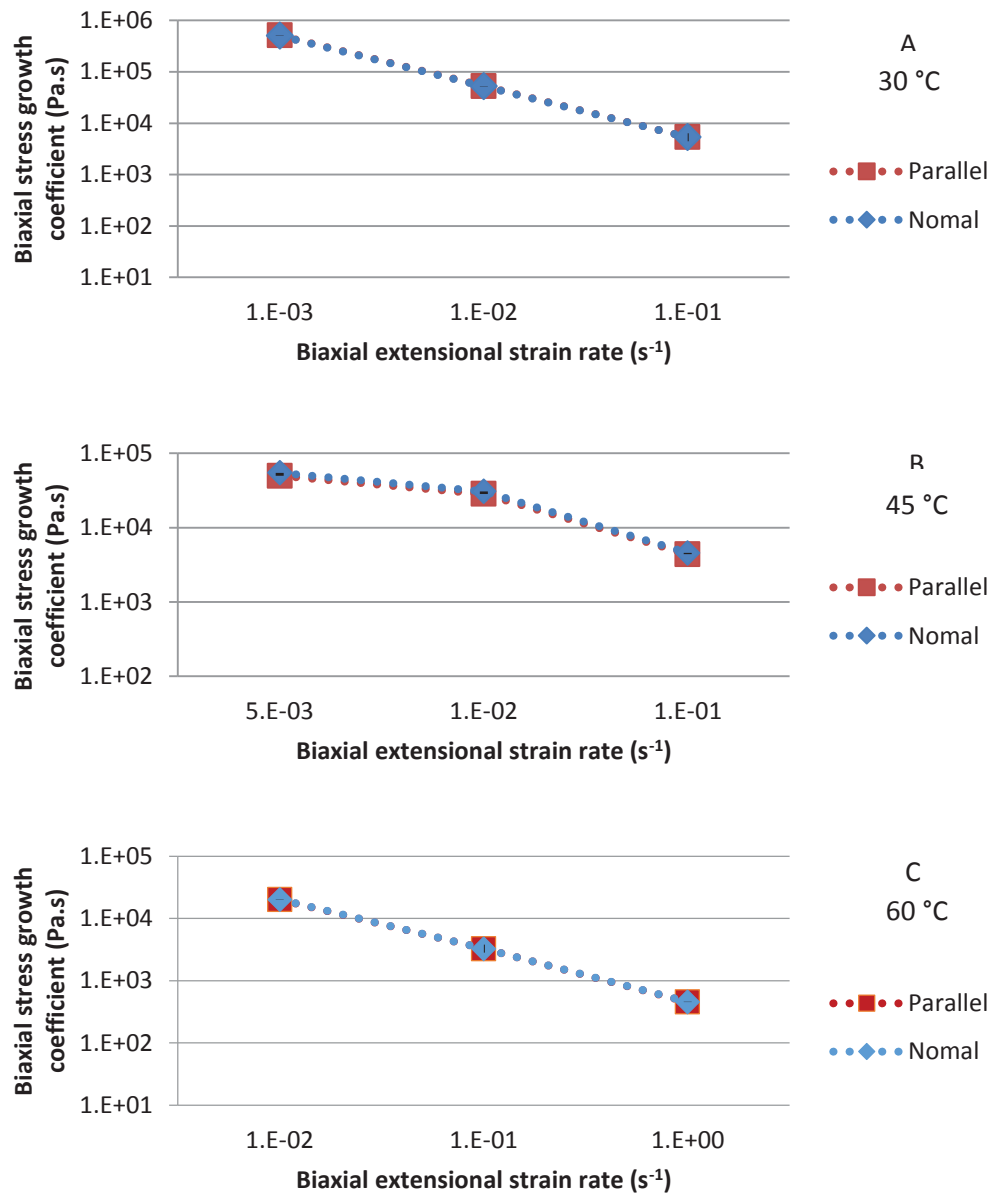


Figure 3 - 20 Biaxial stress growth coefficient vs. biaxial extensional strain rate of mozzarella samples at different temperature

3.8. The effect of EPS modification on rheological property

Wang *et al.* (1998) showed that a change in the compression force in the UW Meltmeter test may alter the correlation between the BESR and BSGC. The addition of a layer of EPS to the top plate of the UW Meltmeter increased the compression force experienced by cheese samples during testing. The weight of aluminium plate and EPS were 38.4 g and 1.0 g respectively. This equates to an increase of 0.01 N of force or approximately 2.6 % of the original total.

To determine if the modification had an impact on the results gained from the UW Meltmeter, triplicate samples of traditional mozzarella cheese (Fonterra, New Zealand) were tested according to the method outlined in section 3.3.3 using the unmodified and modified top plates at a test temperature of 60 °C.

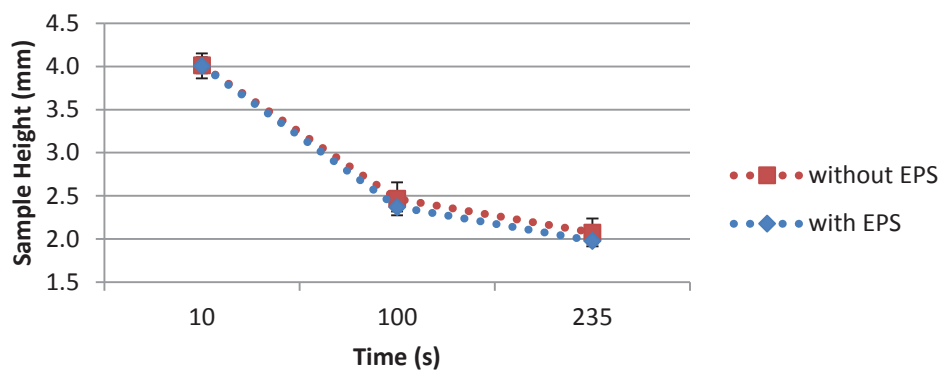


Figure 3 - 21 Height of mozzarella samples vs. time

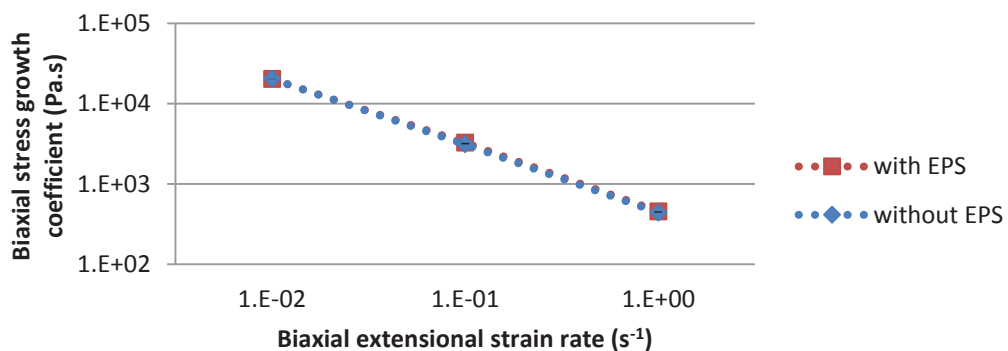


Figure 3 - 22 Biaxial stress growth coefficient vs. biaxial extensional strain rate of mozzarella samples

Each point in figures 3-21 and 3-22 illustrates the mean of three replicates. Three points from beginning, middle and end (10 s, 100 s and 235 s) of the data from the tests (sample height versus time) were selected to compare the effect of EPS addition. Figure 3-21 shows that the weight of EPS causes a very small change in height of the cheese samples at the three times analysed. At 10 s, there was no difference, however, at longer time intervals the height of the samples with EPS was less than those without EPS. These results, however, were not statistically significant by two tailed t tests. The P value at 10 s, 100 s and 235 s were 0.95, 0.46 and 0.37 respectively. All the P value were larger than 0.05 meaning there was no significant difference between two groups of data sets.

The BSGC and BESR were calculated using the method outlined in section 3.6.1. BSGC at BESR's of 1, 0.1 and 0.01 s^{-1} were chosen for comparison between the unmodified and modified UW Meltmeter tests. As shown in figure 3-22, there was no significant difference in BSGC between the samples with and without EPS.

According to Wang *et al.* (1998), the increased force applied to cheese will lead to an increase in the BSGC. The weight change here, however, was very small and was shown to have minimal effect on the rheological results. It should be noted that the improvement in the temperature control could cause a decrease in the BSGC. It is, however, difficult to uncouple the effects of having better temperature control through insulative effects and the effects of additional weight from one another. Furthermore, it is possible that there is a difference in the results but the UW Meltmeter test is not sensitive enough to measure the changes.

3.9. Conclusion

Several changes were made to the UW Meltmeter method to improve the accuracy of the measurement process. They were:

- 1) The template for preparing samples was modified to give samples with a more uniform shape than those from the original cheese cutting template.
- 2) The top plate of UW Meltmeter was insulated to minimise heat losses during testing.
- 3) The method for the data analysis was improved where the MMF was found to better fit the data of sample height versus time.
- 4) The anisotropy of the mozzarella cheese structure was not found to affect melt behaviour. Based on these findings, the accurate characterisation of mozzarella cheese could be carried out. This is the focus of the next chapter.

4. UW MELTMETER RESULTS

4.1. Introduction

To understand the behaviour of cheese during pizza baking, data that describes melt and flow of mozzarella cheese is required. To collect the data, measurements across a range of temperatures and strain rates which are related to pizza baking is needed. The UW Meltmeter is a useful tool to characterise the rheological properties of mozzarella cheese as they relate to melt and flow on pizza. Therefore, this chapter outlines the use of the modified UW Meltmeter to characterise cheese flow under a range of temperatures and moisture contents.

4.2. Temperature effects on rheological properties

In order to create a model to describe melt and flow of mozzarella cheese on pizzas, the rheological properties at varying temperatures under low gravity flow conditions are needed. According to Rudan and Barbano (1998), the main temperature range for cheese melting is between 30 to 80 °C.

4.2.1. Method

The quantification of the rheological properties was carried out at the temperature range of 30 to 80 °C with 10 °C steps using the method outlined in section 3.3.3. Triplicate samples were repeated for each temperature. Traditional bovine mozzarella as used by the pizza food service industry was used.

4.2.2. Results

4.2.2.1. Melt curves

The change in the sample height of triplicate cheese samples at 30 and 80 °C were plotted in figure 4-1. It can be seen that using the UW Meltmeter method to characterize rheological properties of mozzarella cheese was repeatable.

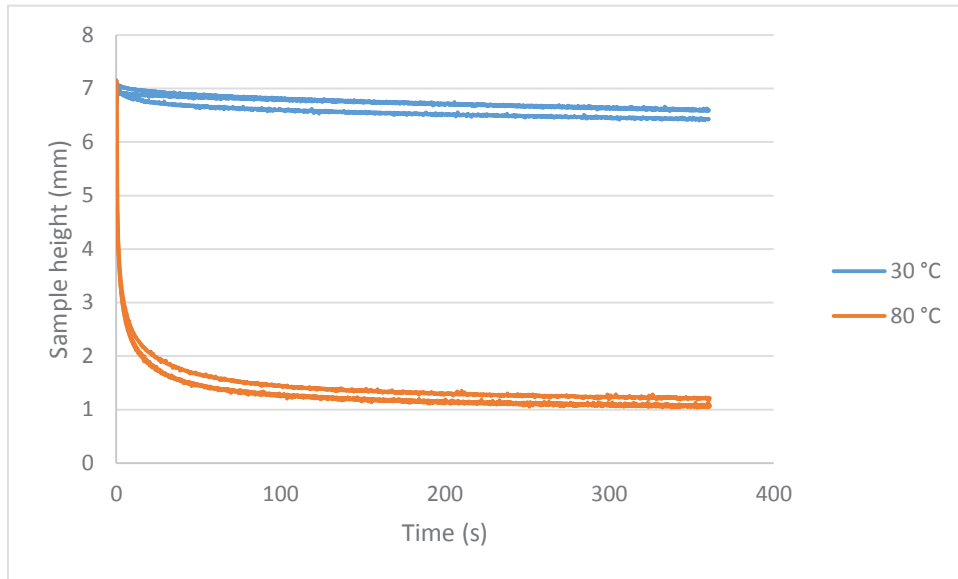


Figure 4 - 1 The height of triplicate cheese samples VS time at 30 and 80 °C

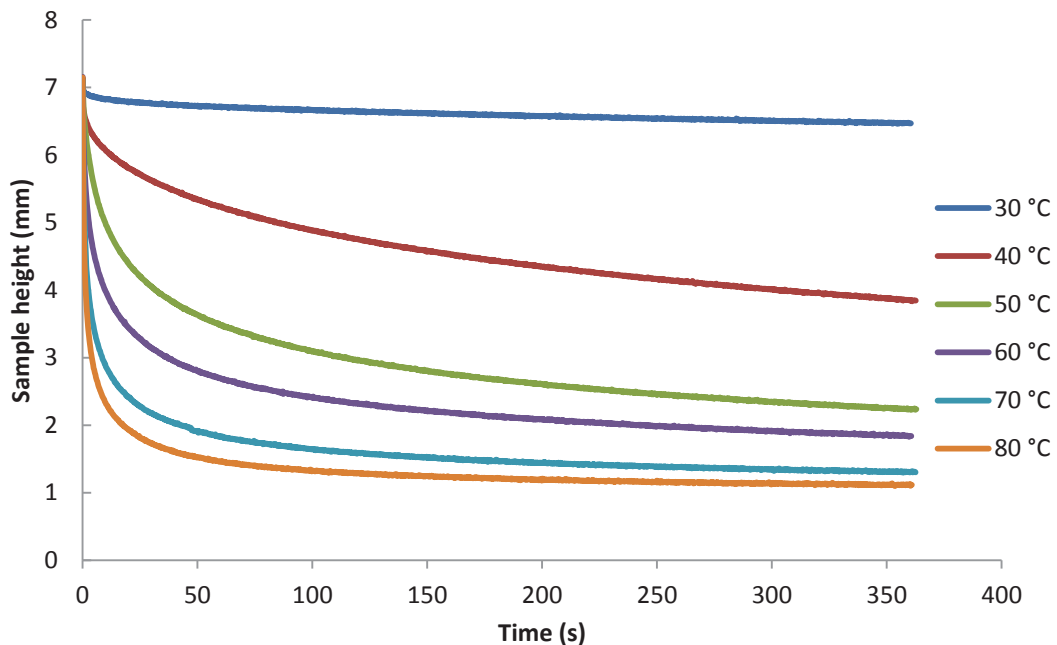


Figure 4 - 2 The height of mozzarella cheese samples VS time at varied temperature

The change in the sample height of mozzarella cheese sample at each temperature is plotted in figure 4-2. The height dropped more rapidly for the samples at high temperatures than the samples at low temperatures. The height of the 30°C samples changed very little while the decrease in height was apparent at temperatures over 40 °C. In a review of the rheological properties of cheese, Lucey *et al.* (2003) pointed out that generally the phenomena of stretch, melt and flow cannot be observed until cheese is heated up to more than 40 °C. The incipient softening at \leq

40 °C is partly attributed to the fat melting; in fact CN-CN interactions in cheese cause the major effects. These findings are supported by Rudan and Barbano (1998), who claimed that the fat in Mozzarella cheese completely melts by about 38 °C, meanwhile the structure of the protein matrix is relatively stable. As the temperature further increases, the interactions of CN-CN and CN-calcium change, causing cheese to flow. Solid fat content as a function of temperature in Emmental cheese was plotted by Lopez *et al.* (2006) shown in figure 4-3.

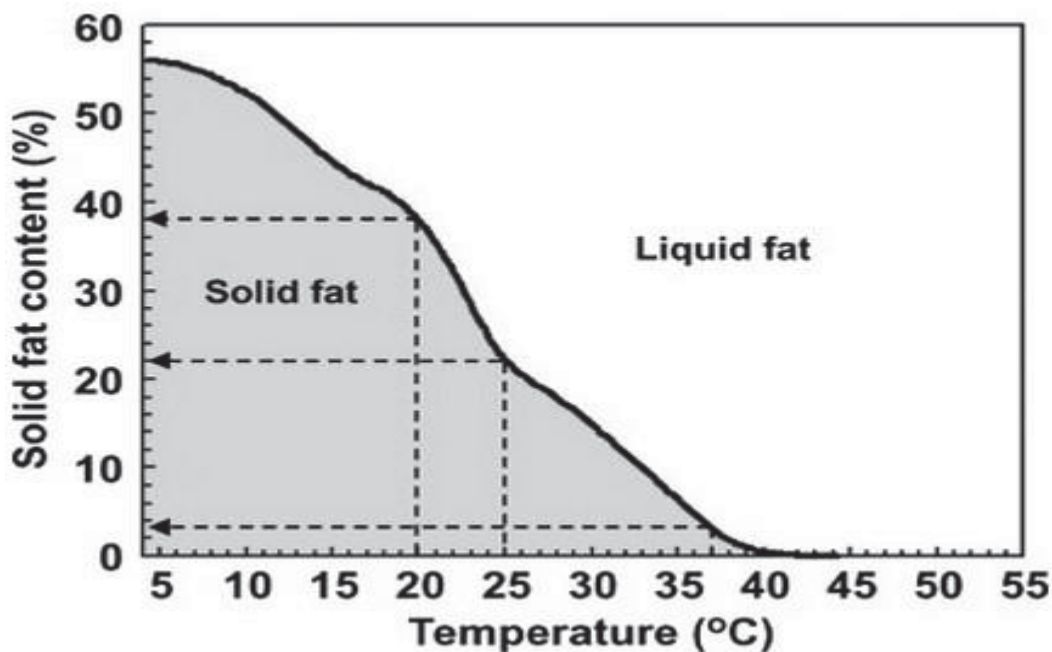


Figure 4 - 3 The solid fat content as function of temperature in Emmental cheese (from Lopez *et al.* 2006)

From the raw data, the biaxial extensional strain rates and biaxial stress growth coefficients were calculated as outlined in section 3.6 and plotted (figure 4-4). The curves of BSGC versus BESR show that η_B^+ decreased as $\dot{\epsilon}_B$ and temperature increased. The strain rate and temperature dependent thinning behaviour have been published for mozzarella cheese (Smith *et al.*, 1980; Wang *et al.*, 1998), processed cheese (Dimitreli & Thomareis, 2004) and cheddar cheese (Gunasekaran & Ak, 2003). The low BESR throughout the test for the samples at 30 °C also indicated that mozzarella cheese under 40 °C exhibited more solid-like behaviour. According to (Wang *et al.*, 1998), the curves of BSGC versus BESR for all cheese samples at their tests were aligned within a narrow band and approximately parallel. The high BSGC

and low BESR were represented on the top left corner as plotted in figure 2-8 in section 2.4.1. A cheese with poor 'meltability' will be located in this area. Inversely, the cheese with good 'meltability' would be close to the bottom right corner with a low viscosity and high flow.

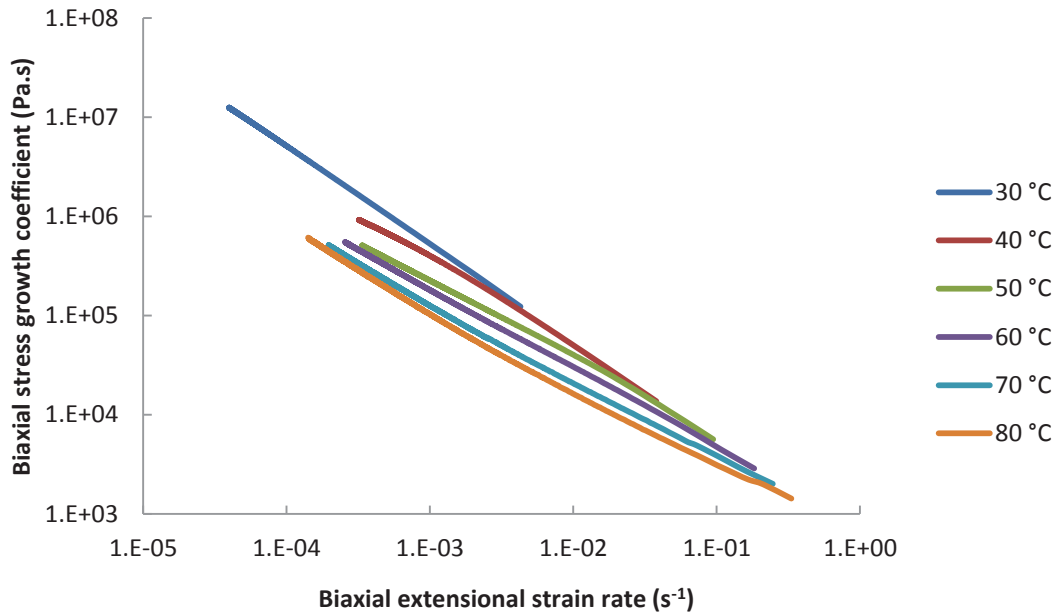


Figure 4 - 4 The BSGC VS BESR plots for Mozzarella cheese samples at varied temperature

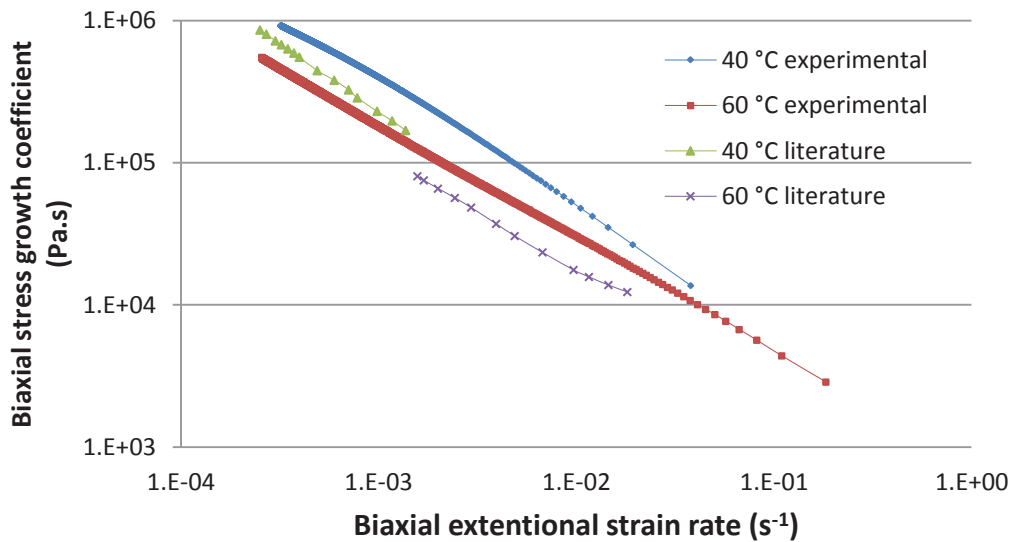


Figure 4 - 5 The comparison between the BSGC VS BESR plots for mozzarella cheese samples at 40 °C and 60 °C from the present study and literature (Wang *et al.*, 1998)

A comparison of BSGC between the present study and literature (Wang *et al.*, 1998) is shown in figure 4-5. The figure shows that the BSGC at any particular BESR in this research were larger than the literature result at 40 and 60 °C. There are, however, differences between the methods used in this study and literature. For example, the force (about 0.4 N) applied to the sample in this study was lower than the force (0.7 N) in the literature. A smaller force applied to the sample should generate a lower BSGC value for a given BESR (Sun & Gunasekaran, 2009; Wang *et al.*, 1998). Furthermore, the higher fat content (about 20 %) in this study compared with the fat content in the literature (14 %) should give a lower BSGC (Cais-Sokolinska & Pikul, 2009; Wang *et al.*, 1998). These explanations are the opposite of the observed results shown in figure 4-5. A potential mistake was found in the calculation of BSGC for the literature (Wang *et al.*, 1998), who used diameter as the radius of the cheese sample to calculate the BSGC as introduced in section 2.4.1. The corrected curves are plotted in figure 4-6. The curves in this research were lower than the curves from literature at the same sample temperatures. Lower curves are likely to be explained by the smaller force applied and the higher fat content of mozzarella cheese in this study as discussed above.

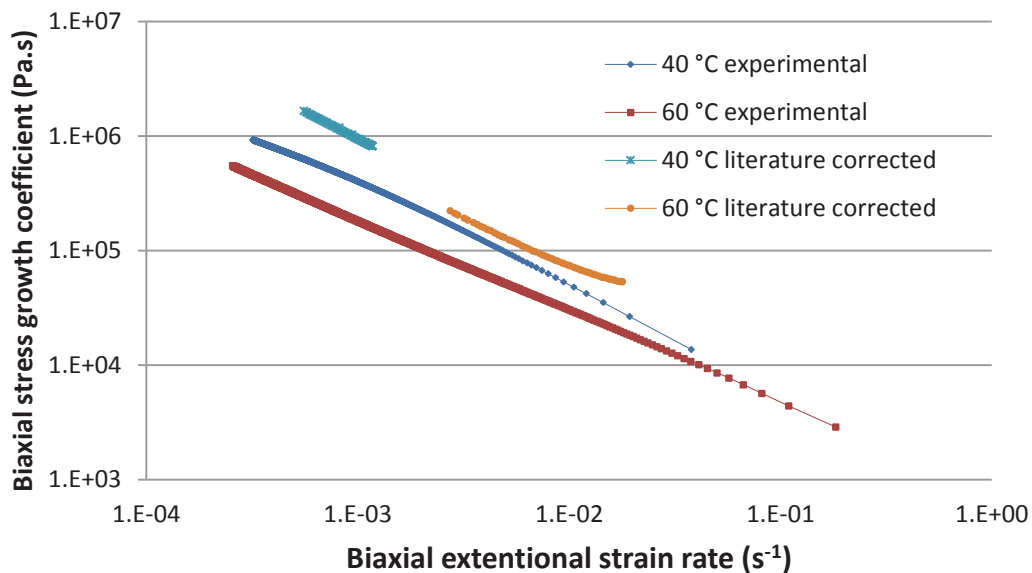


Figure 4 - 6 The comparison between the BSGC VS BESR plots for mozzarella cheese samples at 40 °C and 60 °C from the present study and the corrected literature data (Wang *et al.*, 1998)

4.2.2.2. BSGC as function of temperature

The rheological properties of cheese are temperature dependent with more flow at higher temperatures. In a study by Muthukumarappan *et al.* (1999a), a graph of the BSGC versus temperature for cheddar cheese was plotted (Figure 4-7). They used different models to fit the data, and chose the model which best fitted the data. The function they gained was expressed by:

$$\text{Log}(\eta_B^+) = 0.1284 + 0.7394T - 0,0309T^2 + 4.86 \times 10^{-4}T^3 - 2.51 \times 10^{-6}T^4 \quad (4.1)$$

Although this function fitted the data best, it was not a mechanistic function. The parameters do not have any physical significance.

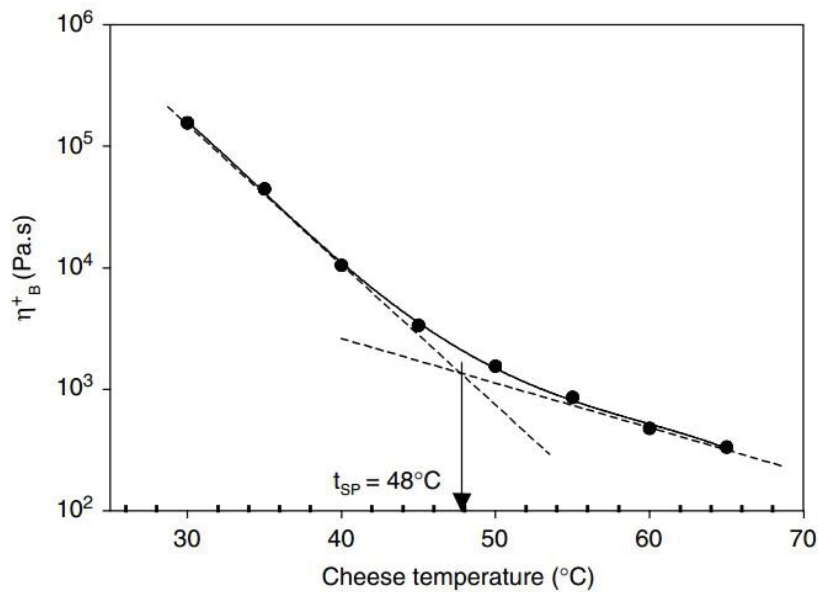


Figure 4 - 7 Biaxial elongational viscosity vs. temperature for Cheddar from a UW Meltmeter (Muthukumarappan *et al.*, 1999a)

The Arrhenius and Williams-Landel-Ferry (WLF) models are commonly used to describe the relationship between viscosity and temperature. The Arrhenius equation has been widely used to describe the relationship between viscosity and temperature for various materials such as melting polymers (Liu *et al.*, 2006), liquid foods (Rao, 2005) and semisolid foods. When the Arrhenius model is not adequate to express the relationship, the WLF model is usually utilised (Peleg *et al.*, 2002). The WLF model is

generally applied to polymer melt or some fluids when a glass transition temperature, T_g , is crossed during heating. The temperature range of this model for polymer applications normally is from T_g to $T_g + 100$ °C (Liu *et al.*, 2006). At higher temperature, the Arrhenius temperature relationship would be better to fit the viscosity as function of temperature.

The WLF equation (Williams *et al.*, 1955):

$$\log(a_T) = \frac{-C_1(T-T_r)}{C_2+(T-T_r)} \quad (4.2)$$

Where T is temperature (°C), T_r is the reference temperature (°C); C_1 and C_2 are empirical constants (K).

The Arrhenius equation can be applied to viscosity with:

$$\eta = A \exp\left(\frac{-E_a}{RT}\right) \quad (4.3)$$

Where A is pre-exponential factor (Pa · s); E_a is the activation energy (J · mol⁻¹); R is the gas constant, 8.314 J · K⁻¹mol⁻¹; T is absolute temperature (K). E_a is the energy required for a protein to diffuse away from the attraction of its neighbours. RT expresses the thermal energy of one mol of proteins at temperature of T .

The effects of temperature can be depicted on an Arrhenius plot; a plot of the natural logarithm of the viscosity versus the reciprocal of the absolute temperature, which should yield a straight line. From such a plot (and/or equation 4.4), E_a and A can be determined by the intercept and gradient of the line.

$$\ln(\eta) = \ln(A) + \frac{-E_a}{R} \cdot \frac{1}{T} \quad (4.4)$$

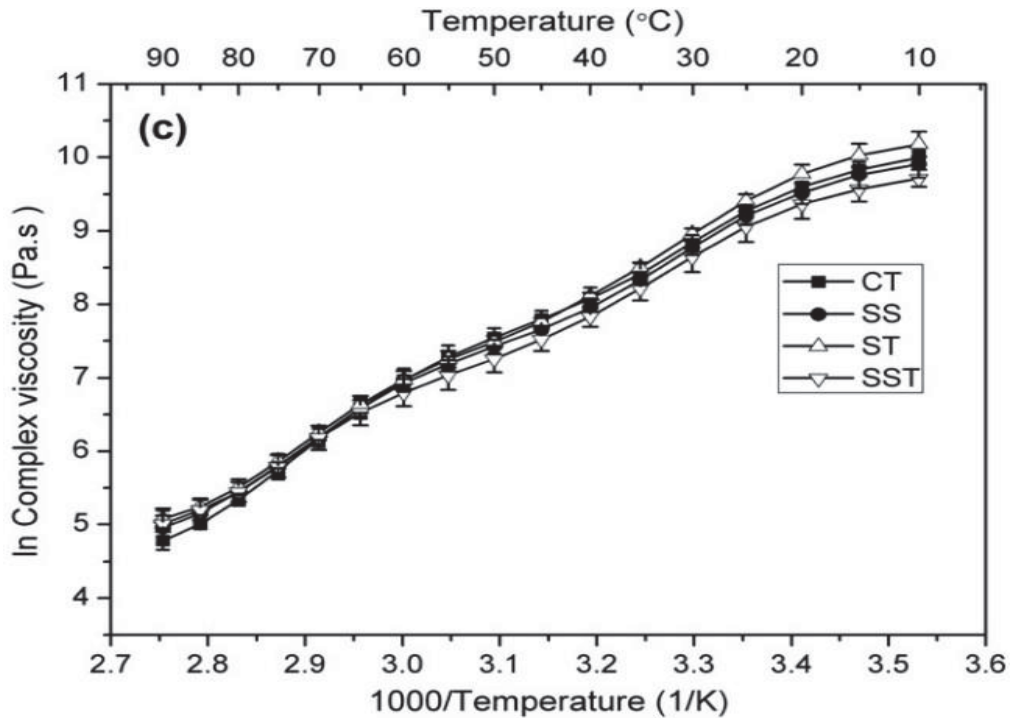


Figure 4 - 8 Arrhenius plots of viscous flow for mozzarella samples with different stretching conditions (Ma *et al.*, 2013)

Tunick *et al.* (1990) showed that the Arrhenius equation explained the change in the complex viscosity of cheddar and cheshire cheeses with temperature. Using the same method (small amplitude oscillatory shear analysis, SAOSA), the complex viscosity of several cheeses including colby, fresco and mozzarella cheese (Ma *et al.*, 2013), shown in figure 4-8, were also shown to obey the Arrhenius equation (Ma *et al.*, 2013; Tunick, 2010).

However, the relationship between the BSGC or elongational viscosity of cheese and temperature is rarely demonstrated. It was reported by Campanella *et al.* (1987) that the elongational viscosity of American process cheese did not follow the Arrhenius temperature relationship (figure 4-9). The plot of elongational viscosity versus the reciprocal of the absolute temperature resulted in a concave curve. Another example is shown in figure 4-7 as discussed earlier, the BSGC of cheddar also failed to follow the Arrhenius temperature relationship (Muthukumarappan *et al.*, 1999a).

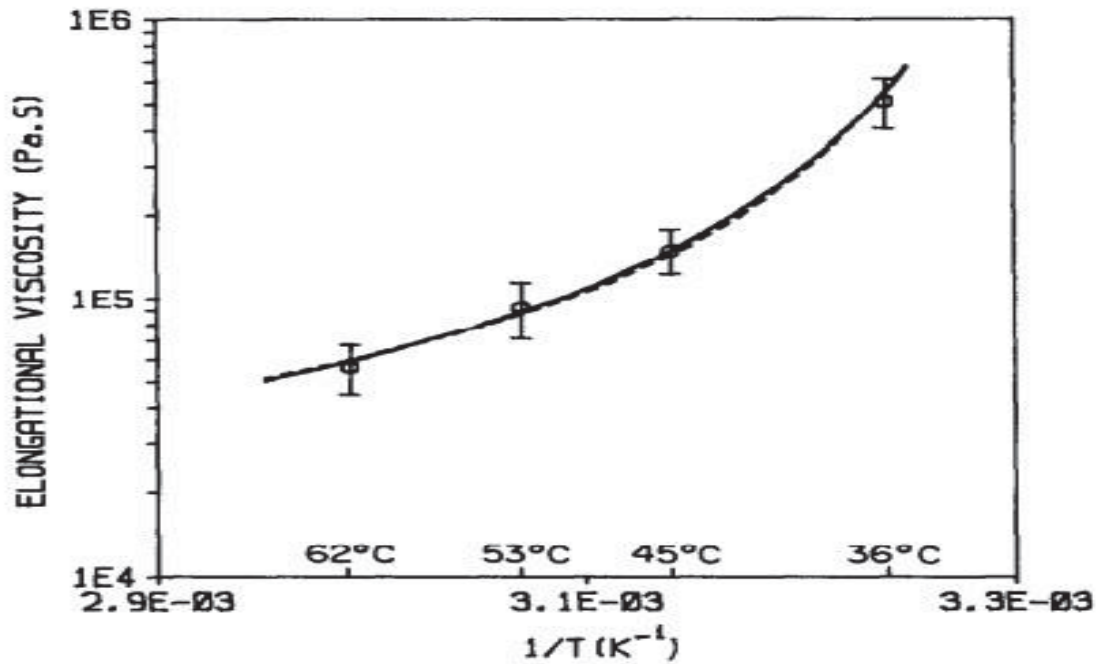


Figure 4 - 9 Effect of temperature on the elongational viscosity of process American cheese at 0.015 s⁻¹ biaxial strain rate (Campanella et al., 1987)

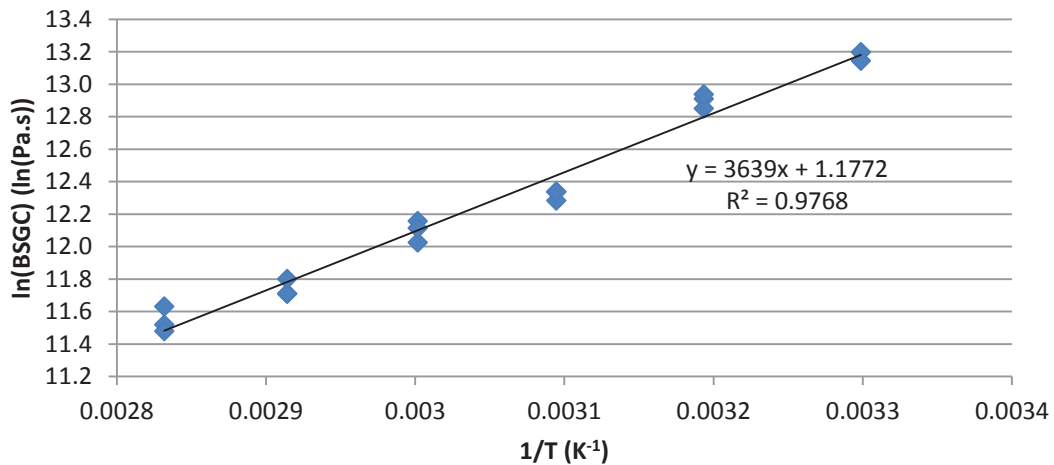


Figure 4 - 10 Effect of temperature on the elongational viscosity of mozzarella cheese at 0.001 s⁻¹ BESR

The Arrhenius plot of the data collected using the UW Meltmeter at the BESR of 0.001 s⁻¹ in present study is shown in figure 4-10. It can be seen that, over the temperature range from 30 °C to 80 °C, there was an approximately straight line which suggests that the data obeyed the Arrhenius equation. Equation 4.4 was fitted to each of the BSGC curves shown in figure 4-4 using the solver function in EXCEL (Microsoft, 2010). The high R-squared value, 97.68%, illustrated that the curve fitted equation 4.4

well. The activation energy of flow was $30.3 \pm 1.2 \text{ kJ} \cdot \text{mol}^{-1}$, pre-exponential factor is $3.3 \pm 1.4 \text{ Pa} \cdot \text{s}$. According to Liu *et al.* (2006), the pre-exponential factor is associated with the chemical composition, molecular weight and distribution of material. In the original Arrhenius equation, the activation energy is defined as the energy required to start a chemical reaction (Kelter *et al.*, 2008). When it applies to viscosity, the E_a can be called activation energy of flow which reflects the attractive energy holding a protein in its position.

Tunick (2010) showed that the E_a was $113.3 \pm 2.0 \text{ kJ} \cdot \text{mol}^{-1}$ for whole milk mozzarella and $104.4 \pm 5.7 \text{ kJ} \cdot \text{mol}^{-1}$ for low-moisture part-skim mozzarella obtained by small amplitude oscillatory shear analysis with temperature sweep test. The author concluded that cheese did not flow when the E_a is under $60 \text{ kJ} \cdot \text{mol}^{-1}$, while cheese with an E_a over $100 \text{ kJ} \cdot \text{mol}^{-1}$ will flow. The E_a discrepancy between present study and the literature may result from the different methods. The situation and mechanism of each test was not the same. Many factors, which influence the E_a value, are not controlled or comparable for the different methods. According to Peleg *et al.* (2002), the viscosity of food is not only shear rate and temperature dependent but also impacted by the mechanical history of the test specimen.

4.3. Moisture effect on rheological properties

For the commercial pizza baking process, pizza is placed in a convection oven which employs high temperature for a baking short time. The hot air movement in the oven across the surface of pizza brings about moisture loss from the pizza including the cheese topping. The characterisation of the rheological properties of mozzarella cheese influenced by moisture content would benefit the more accurate understanding of cheese melting during pizza baking.

4.3.1. Cheese drying

To simulate the moisture loss effect on the rheological properties of mozzarella cheese, samples were dried over salt solutions to lower their moisture contents.

Drying cheese was not discussed in literature, so there was no standard method to dry cheese. Saturated salt solutions, however, are widely used to investigate the moisture sorption isotherms of foods (Bronlund & Paterson, 2004; Duggan *et al.*, 2008; Durakova & Menkov, 2005). Water activity difference between food and its environment creates a driving force for water transport. When their water activities reach equilibrium, the water transport ends.

Sodium chloride (NaCl), sodium bromide (NaBr), potassium carbonate (K_2CO_3) and magnesium chloride ($MgCl_2$) salts were used in this study. The equilibrium relative humidity of each at 20 °C are 77%, 58%, 43% and 33% respectively (Greenspan, 1977). Mozzarella cheese blocks were placed into the different relative humidity air conditions which were provided by desiccators with the different saturated salt solutions at room temperature (approximately 20°C) for one week. Control cheese blocks were placed in a container without salt solution. After drying, the cheese blocks were sealed in separate aluminium foil pouches for ten days to allow time for the moisture in the cheese to redistribute within the cheese.

The moisture contents of the mozzarella cheese samples were determined by a gravimetric method (see appendix 1) based on procedures described previously (New Zealand Dairy Board, 1993). Shredded cheese is weighed before (the initial weight of the shredded cheese is about 10 g) and after the shredded cheese is baked in a 105 °C oven for 16 h. The moisture content can be calculated by the amount of weight loss in the oven. Water activity was determined by the AquaLab 4TE water activity meter (Labomar d.o.o., Zagreb Slovenia). Both moisture content and water activity for each sample were measured twice.

4.3.2. Results of cheese drying

Table 4-1 shows the average moisture contents, water activities of mozzarella cheeses samples dried over different salt solutions and their standard deviations. Their small standard deviations point out the repeatability of both the moisture content and water activity measurements. When the relationship between the moisture content

and water activity was plotted in the scale of water activity from 0 to 1 as an entire moisture sorption isotherm, it was found that relatively large changes in moisture content had little impact on the water activity (figure 4-11, experimental points). This phenomenon was reported by Bronlund and Paterson (2004) and Duggan *et al.* (2008). One of the plots from Duggan *et al.* (2008) is shown in figure 4-11 (literature line), when moisture increased to a high value, the water activity approached 1. Due to the insensitivity of water activity to change in moisture content, the moisture content was used to express the moisture loss.

Table 4 - 1 Moisture content and water activity of mozzarella cheese

drying by	Moisture content (g/g dry matter)	STDEV	Water activity	STDEV
Control	0.954	0.012	0.971	0.001
NaCl	0.788	0.012	0.958	0.001
NaBr	0.713	0.001	0.952	0.002
K ₂ CO ₃	0.697	0.000	0.950	0.002
MgCl ₂	0.654	0.006	0.949	0.000

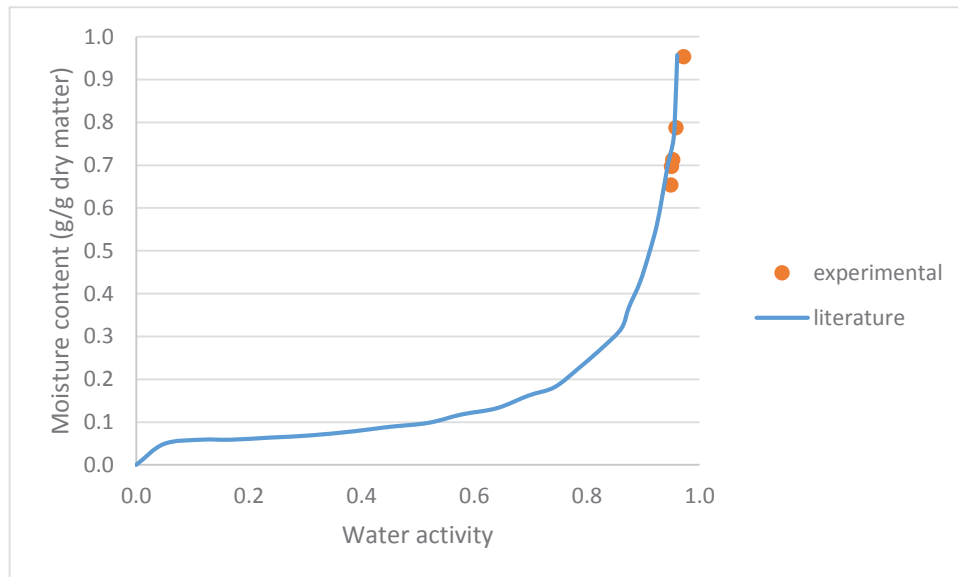


Figure 4 - 11 Relationship between moisture content and water activity of mozzarella cheese, and water sorption isotherms for imitation cheese at 5 °C (Duggan *et al.*, 2008)

4.3.3. Measurement of rheological properties of mozzarella

The rheological properties of the different moisture content mozzarella cheese samples were measured at 50 °C using the UW Meltmeter with triplicate samples (see section 3.3.3 for the full method).

4.3.4. Rheological results

The curves of sample height versus time for triplicate samples of the highest and lowest moisture content respectively were plotted in figure 4-12. This figure shows the repeatability of the UW Meltmeter method to characterize rheological properties of mozzarella cheese.

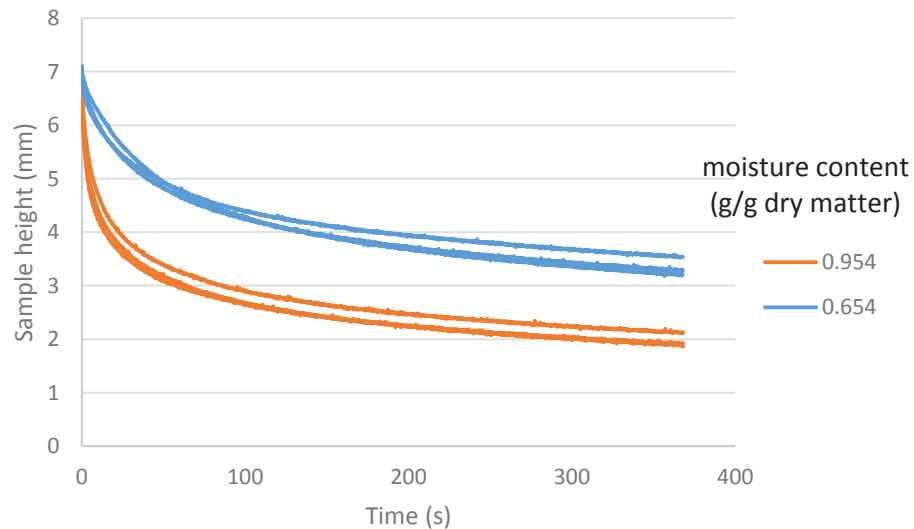


Figure 4 - 12 The height VS time for triplicate cheese samples of the highest and lowest moisture content

The sample heights for the different moisture content samples as a function of time were plotted in figure 4-13. It is hard to distinguish between the curves for each of the dried cheese samples. In other words, the samples had a similar melt and flow behaviour. Only the control sample showed a better ability to melt or flow.

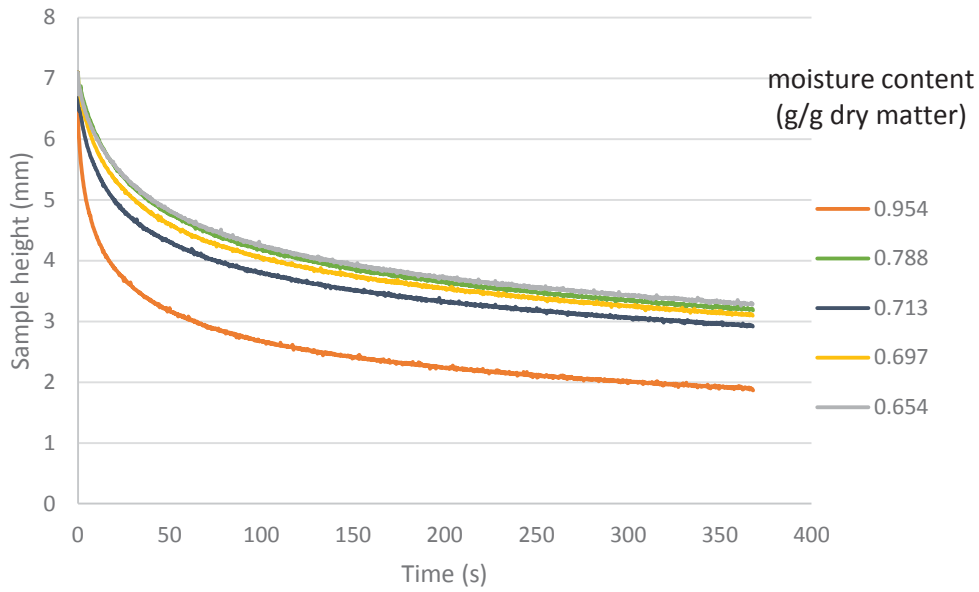


Figure 4 - 13 The height VS time for the different moisture content mozzarella cheese

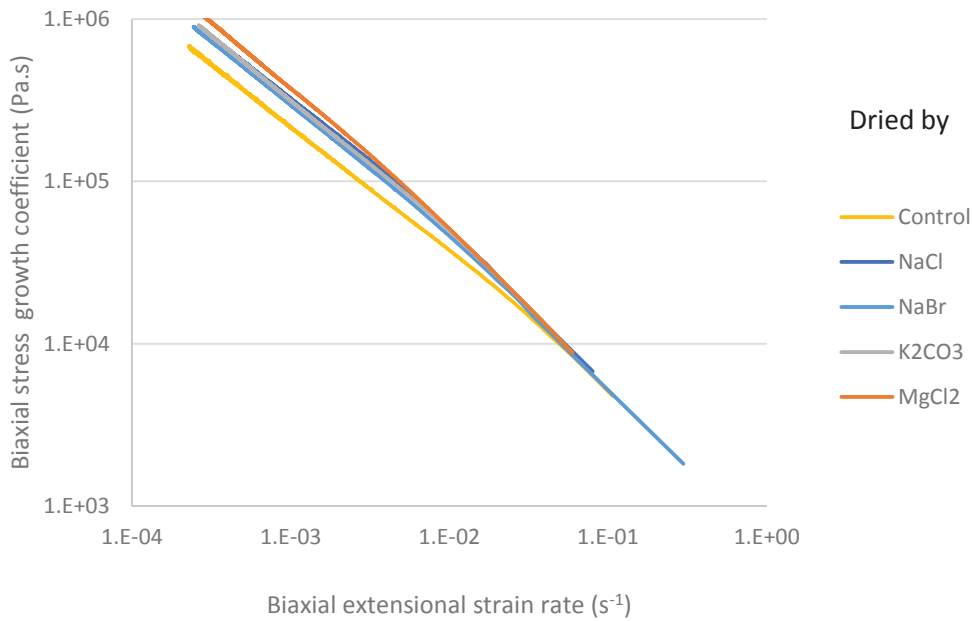


Figure 4 - 14 BSGC vs. BESR for the different moisture content mozzarella cheese at 50 °C

The BSGC and BESR of the mozzarella cheese were calculated as outlined in section 3.6 and plotted (figure 4-14). The same result as the plot of height versus time was observed. The control sample, cheese without drying, had lower BSGCs over the entire range of BESR. However, the curves for each of the dried cheese samples overlapped each other. They did not show a difference in the melt and flow behaviours.

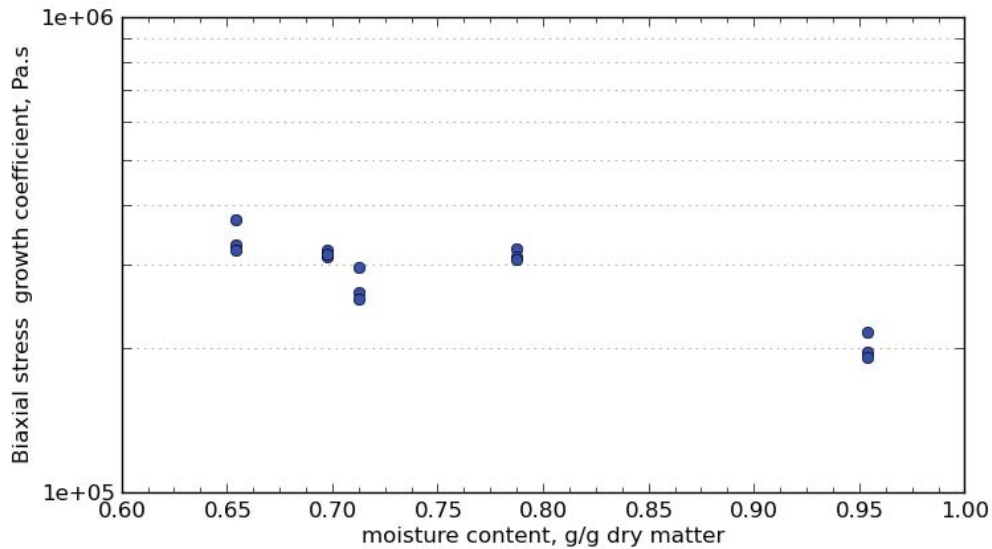


Figure 4 - 15 BSGC of mozzarella cheese as function of moisture content at BESR of 0.001 s^{-1}

The BSGC of mozzarella cheese at BESR of 0.001 s^{-1} for each of the cheese samples is plotted in figure 4-15. This plot gives a more intuitive feel of the moisture effect on the rheological properties. The results suggest that the BSGCs of the dried mozzarella cheeses were slightly higher than the control cheese sample. The BSGC difference between cheeses samples dried over different salt solution was little. Arnott *et al.* (1957) reported that there was not a significant relationship between moisture content and melting behaviour for process cheese. This was supported by Harvey *et al.* (1982), who argued that moisture and fat content did not always influence the melting properties of cheese.

Overall, the mozzarella cheeses dried over different salt solutions had slightly reduced flow behaviours than the control cheese sample as measured by the UW Meltmeter. The different levels of drying had barely any impact on rheological properties of mozzarella cheese.

4.4. Conclusion

The rheological properties of mozzarella were measured at varying temperatures and moisture contents. Results showed that the biaxial stress growth coefficient decreased as temperature and biaxial extensional strain rate increased in

the UW Meltmeter tests. The temperature effect at 0.001 s^{-1} , which is analogous with the flow rate of cheese on pizza baking, obeyed the Arrhenius model. The mozzarella cheese drying over the varying saturated salt solutions resulted in a small decrease in meltability of cheese, and the effect of different drying levels on the rheological properties of mozzarella cheese was not measurable when measured using the UW Meltmeter.

5. ROTATIONAL RHEOLOGY METHOD DEVELOPMENT

5.1. Introduction

In this chapter, an appropriate method to characterise cheese flow under low shear conditions using rotational rheometer was identified and compared with the results gained from the UW Meltmeter (Chapter 4). A MCR301 rheometer (Anton Paar, Austria) was chosen for conducting this analysis as it provided the greatest testing flexibility of the instruments available. In particular, this rheometer has a wide range of measurement systems for many types of rheological tests including the ability to conduct both oscillatory and rotational tests. The rheometer also included accessories that allowed for careful temperature control during testing. Several measurement methods were trialled. These included high stress creep tests, low stress creep and recovery tests, constant shear rate tests, shear rate ramp tests and temperature sweep oscillatory tests.

5.1.1. Rotational rheometer

Rotational rheometers equipped with parallel plates are widely used to measure rheological properties of foods (Djalili-Moghaddam & Toll, 2005; Mezger, 2011; Rao, 2005) . In most cases, the upper plate is rotatable and the bottom plate, whose diameter is equal or larger than the diameter of the upper plate, is stationary. The plate radius, R , represents the size of the upper plate as shown in Figure 5-1.

The distance between the parallel plates, and therefore the height of sample, is defined as H (m). The height of the sample should be less than the upper plate radius. The gap size can impact the results gained from the rheometer. For example a large gap between the two plates can result in problems such as edge failure for viscoelastic materials, inhomogeneous deformation behaviour for paste-like samples and secondary flow effects for liquids with low viscosity. The typical range of R is between

10 and 25 mm. H typically ranges from 0.5 to 3 mm for measuring polymer melting properties (Mezger, 2011).

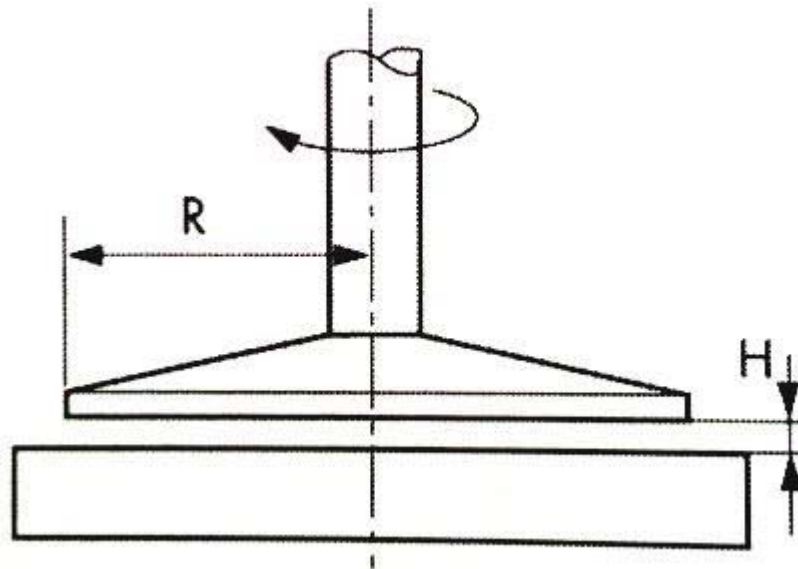


Figure 5 - 1 Parallel-plate measuring system

The shear rate in the parallel plate gap is not constant in the radial direction. The shear rate (s^{-1}) is expressed by:

$$\dot{\gamma} = \frac{r \cdot \omega}{H} \quad (5.1)$$

Where, r is the distance between the centre and a certain point of the plate (m); ω is the rotational speed (rad/s). During a test, H is constant, but the shear rate changes with respect to r even at a constant rotational speed. The shear rate is zero at the centre of the plate ($r = 0$), and it reaches the maximum at the edge of the upper plate ($r = R$).

There are two concepts that are utilised for the shear rate calculation and the data analysis of measurement results:

- (1) Maximum shear rate ($\dot{\gamma}_R$): This shear rate value refers to the edge of the upper plate;

- (2) Mean shear rate ($\dot{\gamma}_m$): the $\dot{\gamma}_m$ sums the contribution of the radius-dependent shear rates, the value is associated to the location of $r_m = (2/3) \cdot R$. Namely, $\dot{\gamma}_m = (2/3) \cdot \dot{\gamma}_R$.

Shear stress is determined from the applied torque according to a force balance on the upper plate, which is integrated over the radius (Steffe, 1996). The shear stress can be given by equation 5.2:

$$\tau_R = \frac{M}{2\pi R^3} \left[3 + \frac{d \ln M}{d \ln \dot{\gamma}_R} \right] \quad (5.2)$$

Where M is the torque on the upper plate (mNm). Similarly, the mean shear stress $\tau_m = (2/3) \cdot \tau_R$.

The viscosity is given by:

$$\eta = \frac{\tau_R}{\dot{\gamma}_R} = \frac{\tau_m}{\dot{\gamma}_m} = \frac{MH}{2\pi\omega R^4} \left[3 + \frac{d \ln M}{d \ln \dot{\gamma}_R} \right] \quad (5.3)$$

The rotational rheometer also can be operated for oscillatory tests. In a small amplitude oscillatory shear measurement (SAOS), the testing sample is subjected to small sinusoidal shear strain with constant frequency, ω , and strain amplitude, γ_o , (Gunasekaran & Ak, 2003):

$$\gamma(t) = \gamma_o \sin(\omega t) \quad (5.4)$$

When γ_o is adequately small (in the linear viscoelastic limit), the response of stress also is sinusoidal and is given by:

$$\sigma(t) = \sigma_o \sin(\omega t + \delta) \quad (5.5)$$

where σ_o is the stress amplitude (Pa); δ is the loss angle. According to the trigonometric identity, the storage modulus is $G' = \sigma_o/\gamma_o \cdot \cos(\delta)$, (Pa) and loss modulus is given as $G'' = \sigma_o/\gamma_o \cdot \sin(\delta)$, (Pa). The shear stress can be expressed as:

$$\sigma(t) = \sigma_o [G'(\omega)\sin(\omega t) + G''\cos(\omega t)] \quad (5.6)$$

The dynamic behaviour of a sample can also be presented by the loss tangent given by:

$$\tan \delta(\omega) = \frac{G''}{G'} \quad (5.7)$$

The complex viscosity, η^* (Pa · s), is an alternative way to express the oscillatory experiment results. It is related to the viscous component $\eta' = G'/\omega$ (Pa · s) and elastic component $\eta'' = G''/\omega$ (Pa · s) as:

$$\eta^* = \sqrt{(\eta')^2 + (\eta'')^2} \quad (5.8)$$

5.1.2. Sample preparation

Sample preparation has a large impact on the results of rheological properties using the rotational rheometer. The sample needs to maintain contact with the upper and lower plates throughout the test. Furthermore, the sample should not be over-compressed to avoid prestressing effects and liquid/fat migration (Muliawan & Hatzikiriakos, 2007). Therefore it is important to supply uniform samples for all experiments. For the tests conducted for this thesis, the procedures of sample preparation include:

- 1) Blocks of cheese were thawed and tempered to 4 °C.
- 2) The cheese blocks were cut into 3 mm slices using a cheese slicer (figure 5-2 A).
- 3) A cork borer (figure 5-2 B) was used to collect 20 mm diameter samples.
- 4) Samples 3 mm thick and 20 mm diameter were therefore obtained.



Figure 5 - 2 Cheese slicer (A) and 20 mm cork borer (B)

5.1.3. Procedures for the parallel plate rheometer tests

The MCR301 rheometer (Anton Paar, Austria) was equipped with fluid circulators and a peltier hood. These two systems ensured rapid and accurate temperature control during pre-heating and testing. A parallel plate PP20/S-SN13685 measuring system (Anton Paar, Austria) was used to conduct tests.

For each experiment, a cheese sample was placed on the centre of the lower plate and compressed between the parallel plates. The outer area, not in contact with the rheometer plates, of the cheese sample was coated with mineral oil in order to avoid moisture loss. Before a test was executed, the sample was heated for two minutes to ensure that the sample reached a uniform temperature (i.e. to ensure the test was carried out under isothermal conditions). Temperature, shear rate, and shear stress can be set depending on the test required.

5.2. Creep and recovery

The creep test is a way to characterise the rheological behaviour of viscoelastic materials. The Kelvin-Voigt model is, most often, utilised to describe cheese creep response (Gunasekaran & Ak, 2003). The main analysis for cheese, or any other food, involves determining the model constants including the Newtonian viscosity (zero shear viscosity), individual viscosities and individual elasticities. In a creep experiment, when a constant stress is instantaneously applied to a sample, the immediate deformation of the sample occurs at the beginning (figure 5-3). While the stress is maintained over a period of time, the strain increases. Creep recovery can be part of the creep test, whereby the stress is removed and reverse deformations may occur (Mezger, 2011).

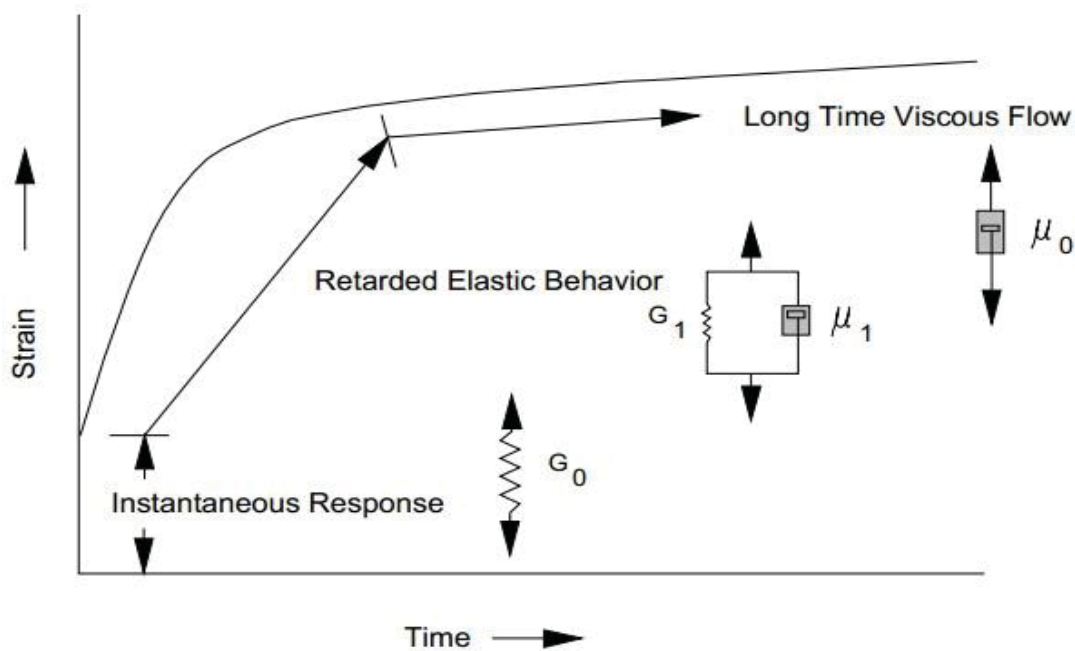


Figure 5 - 3 Typical creep curve showing with the various elements of the Burgers model (Steffe, 1996)

As is well known (Dealy & Saucier, 2000), viscosity varies with both temperature and shear rate for most materials. However, when shear rate is sufficiently low, for some materials (i.e. polymer), the viscosity becomes shear rate independent and approaches a constant value, named the zero shear viscosity. Dealy and Saucier (2000) pointed out that the zero shear viscosity is temperature dependent.

For example, the dependence of the zero shear viscosity of semicrystalline polymers on temperature can be expressed as an Arrhenius relationship Eq. 4.3. The WLF model (Eq. 4.2) is usually used to describe the relationship between the zero shear viscosities of amorphous polymers. These suggest that the zero shear viscosity may be able to describe the flow behaviour of mozzarella cheese as function of temperature.

Therefore, the creep test was carried out to obtain the zero shear viscosity of mozzarella cheese as function of temperature under low shear rate at the interested stress. As discussed in Chapter 3, the stresses which are relevant to pizza baking are approximately 25 to 100 Pa. Therefore, the creep test was trialled at high stress (100 Pa) and low stress (25 Pa).

5.2.1. High stress creep test

In this stress creep test, the setup of the MCR301 rheometer was the same as outlined in 5.1.3, traditional mozzarella samples were tested at 40, 50, 60, 70, and 80 °C. The shear stress applied to cheese samples was set at 100 Pa. Each test lasted 6 minutes. Two replicates were conducted at each temperature.

5.2.2. Results of the high stress creep test

The creep test results are shown in figure 5-4, where the viscosity was plotted as function of shear rate.

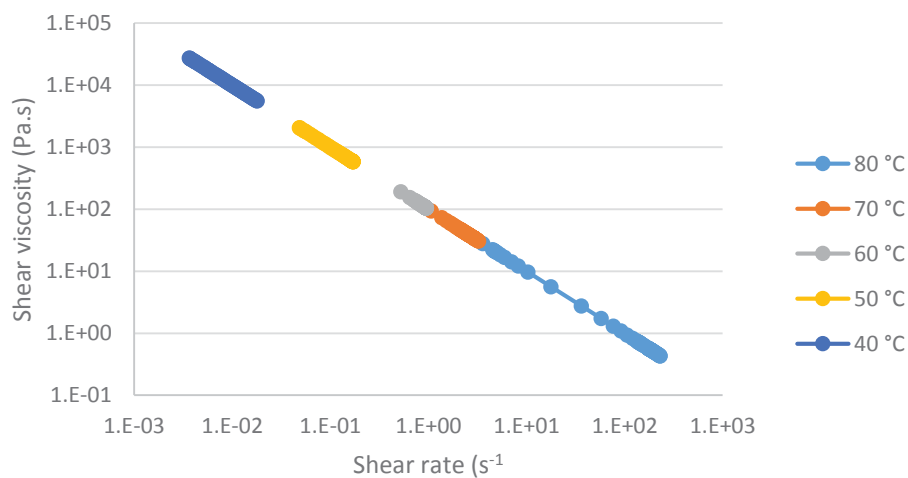


Figure 5 - 4 The shear viscosity VS. shear rate in the high stress creep tests

The shear viscosity versus shear rate on the log scale at different temperature formed a straight line. As is well-known, the shear viscosity equation 2.1, can also be expressed by:

$$\log \eta = -\log \dot{\gamma} + \log \sigma \quad (5.9)$$

The stress was constant, thus, the relationship between log shear viscosity and log shear rate was linear. The shear rate of the sample at 80 °C shows a rapid increase during the test indicating that slip occurred during the test.

The results are presented as shear strain as function of time for each temperature in figure 5-5. The curves were concave upward, and approached straight lines at high temperature. What's more, it was evident that the shear strain was extremely large especially at high temperatures. This relationship between shear strain and time in this high stress creep test did not obey the typical creep curve (figure 5-2), which is a concave downward with three periods of responses. The reason for this could be that the linear viscoelastic range was exceeded during these tests. According to literature, the shear strain limit of linear viscoelastic region was about 0.5% for mozzarella cheese (Ak & Gunasekaran, 1996; Nolan *et al.*, 1989). The viscoelastic behaviour is related to the molecular formulation and structure of the material. As explained in the literature (Mezger, 2011; Ximena & Rao, 2005), when a large deformation is applied, there is a risk of surpassing the linear viscoelastic range. In other words, the basic rheological equations including Newton's law, Hooke's law, Kelvin-Voigt, Maxwell and Burgers functions will no longer apply. There is little doubt that this high stress creep test was conducted beyond the linear viscoelastic region.

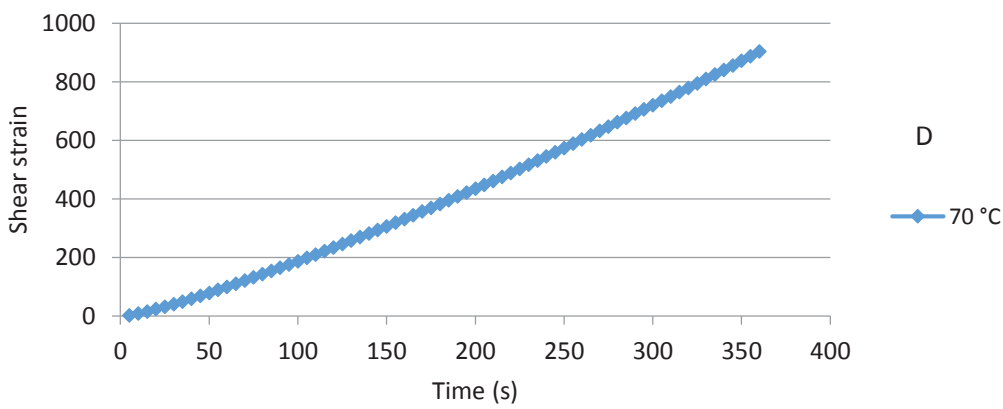
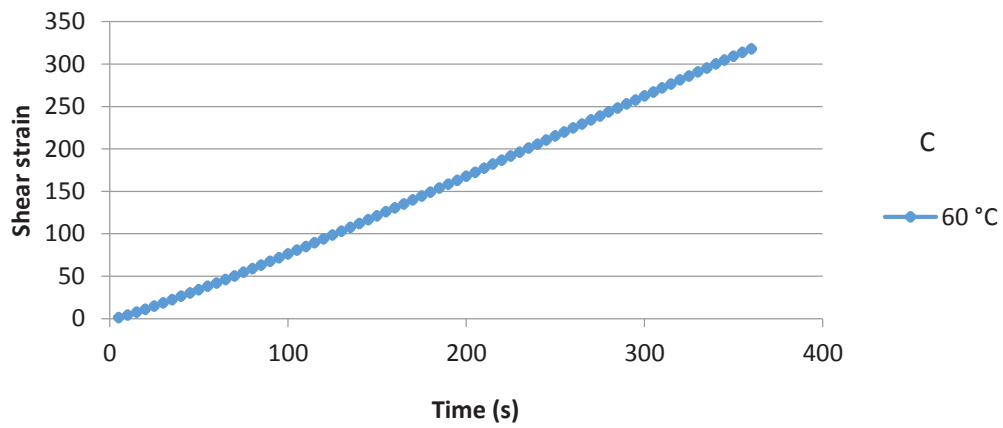
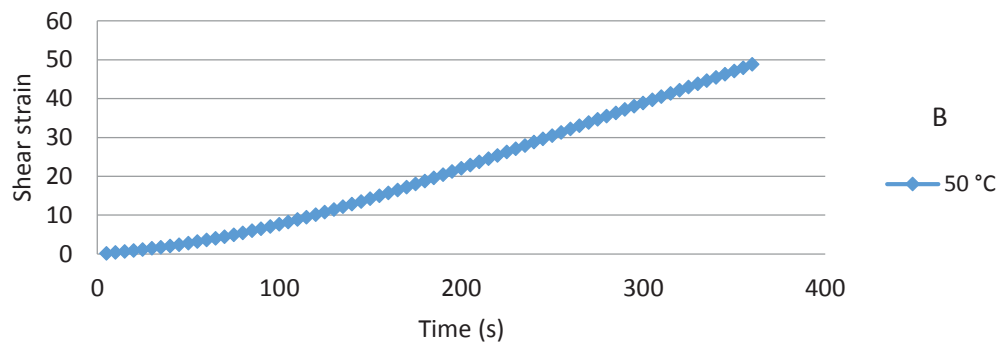
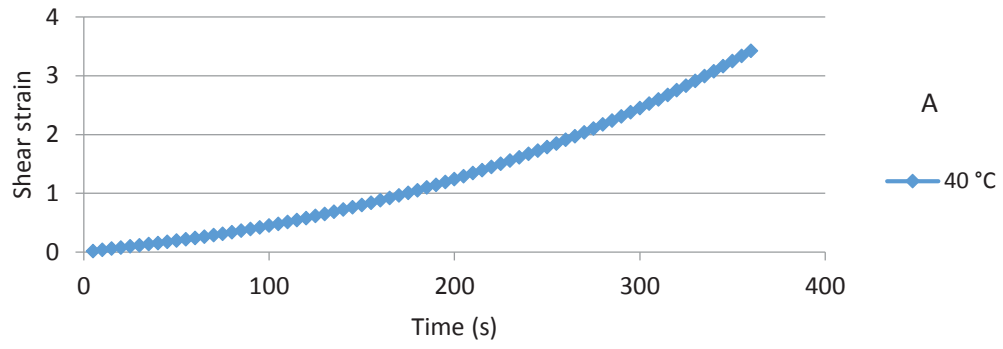


Figure 5 - 5 Shear strain recorded as function of time at different temperatures. A: 40°C; B: 50°C; C: 60°C; D: 70°C

Because the shear strain exceeded the linear viscoelastic limit, there was a failure to obtain the zero shear viscosity of mozzarella cheese in this high stress creep test, hence, inability to develop a model for the zero shear viscosity of mozzarella cheese as function of temperature under low shear rate at the stress range of interest.

5.2.3. Low stress creep and recovery test

For low stress creep and recovery tests, the setup of the MCR301 rheometer was the same as outlined in 5.1.3. According to the literature (Olivares *et al.*, 2009), tests are generally done at 25 Pa so as to ensure that the linear viscoelastic region of mozzarella cheese is not exceeded. This test was conducted at 20, 30, 40 and 50 °C. A stress of 25 Pa was applied to traditional mozzarella cheese samples for 180 s for the creep portion of the test before the stress was removed allowing the sample to relax for 500 s. Three replicates for each condition were conducted.

5.2.4. Results of low stress creep and recovery test

During the experiment, it was found that this test could not be carried out at 50 °C because slip occurred due to fat moving to the surface of the cheese. The creep data usually can be expressed as creep compliance, which is stress independent in the linear viscoelastic region of a material (Gunasekaran & Ak, 2003). The creep compliance is defined as equation 5.10. The curve of the creep compliance versus time is similar to the curve of shear strain versus time (Mezger, 2011).

$$J(t) = \frac{\gamma(t)}{\tau_0} \quad (5.10)$$

Where $J(t)$ is creep compliance (Pa^{-1}); τ_0 is shear stress (Pa) applied to cheese in the creep period; $\gamma(t)$ is shear strain at time t (s).

The creep and recovery curves for the samples at 20, 30, 40 °C are shown in figure 5-6.

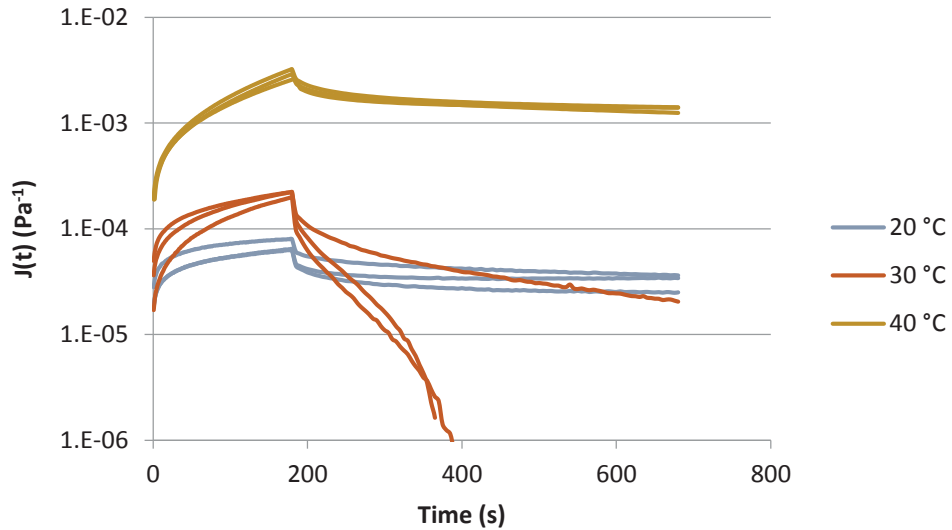


Figure 5 - 6 The creep and recovery curves for mozzarella cheese at different temperatures

For the creep part of the curves, the results followed the typical response for a creep test which is illustrated by the Burgers model as described in figure 5-3. This consists of instantaneous response, retarded elastic and long-time viscous responses. In the recovery period, only the samples at 20 and 40 °C presented the same response as reported the study by Olivares *et al.* (2009). The recovery compliance approached a constant value for each temperature sample and increased as temperature elevated due to the thermal softening.

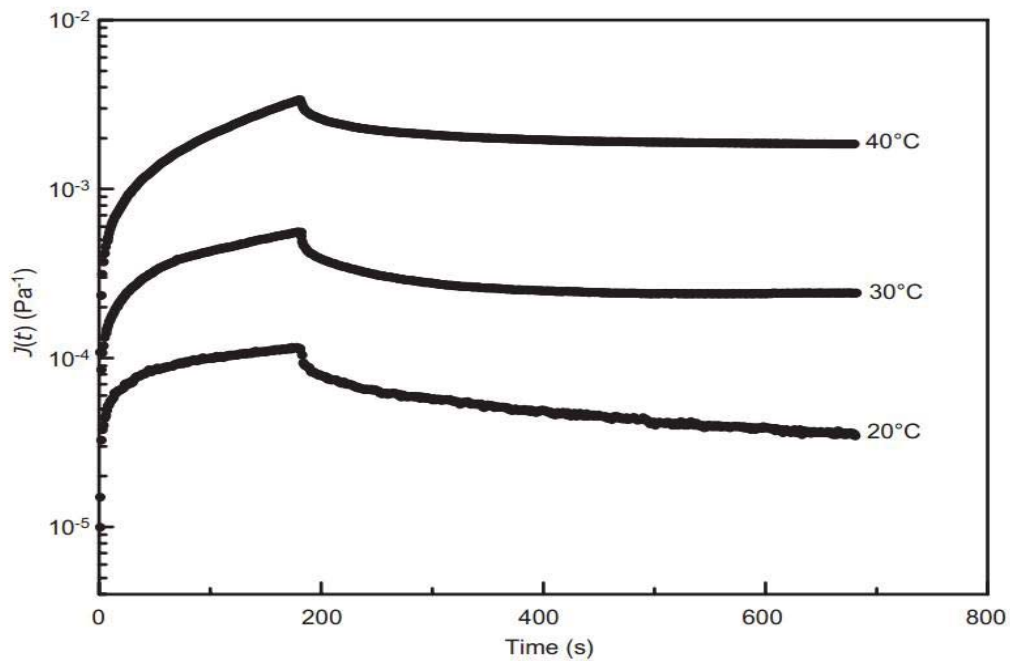


Figure 5 - 7 The creep and recovery curves of mozzarella cheese ripened for 36 days (Olivares *et al.*, 2009)

The recovery compliance of the 30 °C sample was smaller than the 20 °C sample. The reason for this may be attributed to inbuilt strain release at 30 °C. Inbuilt strain can occur in mozzarella as the cheese curd is stretched during manufacture as described in section 2.5.5 (the mozzarella cheese making). On heating this stretch may relax. The inbuilt strain was probably not released at 20 °C and had been released already at 40 °C in the pre-heating period in the rheometer prior to starting the test.

In this low stress creep method, the measurement was unable to be operated at high temperature due to slip effects. The zero shear viscosity could only be determined at low temperatures. Therefore, the desired rheological data of interest in this study could not be obtained using this method.

5.3. Controlled shear rate test

In a controlled shear rate test, a shear rate or rotational speed is controlled and the relative shear stress or torque is recorded. This method is usually applied in investigations of the self-levelling behaviours of materials, measurement of viscosity at a given shear rate or determination of yield stresses of materials. In this method, the shear rate or the rotational speed should not be too high, otherwise, some weak structural bonds may be disrupted before the shear stress or torque reaches a peak (Singh & Wirakartakusumah, 1992).

Controlled shear rate tests were carried out to obtain the viscosity of mozzarella at given shear rates in a range relevant to the flow of cheese on a pizza during baking. The tests included constant shear rate tests and shear rate ramp tests.

5.3.1. Constant shear rate test

The procedure used to setup the MCR301 rheometer was the same as outlined in 5.1.3. Calculations in chapter 3 suggested that a shear rate of 0.001 s^{-1} is relevant to the flow speed of cheese on pizza baking. Therefore, these tests were conducted at

the constant shear rate of 0.001 s^{-1} for 6 minutes (a common pizza baking time). Traditional mozzarella cheese samples were tested at 30, 40, 50, and 60 °C.

5.3.2. Results of the constant shear rate test

The viscosity versus time curves were plotted in figure 5-8 showing that there was a gradual increase in viscosity initially up to a maximum value, followed by a decrease. This is more noticeable at low temperature. According to the typical response of the viscosity at a controlled shear rate test, after the decline, the viscosity should reach an equilibrium value. This was evident at 50 °C in these tests (figure 5-8 B). The time was too short for the samples at 30 and 40 °C to reach this equilibrium. The viscosity at 60 °C slightly increased during the 6 minute test. The increase in viscosity may result from moisture loss at high temperature.

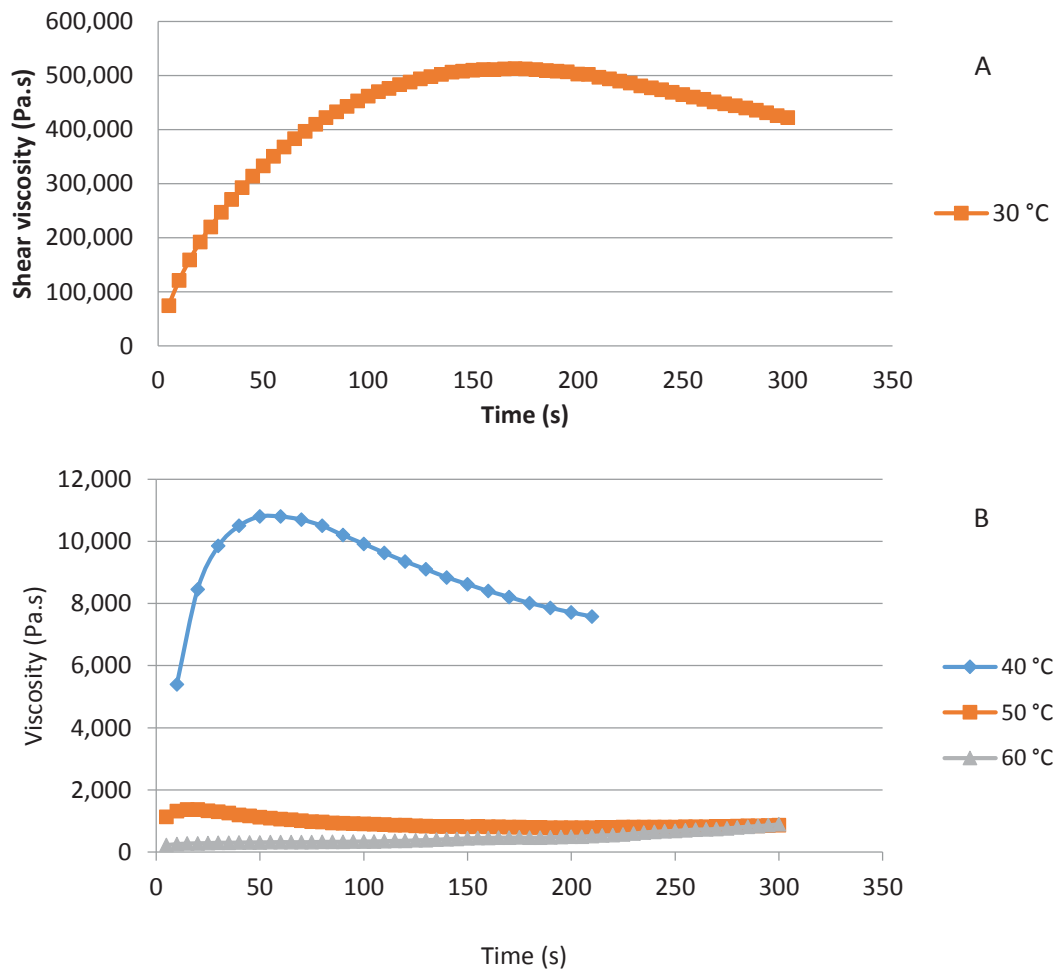


Figure 5 - 8 Time effect on viscosity of mozzarella cheese for different temperature. A: 30 °C; B: 40, 50 and 60 °C

In this constant shear rate method, when testing time is too short, the viscosity of samples at low temperature cannot reach an equilibrium, while it is not able to collect accurate data due to moisture loss at high temperature if the testing time lasts too long. Therefore, it is hard to find a testing condition which can overcome both the disadvantages in the two situations. So the constant shear rate method is not suitable to characterise mozzarella cheese across a wide range of temperatures.

5.3.3. Shear rate ramp test

The shear rate ramp test can be used to observe how the rheological behaviours of materials change with a range of shear rate directly. The MCR301 rheometer setup was the same as outlined in 5.1.3. With the purpose of having a similar process as cheese melting in a baking system, the tests were executed from a high shear rate (0.01 s^{-1}) at the beginning to a low shear rate (0.0001 s^{-1}) at the end with a log ramp decrease. The test time could not be too long to avoid the significant effect of moisture loss. The tests here were carried out over 4 minutes. Traditional mozzarella cheese samples were tested at 30, 50, and 70°C.

5.3.4. Result of the shear rate ramp test

The typical shear viscosity versus shear rate curves obtained are shown in figure 5-9. The shear viscosity increased when the shear rate became slower exhibiting the shear thinning behaviour. The viscosity decreased as temperature increased. The difference in viscosity between the various temperatures was distinct and there were similar trends of shear viscosity affected by the shear rate.

The shear rate ramp test was suitable to collect data that is able to describe cheese melt and flow due to three reasons: 1) the data span across the desired temperature and shear rate range that are relevant to the cheese melt and flow in pizza baking; 2) the results from these tests are sensitive to temperature; 3) this measurement is repeatable.

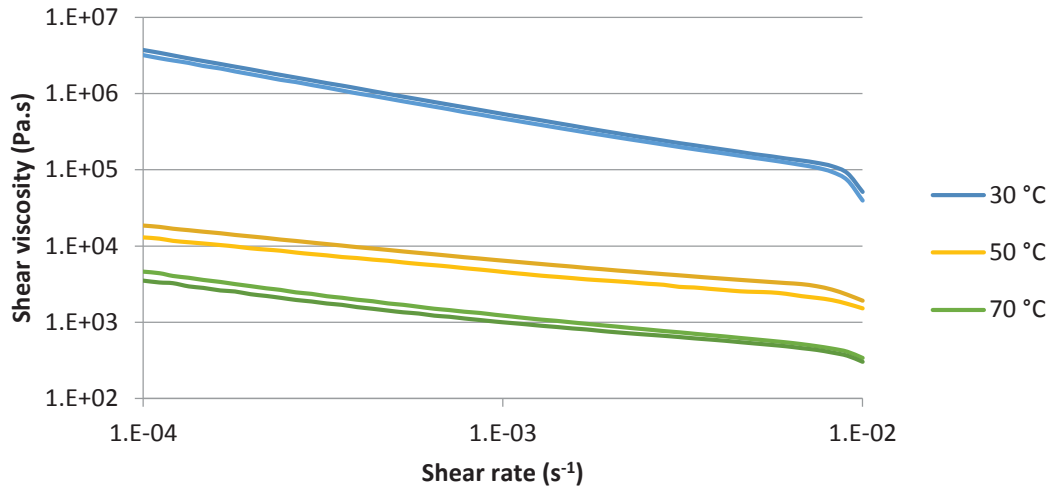


Figure 5 - 9 Shear viscosity VS shear rate plots for mozzarella cheese samples at varied temperature using the rotational viscometer

5.4. Oscillatory Rheometry

The oscillatory test is a common method to investigate the viscoelastic behaviour of materials. The results are sensitive to the physical structure and chemical composition of materials. Therefore, it is very useful for various food applications including observing cheese melting, studying gel strength, evaluating the phenomenon of glass transition etc. (Steffe, 1996). To investigate the rheological behaviour induced by temperature, the temperature sweep test was selected. When operating this kind of oscillatory test, both the amplitude and the frequency are maintained at a fixed value, and temperature is the only varied parameter.

5.4.1. Method

The MCR301 rheometer setup was the same as outlined in 5.1.3. The tests were performed with an amplitude of 0.5 % at a frequency of 1Hz; traditional mozzarella cheese samples were heated from 20 °C to 80 °C with a heating rate of 1 °C/min over the test.

5.4.2. Results of the oscillatory test

The dynamic properties recorded as function of temperature determined at 1 Hz are shown in figure 5-10 and 5-11. As can be seen in figure 5-10, both the viscous and the elastic components decreased with increasing temperature. At temperatures below 50 °C, the elastic component was larger than the viscous component. That means the elastic component was the dominant element in this period displaying a solid-like behaviour. Beyond 50 °C, this situation was contrary, the viscous component dominated the dynamic properties showing a liquid-like behaviour. The increase in the loss tangent with elevated temperature also illustrated the transition of the mozzarella cheese from the solid-like to liquid-like behaviour during the heating. Figure 5-11 shows that the complex viscosity declined as the temperature increased.

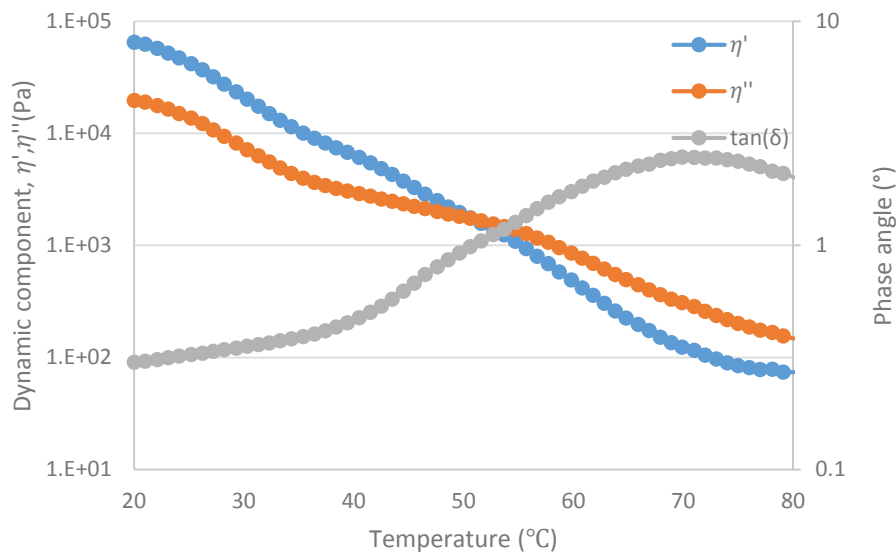


Figure 5 - 10 The complex modulus and loss tangent as a function of temperature in the temperature sweep test using oscillatory method

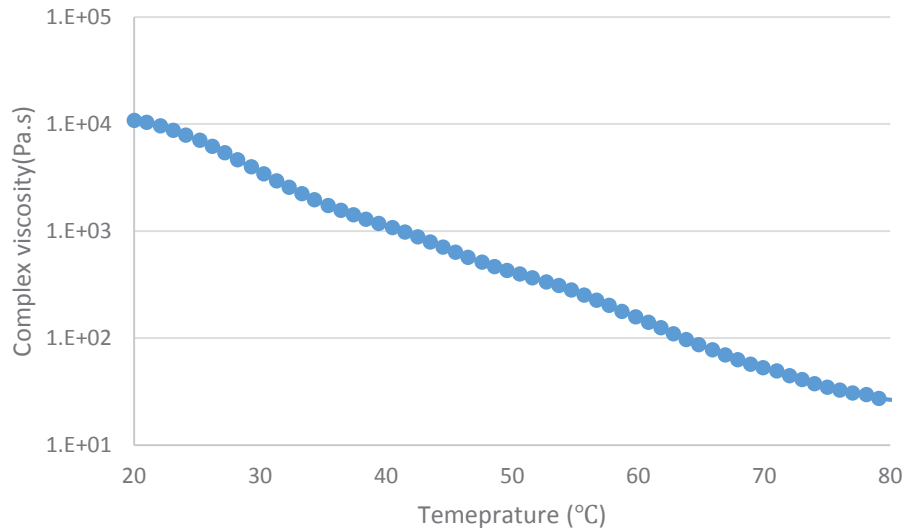


Figure 5 - 11 Complex viscosity as a function of temperature in temperature sweep test using oscillatory method

It is hard to relate the results to the practical situation of mozzarella cheese in pizza baking process, although this method could be a good way to examine the temperature effect on the cheese rheological properties at a given frequency and amplitude. Thus, it may not be appropriate to use the oscillatory method to collect the data describing the cheese melt and flow in pizza baking.

5.5. Conclusion

A number of methods were carried with the aim of identifying and/or developing a suitable method to collect the desired data using the MCR301 rheometer to compare the data obtained by the UW Meltmeter. The high stress creep test failed to yield valid rheological data because the linear viscoelastic limit of the cheese was exceeded. The low stress creep and recovery tests were unable to be conducted at high temperature due to slip. The constant shear tests might not collect accurate data at high temperature in a long time test due to moisture loss. The temperature sweep test using the oscillatory method was hard to relate to cheese flow and so also was not suitable for aim of this study. However, the shear rate ramp tests gave distinguishable results for each temperature sample. The data obtained from this method also spanned across the shear rate range of interest in this study. Therefore, the shear rate

ramp test was selected as the most appropriate method to characterise rheological properties of mozzarella cheese using the rotational rheometer technique.

6. ROTATIONAL VISCOMETER RESULTS

6.1. Introduction

This chapter was aimed at characterising the melt and flow properties of traditional mozzarella cheese using the method selected in chapter 5 (shear rate ramp test). The temperature range of interest was at 30 °C, 40 °C, 50 °C, 60 °C, 70 °C and 80 °C. With appropriate data, there was potential to explore different mathematical methods to describe the flow behaviour. Because the surface of the cheese forms a skin that resists flow, it is likely that the viscosity of the cheese increases as it dries out. For this reason the effect of moisture content on the melt and flow properties was examined.

6.2. Fibre direction effect in rotational rheometer

Anisotropy is a feature of the mozzarella cheese that is discussed in section 3.7. If it has some effect on rheological measurements, it needs to be controlled. In order to avoid the possible fibre direction effect on the rheological properties of mozzarella cheese using the rotational rheometer, the fibre direction effect was investigated here.

6.2.1. Method

The parallel and normal directions in the cheese were defined the same as in section 3.7 (see figure 3-19). Samples of traditional mozzarella were taken from a large block of cheese according to the method outlined in section 5.1.2. The setup of the MCR301 rheometer was the same as detailed in section 5.1.3. Triplicate samples with parallel and normal directions respectively were measured at 30 and 60 °C using the method described in section 5.3.3.

6.2.2. Results

The mean of the measured viscosities, with error bars based on standard deviation, are plotted in figure 6-1. There was little difference in the shear viscosities

between the cheese samples at 30 °C with different fibre directions. The samples tested in the parallel direction had a slightly higher viscosity at the high shear rate compared with the sample with normal direction at 60 °C. However, all results for both tests were within the error bars i.e. the error is larger than the difference between the results. Therefore, it was concluded that the effect of fibre direction on the rheological behaviour of mozzarella cheese is not measurable in rotational tests and so does not need to be controlled in future tests. These results agree with the results of the investigation carried out in UW Meltmeter and presented in section 3.7.

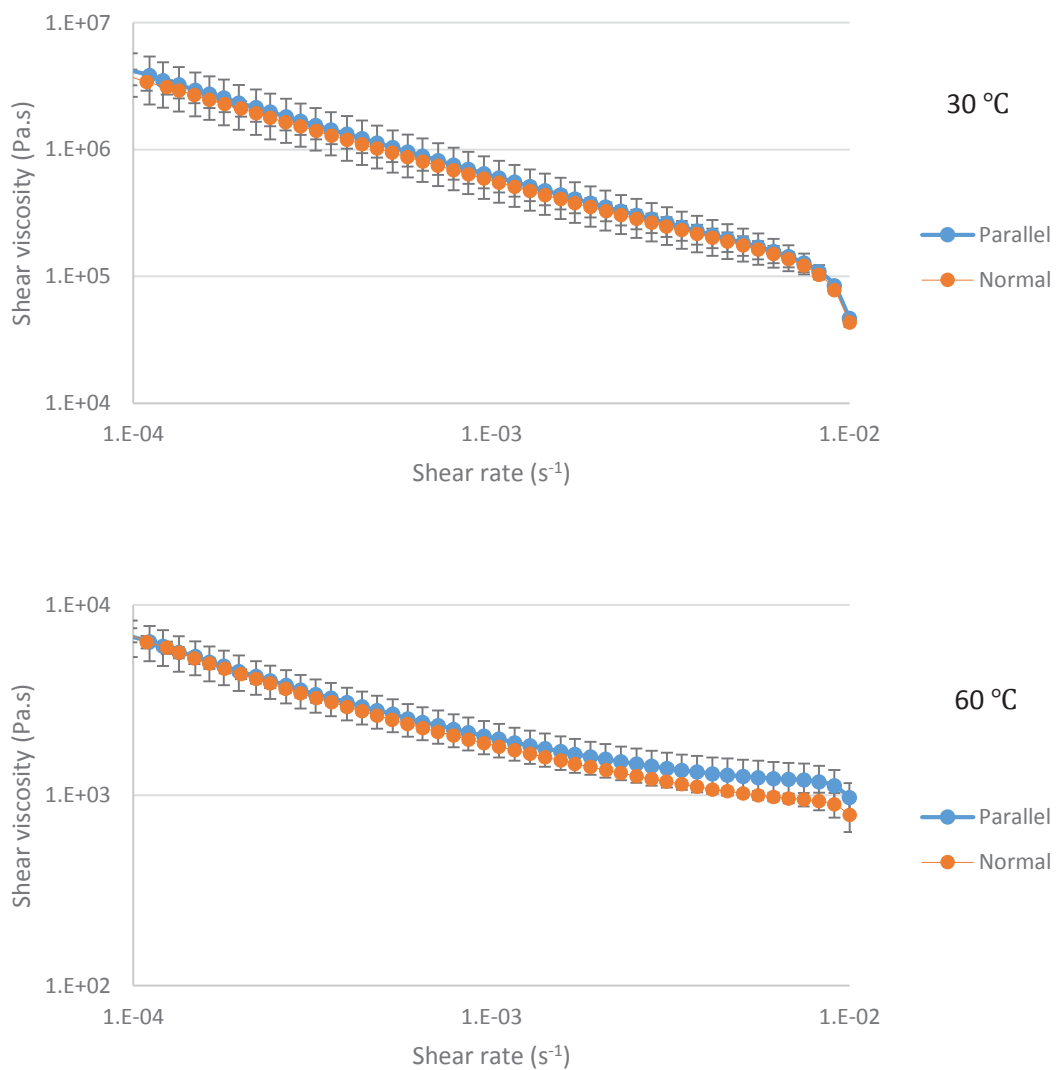


Figure 6 - 1 Comparison of the shear viscosity between the samples with two fibre directions

6.3. Temperature effects on rheological properties

It is well known that temperature is an important factor that influences the melt and flow behaviour of cheese. Mozzarella cheese on pizzas during baking is accompanied by temperature change. Accordingly, the viscosity of mozzarella cheese changes during pizza baking. For this reason quantification of the viscosity of mozzarella cheese at varying temperatures was required.

6.3.1. Method

The sample preparation was specified in the section 5.1.2. The quantification of the rheological properties of traditional mozzarella cheese was carried out in the temperature range of 30 to 80 °C with 10 °C steps using the shear rate ramp test as outlined in section 5.3.3. Triplicate samples were repeated for each temperature.

6.3.2. Results

The shear viscosity, with error bars (based on standard deviations), versus shear rate at different temperatures are plotted in figure 6-2. As can be seen, the small standard deviations in the viscosity from the triplicate samples for each temperature indicate that the method is repeatable. This method also showed good sensitivity of the shear viscosity to the different temperatures. The viscosity curves did not overlap each other for each temperature. As expected, the mozzarella showed shear thinning behaviour. The shear viscosity decreased as temperature and shear rate increased. There was a significant change in the shear viscosity when temperature was under 50 °C, while the change became smaller at higher temperatures. These differences are probably the result of a change in microstructure as temperature changed. At 30 °C, the fat in the cheese is not completely melted and the bonds of casein matrix are strong, which is indicated by solid-like behaviour of the cheese. When the temperature is elevated to 40 °C, the fat is completely melted and the casein matrix becomes weaker, which result in the significant decrease in viscosity. Subsequently, at 50 °C collapse of casein matrix leads to the further reduction of viscosity (Lucey *et al.*, 2003).

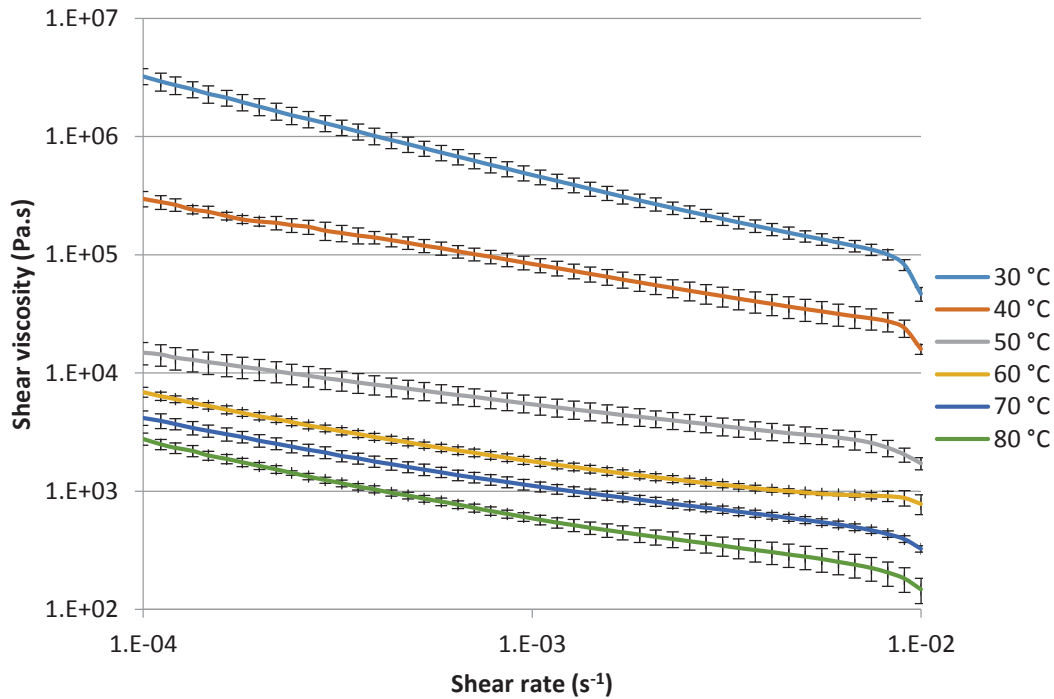


Figure 6 - 2 The shear viscosity of mozzarella as function of shear rate at different temperatures

There are not many studies that investigate the temperature effect on the shear viscosity of mozzarella cheese. Lee *et al.* (1978) and Savage and Mullah (2000) used helical viscometry to examine the apparent viscosity of mozzarella. They did their measurement at a steady shear rate, which makes a comparison with the data of this study difficult. A study using the rotational method with parallel plate geometry to measure shear viscosity could not be found. Data from capillary Rheometry (Smith *et al.*, 1980) and Oscillatory methods (Muliawan & Hatzikiriakos, 2007) are available and may be comparable with the data of this study. The shear viscosity or complex viscosity of mozzarella cheese at 40 and 50 °C from different methods is plotted in figure 6-3. They cannot be compared directly because of the different range of shear rate or frequency, but by extrapolation, the disparity between each method is small if it is considered that the composition of the mozzarella cheeses are likely to vary. Taking into account the potential differences between the testing cheese samples, the results from the different methods are in good agreement, especially at 40 °C. It should be highlighted that the shear viscosity curves from the rotational test exhibit more temperature sensitivity than the curves obtained from the other two methods.

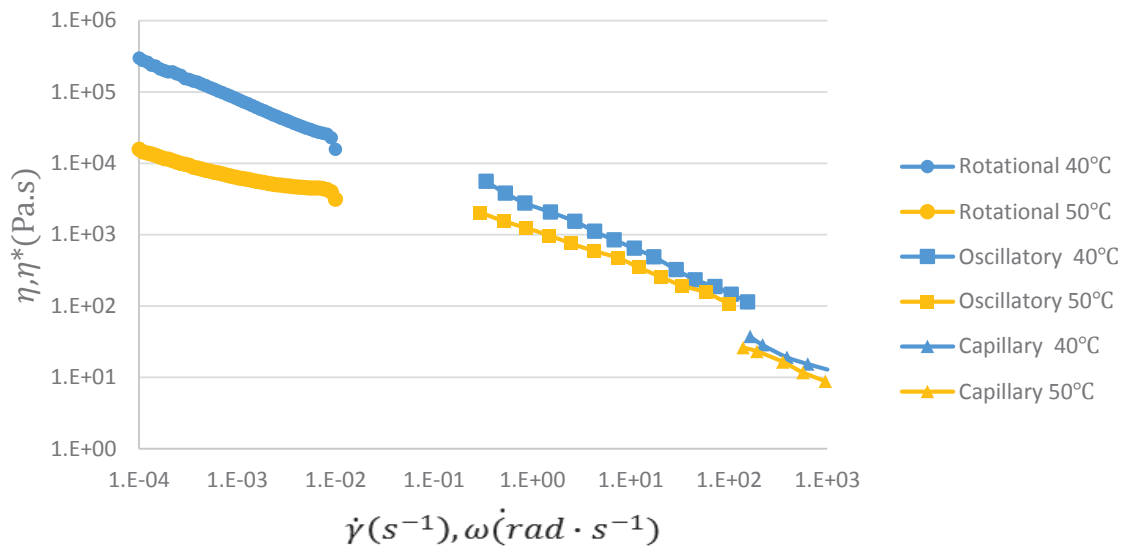


Figure 6 - 3 Comparison of rheological properties of mozzarella cheese obtained from different methods (Muliawan & Hatzikiriakos, 2007)

6.4. Model development

6.4.1. Power law model fitting raw data

The shear thinning behaviour of materials can be described by the power law model (Ostwald and de Waale model) which has been widely used for a variety of materials including cheese, other food products and polymers (Dimitreli & Thomareis, 2004; Jao *et al.*, 1981; Lee *et al.*, 2004; Solorza-Feria *et al.*, 2011; Sopade & Filibus, 1995; Sopade & Kiaka, 2001; Yamasaki & Irvine, 1990). The power law equation is:

$$\eta = k\dot{\gamma}^{n-1} \quad (6.1)$$

Where, k is the consistency index ($\text{Pa}\cdot\text{s}^n$), which is related to the magnitude of the shear viscosity; n is the flow behaviour index, which can be used to indicate the type of behaviour of material. When $n=1$, the material is a Newtonian fluid. If $n>1$, a curve of the $\log \eta$ versus $\log \dot{\gamma}$ has a positive gradient, representing shear thickening behaviour. For $n<1$, the curve has a negative gradient, representing shear thinning behaviour; as n decreases, the material becomes more shear thinning (Kontopoulou, 2011; Morrison, 2001).

6.4.1.1. Model Fitting Method

According to equation 6.1, the plot of the logarithm of the viscosity versus the logarithm of the shear rate should yield a straight line.

$$\log(\eta) = \log(k) + (n - 1)\log(\dot{\gamma}) \quad (6.2)$$

From such a plot (equation 6.2), k and n can be determined by the intercept and gradient of the line. The linear regression of data for all samples at different temperatures were obtained by Excel (Microsoft, USA).

6.4.1.2. Results

The consistency index and flow behaviour index of the power law for all samples at different temperatures are shown in the table 6-1. It was observed that the flow behaviour index did not change much with the temperature variation; the only exception being the samples at 30 °C. The exception at 30 °C is attributed to the difference in the states of the fat phase. As shown in the UW Meltmeter test (figure 4-1 in section 4.2.2), mozzarella cheese almost did not flow at 30 °C and behaved as solid-like. Figure 6-4 demonstrates the transformation of cheese from solid like behaviour to viscous behaviour when the temperature is increased. Based on that cheese does not flow significantly at 30 °C. The flow data for this temperature therefore should not be fitted using the power law model which is designed for fluids, not solids.

The temperature insensitivity of the flow behaviour index has been widely reported for a variety of materials including ketchup-processed cheese mixtures (Yılmaz *et al.*, 2011), sago starch (Sopade & Kiaka, 2001) and Akamu (Sopade & Filibus, 1995), and for each the n value did not show a significant change with temperature.

Table 6- 1 The consistency index k and behaviour index n at the different temperatures

Temperature (°C)	Sample 1			Sample 2			Sample 3		
	k(Pa·s ⁿ)	n	R ²	k(Pa·s ⁿ)	n	R ²	k(Pa·s ⁿ)	n	R ²
30	1645.6	0.16	0.99	1532.5	0.17	0.99	1390.7	0.18	1.00
40	1714.2	0.43	0.99	1386.7	0.43	1.00	2764.8	0.49	0.98
50	242.5	0.57	1.00	586.9	0.68	1.00	296.6	0.55	1.00
60	58.4	0.49	0.99	53.4	0.48	0.99	41.2	0.46	0.99
70	25.6	0.44	1.00	27.3	0.48	0.99	23.5	0.44	0.99
80	6.0	0.34	0.99	8.4	0.37	0.99	6.6	0.36	0.99

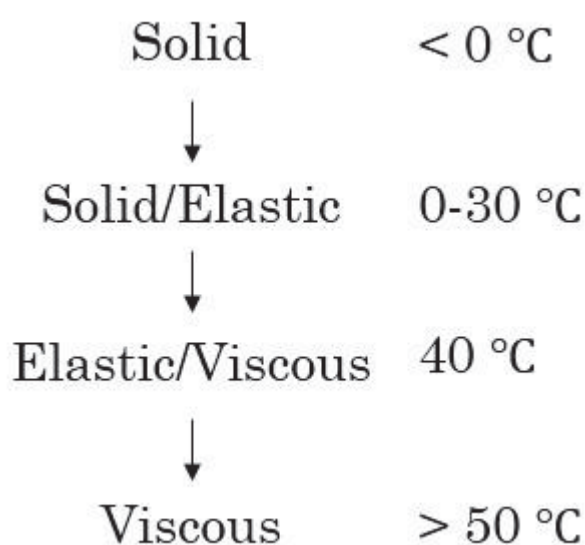


Figure 6 - 4 Schematic of the form transformation of cheese with varied temperature

Except for the samples at 30 °C, the consistency index of samples for the temperature range from 40 to 80 °C decreased as temperature increased (table 6-1). The increasing trend of the consistency index was observed in studies (Dimitreli & Thomareis, 2004) on processed cheese, on ketchup-processed cheese mixtures (Yılmaz *et al.*, 2011) and for Akamu (Sopade & Filibus, 1995).

Because n did not change much over temperature (when the 30° data was removed), n was held in a constant value and the results were refitted. The value of n determined by the average of the flow behaviour index of the data gathered at temperatures above 30°C was used in the power law equation to fit the curves of shear stress versus shear rate for each temperature again. The regression results are given

in table 6-2. The mean value for n was 0.47. The coefficient of determination for each temperature was all close to 1 in all cases. In other words, the power law equation with the new fitted values of the k and n was able to describe mozzarella cheese flow as measured by the rotational tests.

In table 6-2, it can be seen that the consistency index decreased as the temperature increased. The similar pattern was observed in studies by Diefes *et al.* (1993) and Dimitreli and Thomareis (2004).

Table 6- 2 The consistency index k regressed from the power law equation with a constant n=0.47

Temperature (°C)	Sample 1			Sample 2			Sample 3		
	k(Pa·s ⁿ)	n	R ²	k(Pa·s ⁿ)	n	R ²	k(Pa·s ⁿ)	n	R ²
40	2396.1	0.47	0.99	1896.0	0.47	0.99	2259.2	0.47	0.98
50	105.4	0.47	0.97	110.0	0.47	0.95	149.5	0.47	0.98
60	51.3	0.47	0.99	49.5	0.47	0.99	44.7	0.47	0.99
70	32.9	0.47	0.99	26.1	0.47	0.99	30.8	0.47	0.99
80	18.4	0.47	0.97	19.4	0.47	0.97	16.3	0.47	0.98

6.4.2. Arrhenius model fitting to consistency index

The results of the power law fitting (table 6-2) showed that the k value for the samples at 40 °C were higher than the others. This may be because the cheese samples at 40 °C were in a phase transition between a solid-like to a liquid-like material. The cheese samples at 50°C and higher all show liquid-like behaviour. As described in figure 6-4, at around 40 °C the cheese shows both elastic and viscous behaviours. The elastic component is probably more dominant at 40 °C. The relationship between rheological properties and temperature for the cheese may not be explained using the Arrhenius law when the cheese is going through a phase or state change. This can be seen in section 4.2.2.2 in figure 4-7 and 4-9 (Campanella *et al.*, 1987; Muthukumarappan *et al.*, 1999b).

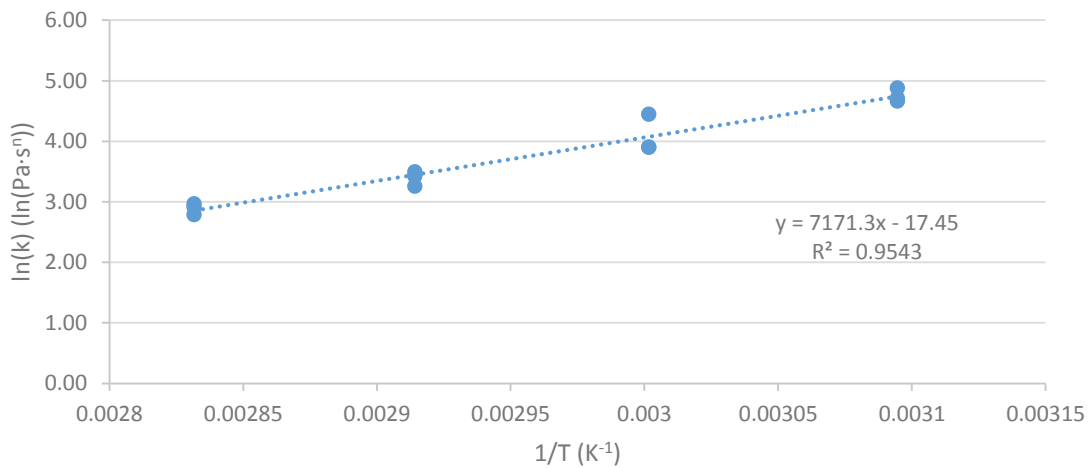


Figure 6 - 5 The Arrhenius relationship between the consistency index and temperature

Considering the limited time during pizza baking and the very slow flow of cheese at 40 °C it can be assumed that, from a practical standpoint, mozzarella cheese does not flow at temperatures below 40°C. The plot of the natural logarithm of the consistency index versus the reciprocal of the absolute temperature in the present study is shown in figure 6-5 (Arrhenius plot). It can be seen that over the temperature range from 50 °C to 80 °C, the consistency index and temperature could be coupled using the Arrhenius relationship, equation 6.3.

$$k = k_0 \cdot \text{EXP} \frac{E_a}{RT} \quad (6.3)$$

where, k_0 is pre-exponential factor (Pa·sⁿ). By regression, the intercept and gradient of the curve were -17.45 and 7171.3 respectively. By further calculation, the activation energy of flow was shown to be 59.6 kJ · mol⁻¹, and the pre-exponential factor was 9.34E-15 Pa·sⁿ.

For the purpose of making the equation 6.3 more relevant to the temperatures experienced during pizza baking, equation 6.3 can be expressed as:

$$k = k_{70} \cdot \text{EXP} \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{70}} \right) \quad (6.4)$$

where, k_{70} is the average, experimentally determined, consistency index at 70 °C; T_{70} is the absolute temperature at 70 °C (343.15 K). When equation 6.4 was

substituted into the power law, equation 6.1, the shear viscosity could be expressed as function of temperature and shear rate by:

$$\eta = k_{70} \cdot EXP\left(\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{70}}\right)\right) \cdot \dot{\gamma}^{n-1} \quad (6.5)$$

The parameters in the equation 6.5 are listed in the following table 6-3.

Table 6- 3 Viscosity model parameters for mozzarella cheese as function of shear rate and temperature

Parameters	k_{70} (Pa·s ⁿ)	E_a (kJ/mol)	R (kJ/mol K)	T_{70} (K)	n
value	30	59.63	0.008314	343.15	0.47

6.4.2.1. Comparison between Model and Experimental Data

The lines in figure 6-6 represent the predicted shear viscosity of mozzarella cheese over the shear rate range from 0.0001 to 0.01 s⁻¹ at different temperatures using the equation 6.5 with the parameters in table 6-3. The points are the experimental data (average of triplicate samples). The overall agreement between the predicted curves and the experimental data was good, especially at high temperatures. The small divergences for the samples at 50 and 60 °C in the high shear rate area were possibly attributed to the start effect of the tests (at beginning of testing, an shear rate instantaneously is applied to the cheese sample which may result in inaccurate data). In other words, the model (equation 6.5) is suitable to be used to predict the shear viscosity of mozzarella cheese at low shear rate and melting conditions.

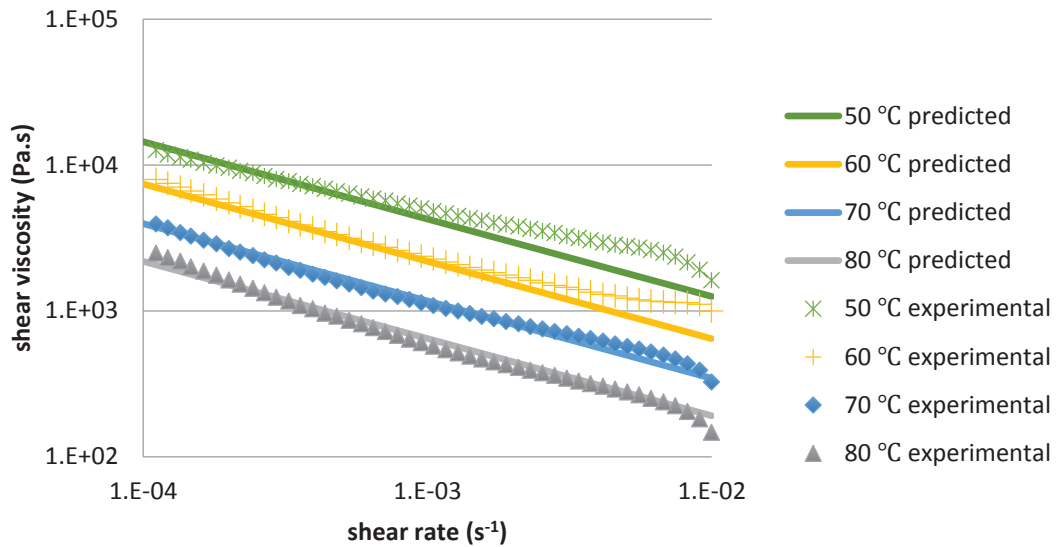


Figure 6 - 6 Comparison between the experimental data and model predictions for shear viscosity vs. shear rate

6.4.3. WLF model fitting to consistency index

A second model commonly used to predict the effects of temperature in cheese flow is the WLF model (Nicoli, 2012). While the Arrhenius model fitted the experimental data well, the lower temperature data was omitted to do so. The WLF is commonly used when transition periods such as glass transitions are crossed. The WLF model, therefore, is an alternative that may provide equally good predictions without needing to exclude low temperature data.

Therefore, the k at different temperatures in table 6-2 were fitted to the WLF equation (6.6):

$$\log \left(\frac{k(T)}{k(T_r)} \right) = \frac{-C_1(T-T_r)}{C_2+(T-T_r)} \quad (6.6)$$

Where the reference temperature T_r was 40 °C in this study; the consistency index at the reference temperature, $k(T_r)$, was determined by the average k at 40 °C. After the regression, the empirical constants C_1 and C_2 were 2.61 and 11.53 K respectively. Both experimental data and predicted curve are plotted in figure 6-7. It is obvious that the predicted curve had a good agreement with the experimental data.

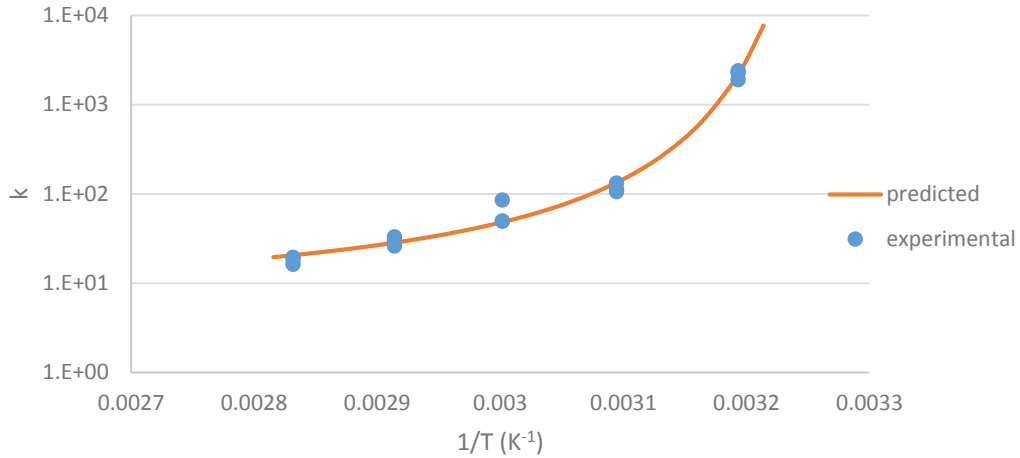


Figure 6 - 7 The WLF relationship between the consistency index and temperature

According to the WLF equation 6.6, the consistency index can be expressed as function of temperature:

$$k(t) = k(T_r) \cdot 10^{\left(\frac{-C_1(T-T_r)}{C_2+(T-T_r)}\right)} \quad (6.7)$$

When this relationship between the consistency index and temperature was substituted into the power law equation 6.1, the shear viscosity can be expressed as function of temperature and shear rate by:

$$\eta(t) = k(T_r) \cdot 10^{\left(\frac{-C_1(T-T_r)}{C_2+(T-T_r)}\right)} \cdot \dot{\gamma}^{n-1} \quad (6.8)$$

The parameters in the equation 6.8 are listed in the following table 6-4.

Table 6- 4 WLF model parameters for mozzarella cheese as function of shear rate and temperature

Parameters	$k(T_r)$ (Pa·s ⁿ)	C_1 (k)	C_2 (k)	T_r (°C)	n
value	2184	2.61	11.53	40	0.47

6.4.3.1. Comparison between model and experimental data

A comparison between the experimental data from the shear rate ramp tests and the predicted shear viscosity of mozzarella cheese over the shear rate range from

0.0001 to 0.01 s⁻¹ at different temperatures using the equation 6.6 is shown in figure 6-8. It can be seen that the model (equation 6.8) provided a good fit to the experimental data except the shear viscosity at high shear rate due to the start up effect discussed above. Overall, this function is good to model the variation of shear viscosity at different shear rate and temperature.

The model (equation 6.8) is, therefore, suitable to be used to predict the shear viscosity of mozzarella cheese at low shear rate and melting conditions.

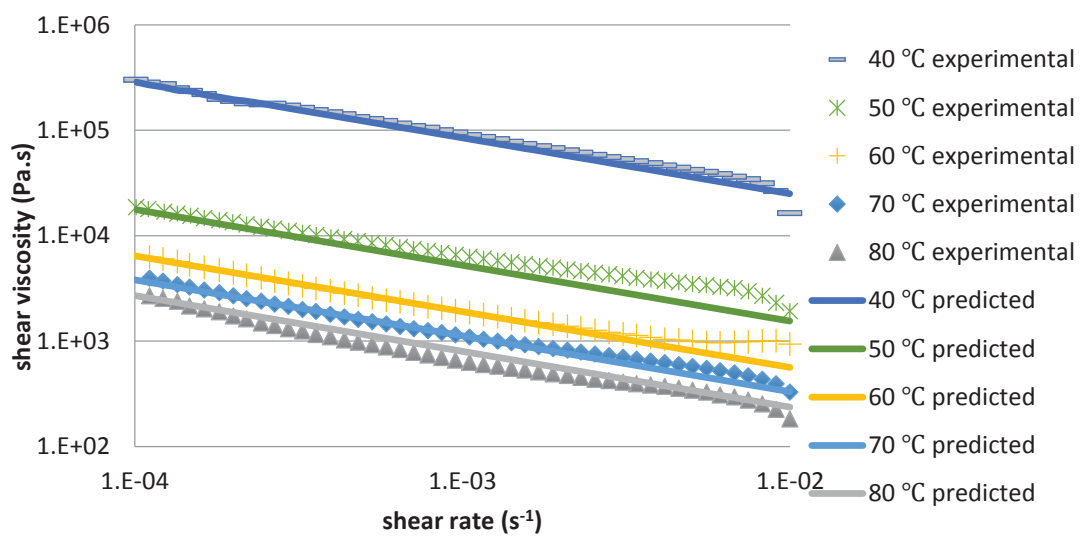


Figure 6 - 8 Comparison between the experimental data and predicted curve of shear viscosity vs. shear rate using the WLF model

6.4.4. Comparison between two models

Both the Arrhenius and WLF models well fit the relationship between the consistency index and temperature if the temperature is larger than 50 ° and both the models (equation 6.5 and 6.8) are able to make a good prediction of the shear viscosity at these temperatures. However, the WLF model can include the low temperature data. The model (equation 6.8) is applicable for a wider temperature range. Therefore, the WLF model (equation 6.8) is better than the Arrhenius model (equation 6.5) to predict the shear viscosity of mozzarella cheese.

6.5. Moisture effect on rheological properties

6.5.1. Mozzarella cheese dried by salt solutions

The process of the cheese drying is described in section 4.3.1. The moisture content information of the different moisture content mozzarella cheeses used are given in table 4-1 (section 4.3.2). Triplicate mozzarella samples, for each moisture content, were tested using the shear rate ramp test (section 5.3.3) at 50, 60 and 70 °C respectively.

The shear viscosity of mozzarella cheese, with error bars (based on standard deviations), versus shear rate for each moisture content at three temperatures are plotted in figure 6-9, 10, 11. The results show that the moisture effect on viscosity was weaker when the cheese samples were tested at higher temperatures. This moisture effect agreed with the results of Dimitreli and Thomareis (2004) and Yanniotis *et al.* (2006). At 50 °C, it was observed that the shear viscosity curves of cheese samples with 71 and 65 % moisture (g H₂O/ g dry matter) were under that of 79 % moisture samples. In some cases (figure 6-9) there was a decrease in the viscosity at the beginning period of the testing. However, as shown in figure 6-2, for a typical curve of shear rate ramp test, the shear viscosity jumped up rapidly (several data points at the beginning) at the start followed by a smooth increase. This phenomenon disappeared when temperature was elevated to 60 and 70 °C. But the shear viscosity curves of the cheese samples with 65 % moisture still were under the curves of the cheese sample with 70 %.

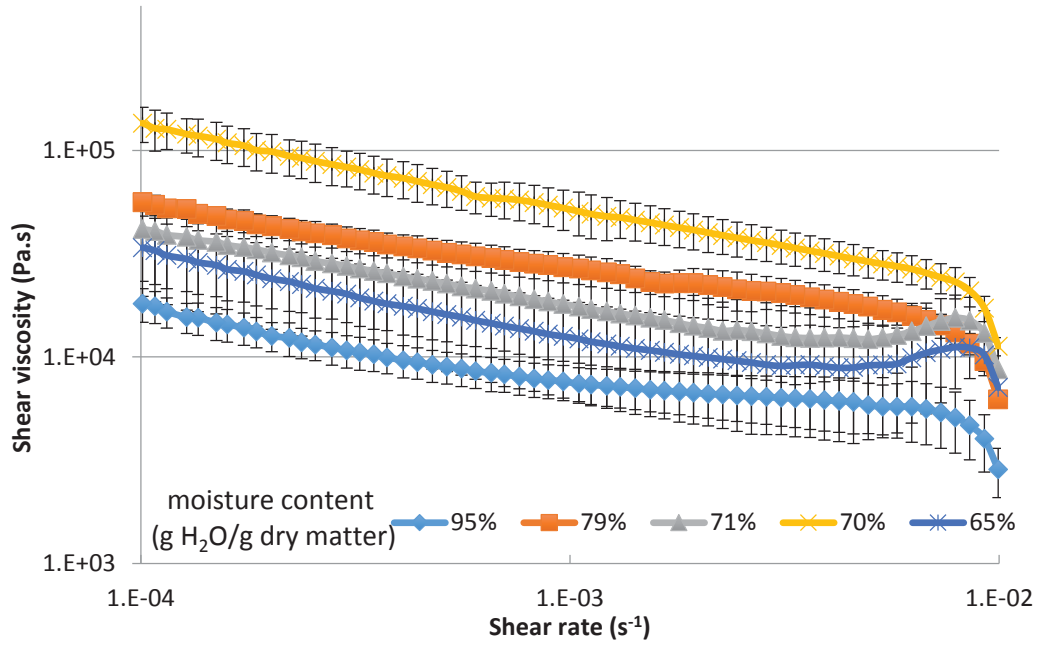


Figure 6 - 9 Viscosity as function of shear rate for different moisture content cheeses at 50 °C

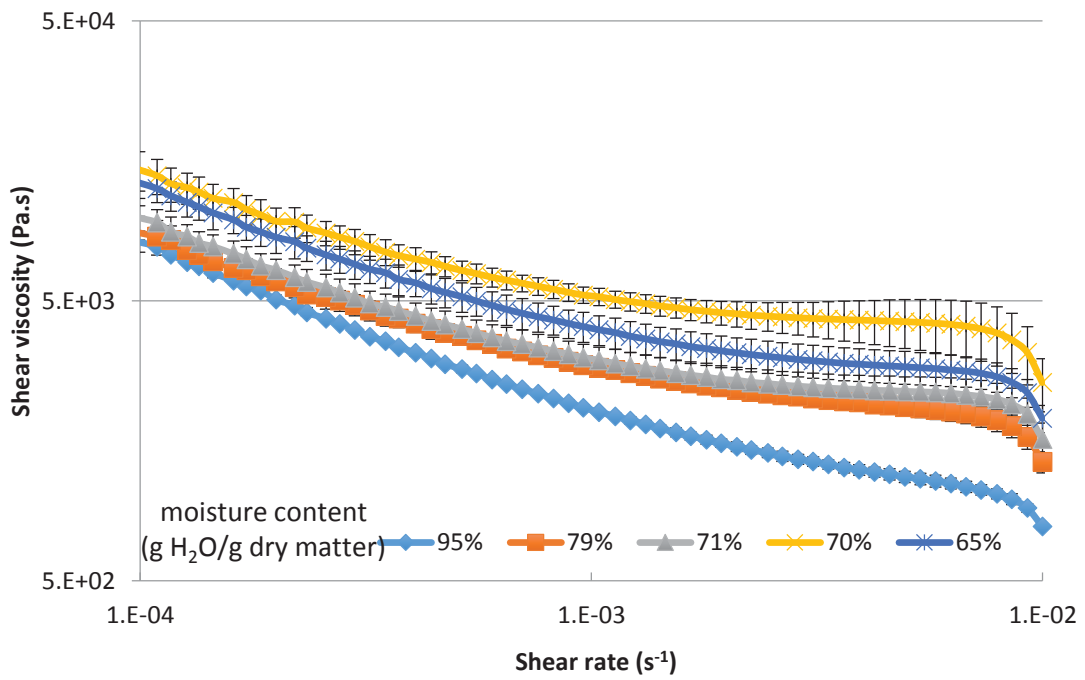


Figure 6 - 10 Viscosity as function of shear rate for different moisture content cheeses at 60 °C

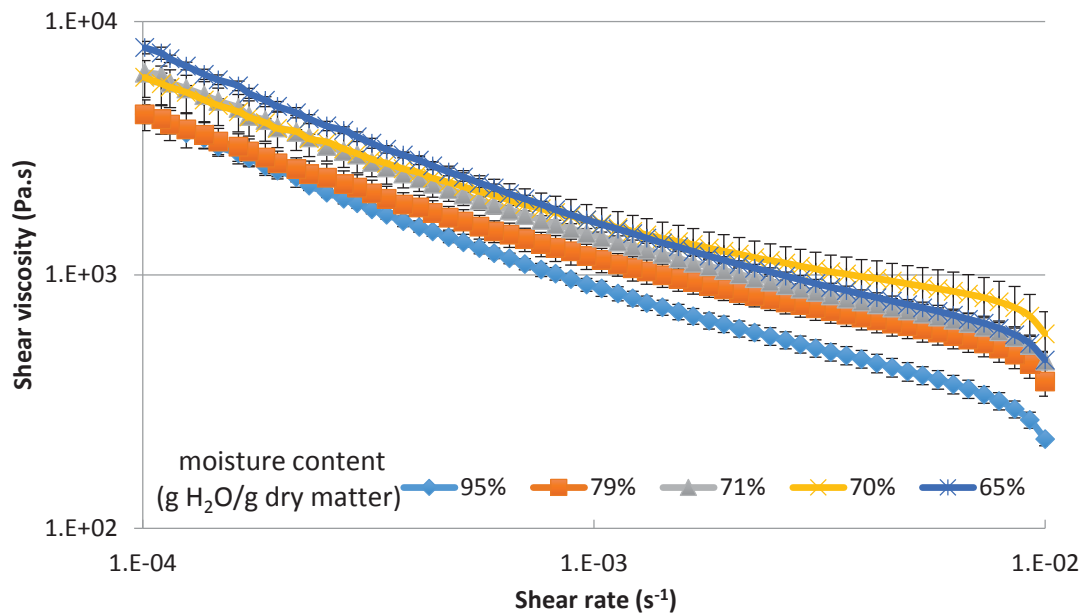


Figure 6 - 11 viscosity as function of shear rate for different moisture content cheeses at 70 °C

The relationships between the shear viscosity and moisture content at three temperatures are more intuitively demonstrated in figures 6-12, 13, 14, where the shear viscosity at three different shear rates (0.0003, 0.001 and 0.003 s⁻¹) were plotted. The shear viscosity increased after drying, but it was not significant especially at high temperature.

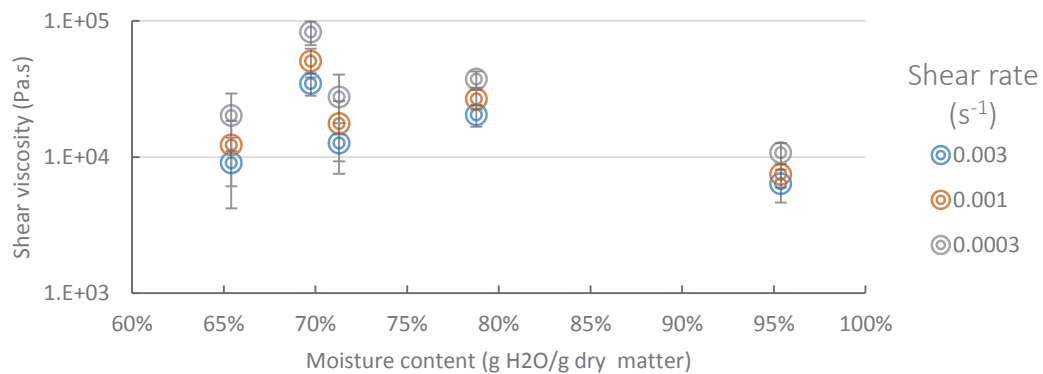


Figure 6 - 12 Relationship between shear viscosity and moisture content of mozzarella at 50 °C

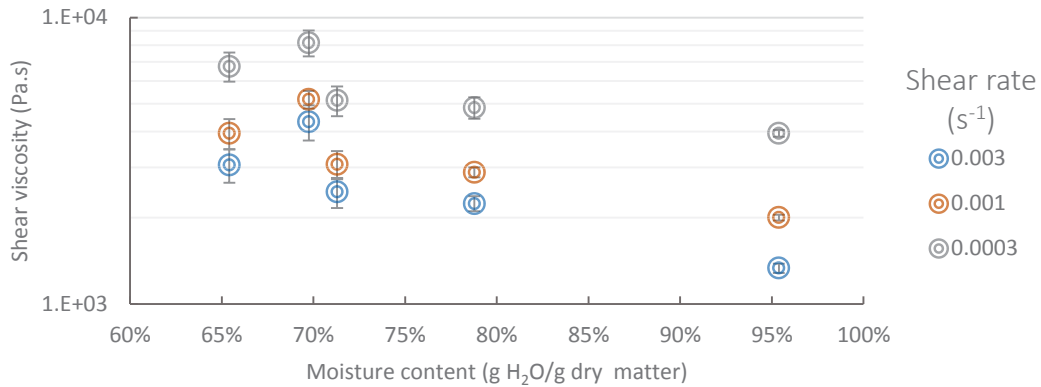


Figure 6 - 13 Relationship between shear viscosity and moisture content of mozzarella at 60 °C

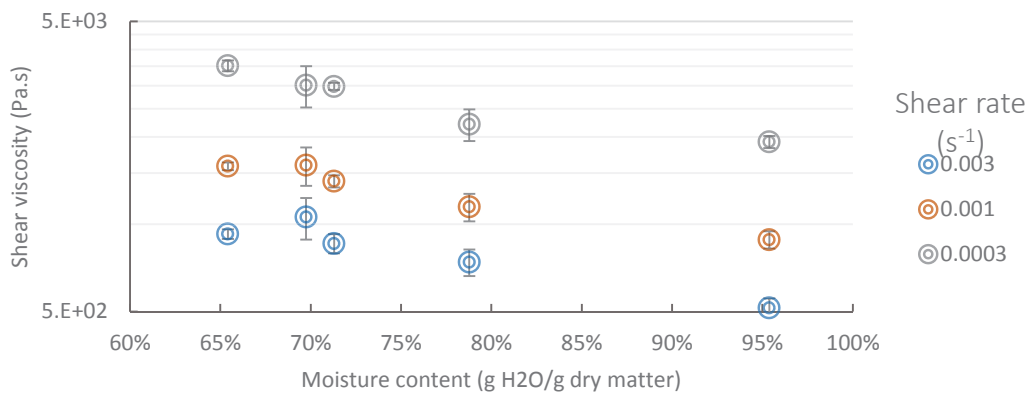


Figure 6 - 14 Relationship between shear viscosity and moisture content of mozzarella at 70 °C

The viscosity of cheese is expected to increase with decreasing moisture as suggested by Lee *et al.* (2004), Jao *et al.* (1981) and Fife *et al.* (1996). But the cheeses they studied were all the fresh cheeses, which were directly made to have different compositions. Few literature reports were found to explain the results of this study.

The samples were stored at -18°C until required for experiments. It was then thawed for 1 days at 4 °C. Then the mozzarella cheese was dried and equilibrated for 20 days in total. Several changes in the cheese might occur during these periods, which may have influenced the flow properties of the cheese.

According to Diefes *et al.* (1993) and Kuo *et al.* (2003), ice crystals are generated when cheese is frozen. Due to the protein dehydration and recrystallization of ice, it was suggested that the protein matrix of cheese was damaged and serum pools were created. These could result in an increase in the melting ability of cheese.

Additionally, cheese ripening would have proceeded to some extent during the period of the drying and equilibrium. Everett and Auty (2008) pointed out that the cheese ripening had a profound impact on water distribution, fat globule microstructure, casein network and even their interactions further influenced the structure and texture of cheese. The proteolysis in cheese during ripening caused the softer texture of cheese because the casein matrix was hydrolysed (McSweeney, 2004). Tunick *et al.* (1993) also suggested that development of meltability and texture properties of mozzarella cheese were connected to the increase in the proteolysis of α_{s1} -casein. A review by Everett and Auty (2008) suggested that aggregation and coalescence of fat globules took place within mozzarella cheese during cheese ripening. The larger the fat globules were, the lower Laplace pressure was required to cause rupture. According to McMahon *et al.* (1999) and Kuo, Gunasekaran, *et al.* (2001), mobility between different states of water and their redistribution were observed during mozzarella cheese ripening. The fraction of entrapped water increased because of the absorption of bulk water from the serum channels to the protein matrix.

Mould also grew on the samples during drying. The environments with different water activity due to the different salt solution might give rise to different metabolism by moulds in cheeses (Fox, 2004). The different metabolism might have different influences on the rheological properties of cheese (e.g. different enzymes produced). Furthermore, contaminant microbial growth during cheese ripening would produce fatty acids, and further give rise to curd softening, off-flavour and poor attributes of melting (Coppola *et al.*, 1995).

When all these factors were taken into account plus the drying, the situation became very complicated.

Because the mozzarella cheese blocks were frozen after the cheese manufacture in this study, the structure of protein matrix probably was weakened forming a porous protein matrix structure due to the formation of ice crystals. Once

they were thawed, water pools in protein matrix may have been formed. The structure of the protein matrix was softened. After the thawing, cheese blocks were exposed in the low relative humidity surroundings, the bulk water in the cheese was quickly evaporated bringing about a large amount of water transformation from the trapped water pools in the protein matrix into expressible water. The release of water might have led to the further disruption of protein matrix. The decrease in the viscosity at the beginning period of the testing might result from the cheese structure disruption. The mould growth might also influence the cheese structure.

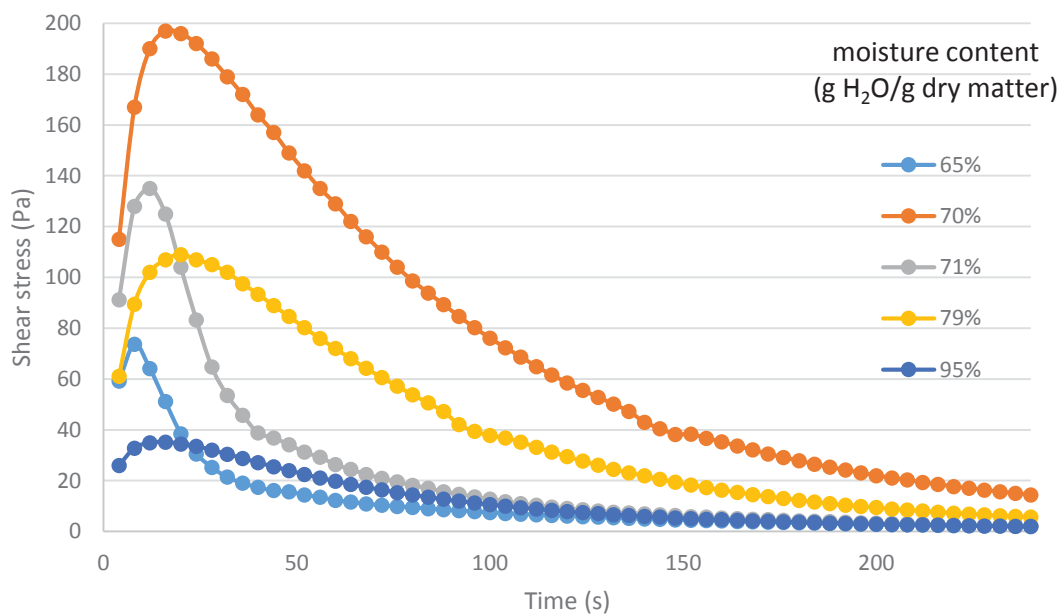


Figure 6 - 15 Shear stress change during the testing

Figure 6-15 shows the change in shear stress applied to cheese samples over the testing time. At the beginning of the test, there was an increase in shear stress because of the increasing resistance due to the sudden and large deformation of the cheese samples at the high shear rate. As the shear rate slowed down, the resistance required to overcome the smaller deformation became small, thus, a decrease in the shear stress. However, the shear stress for the cheese samples with 65 and 71 % moisture (g H₂O/ g dry matter) dropped earlier and faster than those of other samples. This suggested that the structures of the cheese samples with 65 and 71 % moisture content were weak. A small shear stress was required to disrupt the protein structure.

At 60 and 70 °C, the cheese samples were more liquid-like, so the structural change was not apparent in the test results.

6.5.2. Mozzarella cheese drying in a fridge

Because a cold environment can reduce mould growth and there is a large driving force for mass transfer in fridge, drying cheese in a fridge was carried out. Cheese blocks were exposed to air in a 4°C fridge. The weight of each cheese block was recorded during the drying period in order to monitor the amount of the moisture loss. The cheese blocks without drying (control sample) and with drying for 1, 3, 5, 8 day were sealed into aluminium foil bag after their drying period. The sealed cheese blocks were put back to the fridge to allow the inside moisture to equilibrate. The minimum period that the cheese was left to equilibrate was 12 days (i.e. 20 days total minus 8 days of drying).

The moisture content of the cheese samples was determined by drying the samples for 16 h in a 105° oven. This gravimetric measurement process (See Appendix 1 for details) was based on procedures described previously (New Zealand Dairy Board, 1993). Water activity was determined by the AquaLab 4TE water activity meter (Labomar d.o.o., Zagreb Slovenia). Both moisture content and water activity for all samples were measured twice.

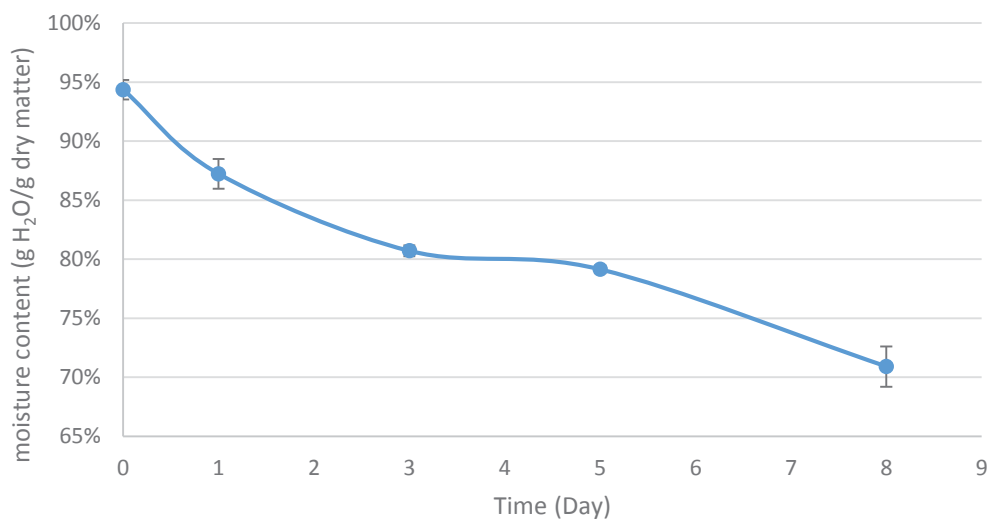


Figure 6 - 16 Moisture loss during fridge drying over time

Figure 6-16 illustrates the moisture content (expressed by dry basis) loss during the eight day drying. There was 25% moisture loss from about 95 % to 70 %.

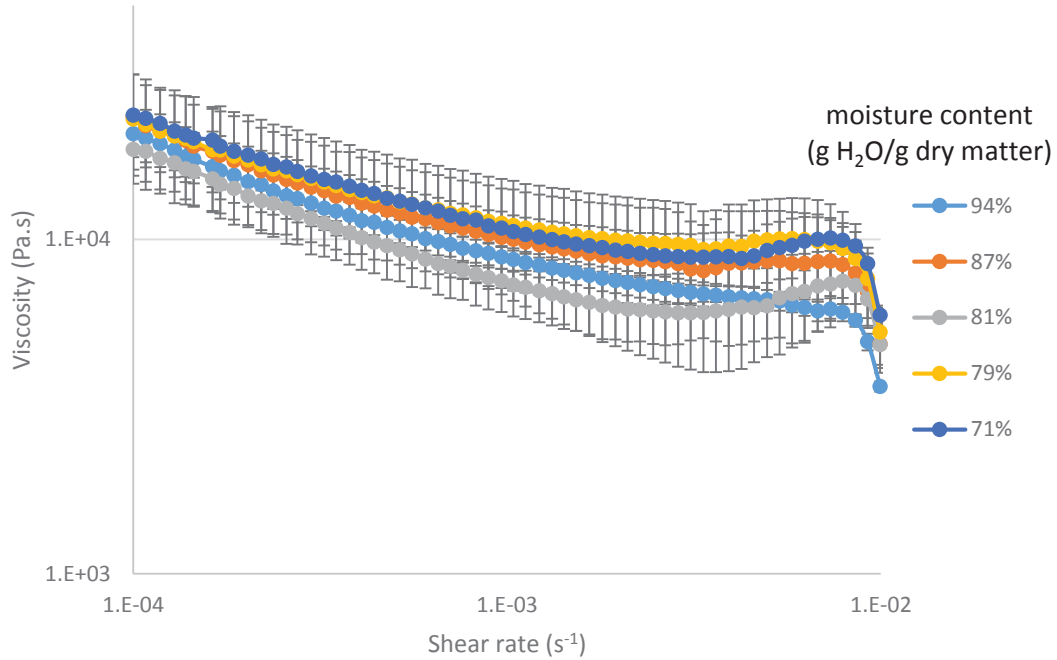


Figure 6 - 17 Viscosity as function of shear rate for different moisture content cheeses at 50 °C

The rheological properties of the different moisture content mozzarella cheeses were measured at 50 °C using the shear rate ramp test (section 5.3.3). The abnormal curve discussed in section 6.5.1 occurred for the all cheese samples except the cheese samples without drying (figure 6-17). The insignificant effect of moisture content on the shear viscosity was shown in 6-18. Overall, the moisture content effect on the rheological properties was shown to be not significant using both these two methods to reduce the moisture content of mozzarella cheese.

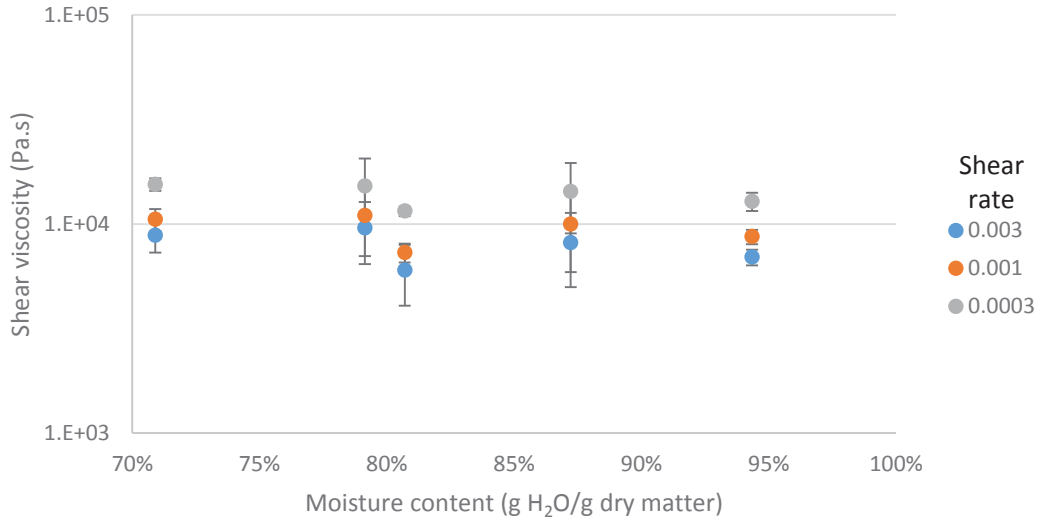


Figure 6 - 18 Relationship between shear viscosity and moisture content of mozzarella

6.6. Comparison/explanation of the results from UW

Meltmeter and rotational viscometry

Trouton (1906) found that the coefficient of viscous traction (extensional viscosity) of several materials was about three times larger than their shear viscosity. This relationship between extensional viscosity and shear viscosity was defined as the Trouton ratio.

$$T_R = \frac{\eta_E(\dot{\epsilon})}{\eta(\dot{\gamma})} \quad (6.9)$$

Where, $\eta_E(\dot{\epsilon})$ is extensional viscosity (Pa·s); $\eta(\dot{\gamma})$ is shear viscosity (Pa·s). As Jones *et al.* (1987) proposed, the shear rate should be numerically equal to $\sqrt{3}$ strain rate to calculate the Trouton ratio.

$$T_R = \frac{\eta_E(\dot{\epsilon})}{\eta(\sqrt{3}\dot{\epsilon})} \quad (6.10)$$

For Newtonian fluids, the extensional viscosity is 3 times the shear viscosity (Barnes *et al.*, 1989). According to Gunasekaran and Ak (2003), the biaxial elongational

viscosity is 6 times the shear viscosity for a Newtonian fluid. However, the Trouton ratio of non-Newtonian flow may depart from the nominal value of 3.

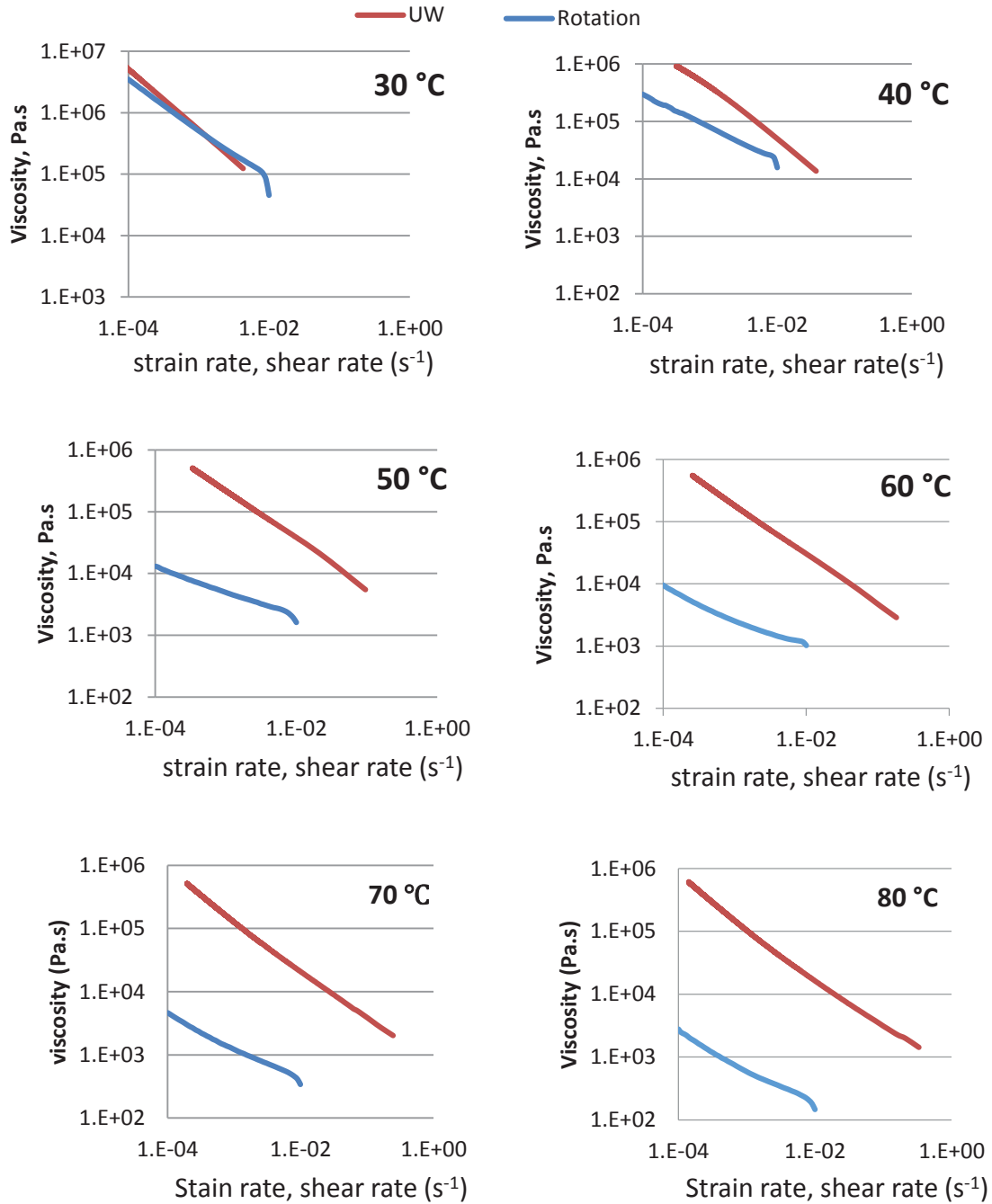


Figure 6 - 19 Comparison between the data obtained from UW Meltmeter and rotational tests

The comparison between the data obtained from UW Meltmeter tests and rotational tests is shown in figure 6-19. It is clearly seen that the Trouton ratio increased dramatically with increasing temperature. The Trouton was around 1 at 30 °C

while it reached about 100 at 80 °C. It was not surprising that the Trouton was not 6 between shear viscosity and biaxial elongational viscosity, because mozzarella is not a Newtonian fluid. According to Chan *et al.* (2007), the difference between extensional and shear behaviours of materials is due to the different mechanism of the deformation. For the extensional deformation, the particles of the material either move towards or away from each other as they are either compressed or stretched. For the shear deformation, however, the particles of the material slide over each other.

During the UW Meltmeter tests, it was found that mozzarella cheese became stickier when the testing temperature was elevated. The mozzarella cheese was even stuck to the UW Meltmeter at high temperature. This indicates that not only the extensional deformation but also shear deformation existed in the UW Meltmeter testing particularly at high temperature. The higher temperature was, the more shear deformation existed. This also explains the Trouton ratio was higher at higher temperature. This opinion was supported by Cogswell (1978) and Padmanabhan (1995), who pointed out the issue during extensional tests was that the tests were not only governed by the kinematics of the pure extensional deformation but were corrupted by some shear flow as well.

It is a large challenge to compare rheological data obtained from different methods, especially for extensional methods, not only in current study but also in this field. Petrie (2006) compared extensional viscosity obtained from ten different methods. The Trouton ratios showed a huge difference from 6 to 3000. Padmanabhan (1995) failed to verify the accuracy of extensional viscosity due to the values gained from three different methods being different. He explained the primary reason was the different molecular orientation, deformation history and deformation rates during the testing. As Petrie (2006) concluded, the extensional viscosity was defined for the steady uniform extensional flow. In practice, however, this concept was inaccurately used in the measurements where the flows were not steady and uniform by researchers and has led to much confusion. In the most of the measurements, the flow should be called transient extensional flow. Because it was a transient situation, results

may be influenced by many factors like deformation history. Petrie (2006) also advised the transient extensional viscosity should not be utilised unless the condition of testing was very restricted and clear.

6.7. Conclusion

As in the UW Meltmeter test, the fibre direction effect on the flow behaviours of mozzarella cheese was tested before characterising the rheological properties of mozzarella cheese influenced by temperature and moisture content. In the present study, the fibre direction effect was not measurable for the rotational method. Temperature showed a significant impact on the shear viscosity. As temperature increased, the shear viscosity declined rapidly. The shear viscosity against shear rate for each temperature was fitted into a power law model. It was observed that the consistency index was temperature sensitive but the flow behaviour index displayed a temperature independence. The relationship between the consistency index and temperature was fitted into the Arrhenius law and WLF model. Ultimately, these relationships were substituted into the power law equation to create models to predict the viscosity at varying shear rate and temperature. The developed models based on Arrhenius and WLF law had a good fit at temperature larger 50 and 40 °C respectively. The characterisation of moisture content effect was not successful, likely due to the protein structure disruption within the mozzarella cheese during the drying procedure. In comparison of the UW Meltmeter and rotational techniques, the data obtained from rotational viscosity was more temperature dependent than that from the UW Meltmeter.

7. CONCLUSION

7.1. Conclusion

In this study, the flow behaviour measurement method using the UW Meltmeter was improved by designing and building a new sample preparation template to improve the ability to cut uniform cheese samples; the addition of insulation to the UW Meltmeter to ensure isothermal conditions during experiments; and the development of a modified data analysis method that improved the accuracy of the transformation of raw results into more traditional rheological information that describe shear and strain. While the changes made to the UW Meltmeter equipment and analysis method improved the accuracy of the measurement results, it was found that the results, expressed by biaxial stress growth coefficient versus biaxial extensional strain rate at varying testing conditions, were not significantly different i.e. the process changes gave similar results. This indicated that the UW Meltmeter might be not sensitive enough to deliver the extensional rheological properties of cheese required for this project and outlined in Chapter 1.

A rotational method, a shear rate ramp test, was developed to measure the flow and melting behaviour of mozzarella cheese. The test method was developed to mimic the stresses and strain rates that cheese experiences on pizzas during baking. The test showed good repeatability and sensitivity. The viscosity of mozzarella cheese was characterised for a range of temperatures. The results showed that shear viscosity increased as temperature and shear rate decreased. The power law and WLF models were applied to the experimental results and used to predict the viscosity of mozzarella cheese at varying shear rate and temperature conditions. This is a new method to quantify and predict the flow behaviour of cheese as a function of temperature under low shear conditions. In order to facilitate the usage of this method in the future, the procedure for this method is summarised in appendix 9.2.

The new method was used to characterise the effect of moisture content on the viscosity of mozzarella cheese. Mozzarella cheese samples were dried using two methods; in a fridge and over salt solutions. While the drying methods were able to provide samples with significantly different moisture contents, the resulting rheological investigation was unable to detect differences between the samples. This was likely caused by the destruction of the protein structure due to the relatively rapid drying of the mozzarella cheese samples. A slower rate of drying is suggested as the next step in this analysis. Time restrictions, however, prevented this from being possible during this project.

7.2. Recommendation

The work done in this study is a primary step to quantify the flow properties of cheese on a pizza baking system. Some further investigations are recommended to better the method developed in this study and extend applications of this method.

1. Based on the unsuccessful characterisation of mozzarella cheese with different moisture content due to the inappropriate drying methods, further work is suggested using an appropriate method for testing. The drying speed of cheese should be gentle during cheese drying to avoid structure damage of mozzarella cheese. The drying surroundings is recommended to be at low temperature in order to lessen the likelihood of mould growth.
2. Only mozzarella cheese was characterised in the current research. Further work on characterisation of alternative cheese is recommended. The current measurement method and model may be also suitable to collect rheological data and model the flow and melting of other cheeses.

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9. APPENDIX

9.1. Moisture content method (16 hour oven)

Cheese Method based on procedures described previously (New Zealand Dairy Board, 1993).

1. Risk Assessment

HAZARD	RISK	EFFECTS OF HAZARD	MANAGEMENT OF HAZARD	RECOVERY
1. Hot oven	LOW	Burns from hot oven	<ul style="list-style-type: none">• Use oven gloves to remove trays from oven.• Use tongs to pick up hot moisture dishes.	<ul style="list-style-type: none">• Run burn under cold water for 10 minutes.

2. Background/Purpose

To measure the moisture of cheese.

3. Scope

All cheese types.

4. Test Principle

A sample of grated cheese is dried in an oven at 105°C to constant weight.

5. Apparatus

- Aluminium containers, flat-bottomed, approximately 90-100 mm diameter and 20-24 mm deep.
- Small pieces of greaseproof kitchen paper can be placed in the container to prevent the sample sticking to the container.
- Drying oven thermostatically controlled at 105°C +/- 2°C for all cheese dish locations. The oven should have a circulation fan and a vent in the top. Shelves should allow good air circulation.
- Tongs.
- Desiccator, with silica-gel desiccant.
- Laboratory balance, weighing to 0.001 g.

6. REAGENTS

None.

7. Procedures

7.1 Calibration

The oven is calibrated annually.

7.2 Sample preparation

Grate the cheese samples with a fine grater or food processor.

Method

1. Place the greaseproof paper in the container.
2. Dry the empty container in the preheated oven for at least 30 minutes.
3. Use the tongs to place the containers into the desiccator and allow to cool to room temperature.
4. Place the container on the balance and record this weight in the lab moisture book. (W1)
5. Tare the balance and place approximately 10g of shredded cheese into the container. Spread the cheese out evenly.
6. Record the weight of the cheese. (W2)
7. Place the container in the oven at 105°C for 16 hours.
8. Remove the container from the oven and cool to room temperature in the desiccator.
9. Weigh the container and record the weight. (W3)

8. Calculations

$$\% \text{ solids} = (W3 - W1) \div W2 \times 100$$

Where:

- W1 = empty weight container
- W2 = weight of cheese
- W3 = weight of container plus dried cheese

% moisture = 100 - % solids

9. Definitions

Moisture

Defined as the percentage loss in weight when the sample is oven dried to constant weight at 105°C.

WFS

The weight percentage remaining is known as the water-free substance.

10. History

Version 1 18 February 2002 Craig Dodds

Version 2 22 July 2013 Ruth Mabbitt

11. Related Documents

New Zealand Dairy Industry NZTM3: Chemical Methods Manual, Section 12.

12. Attachments

N/A

9.2. Procedure summary of the model development

To collect the relevant rheological information that describes mozzarella cheese melt and flow and to predict the rheological properties with the power and Arrhenius laws, the following process should be followed:

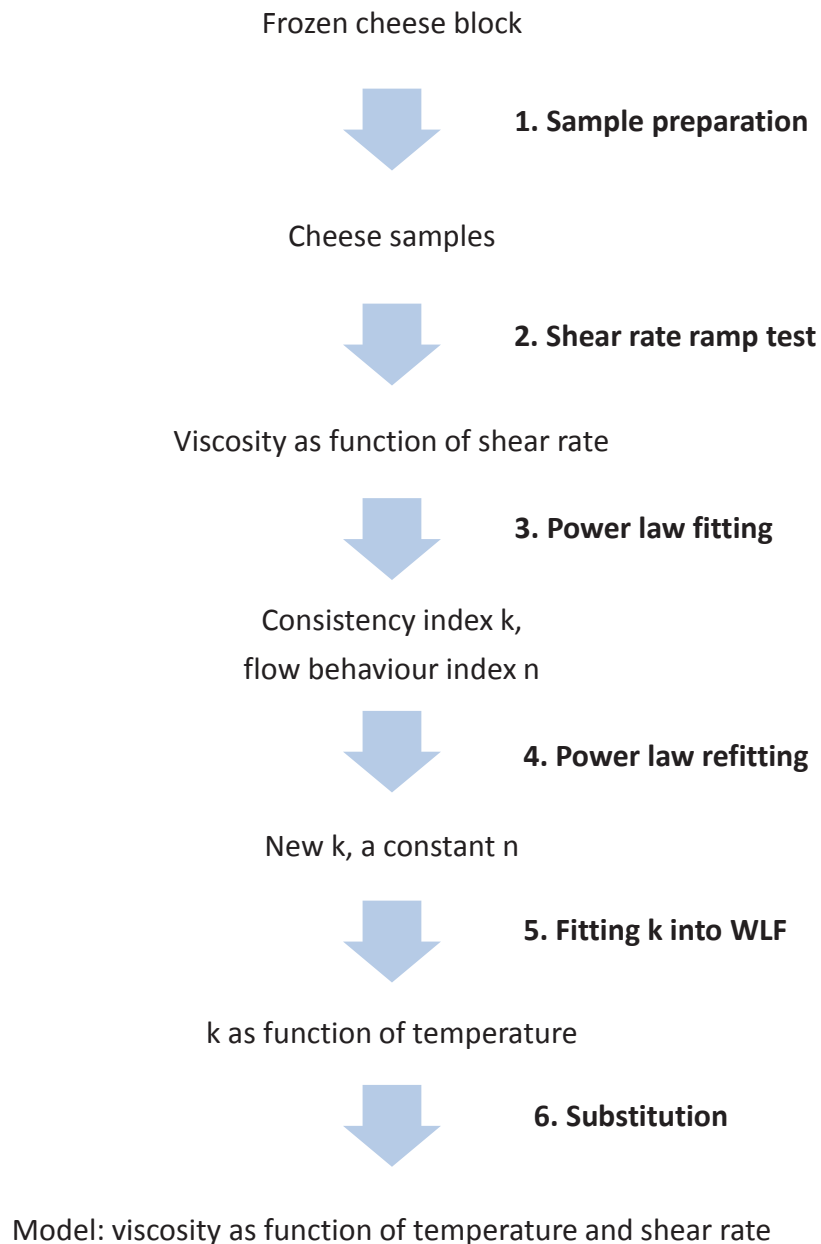


Figure 9 - 1 Procedure of characterisation of cheese

1. Sample preparation

- a. Blocks of cheese tempered to 4 °C for an hour.
- b. The cheese blocks are cut into 3 mm slices using a cheese slicer (figure 9-2 A).
- c. A cork borer (figure 9-2 B) is used to collect 20 mm diameter samples.
- d. Samples 3 mm thick and 20 mm diameter are therefore obtained.



Figure 9 - 2 Cheese slicer (A) and 20 mm cork borer (B)

2. Shear rate ramp test

The MCR301 rheometer (Anton Paar, Austria) is equipped with fluid circulators and a peltier hood. These two systems ensure rapid and accurate temperature

control during pre-heating and testing. A parallel plate PP20/S-SN13685 measuring system (Anton Paar, Austria) was used to conduct tests.

For each experiment, a cheese sample is placed on the centre of the lower plate and compressed between the parallel plates. The outer area of the cheese sample, not in contact with the rheometer plates, is coated with mineral oil in order to avoid moisture loss. Before a test is executed, the sample is heated for two minutes to ensure that the sample reaches a uniform temperature (i.e. to ensure the test is carried out under isothermal conditions). Temperature, shear rate, and shear stress can be set depending on the test required.

The tests are executed from a high shear rate (0.01 s^{-1}) at the beginning to a low shear rate (0.0001 s^{-1}) at the end with a log ramp decrease over 4 minutes. Samples are tested at temperature range of 40 to 80 °C with 10 °C step. Triplicate samples are required for each temperature.

The data of shear viscosity and shear rate are obtained.

3. Power law fitting

The power law equation is:

$$\eta = k\dot{\gamma}^{n-1} \quad (9.1)$$

Where, k is the consistency index; n is the flow behaviour index. According to equation 9.1, the plot of the logarithm of the viscosity versus the logarithm of the shear rate should yield a straight line.

$$\log(\eta) = \log(k) + (n - 1)\log(\dot{\gamma}) \quad (9.2)$$

From such a plot (equation 9.2), k and n can be determined by the intercept and gradient of the line. The linear regression of data for all samples at different temperatures are obtained by Excel (Microsoft, USA).

The power law equation (Eq. 9.2) is used to fit these data for each temperature. The consistency index (k) and flow behaviour index (n) for each temperature is gained.

4. Power law refitting

If the n values from previous step do not change much over temperature, then the n is held in a constant value (average of n from all samples) and to refit the results using equation 9.2. The new k for each sample is generated.

If the n values fluctuate greatly, this method may not be suitable to develop a further model.

5. Fitting k into WLF

The k for each temperature from previous step is fitted into WLF equation:

$$\log \left(\frac{k(T)}{k(T_r)} \right) = \frac{-C_1(T-T_r)}{C_2+(T-T_r)} \quad (9.3)$$

Where T_r is the reference temperature; $k(T_r)$ is the consistency index at the reference temperature, which is determined by the average k at the reference temperature; C_1 and C_2 are the empirical constants. $k(T)$ is the consistency index at temperature, T .

According to the WLF equation 9.3, the consistency index can be expressed as function of temperature:

$$k(t) = k(T_r) \cdot 10^{\left(\frac{-C_1(T-T_r)}{C_2+(T-T_r)} \right)} \quad (9.4)$$

The relationship between k and temperature is created.

6. Substitution

This relationship (Eq. 9.4) between the consistency index and temperature is substituted into the power law equation 9.1. The model (Eq. 9.5) to predict the viscosity of cheese at varying temperatures and shear rates is developed.

$$\eta(t) = k(T_r) \cdot 10^{\left(\frac{-C_1(T-T_r)}{C_2+(T-T_r)}\right)} \cdot \dot{\gamma}^{n-1} \quad (9.5)$$