RHEOLOGY AND PROCESSING OF MOZZARELLA CHEESE

by

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ABSTRACT

Taken as an engineering material, mozzarella cheese can be considered as a complex food system that has dynamic structure and complex flow properties. Food scientists have been actively developing methods to characterize mozzarella cheese rheologically, but most of these methods are empirical in nature. In the past decades, there has been a paradigm shift towards the utilization of well-developed rheological methods which have been widely applied in the study of commercial synthetic polymers.

In this work, the rheology of mozzarella cheese was studied using well-developed rheological techniques. Utilizing various rheometers, the linear and non-linear rheology of mozzarella cheese was examined. General practical properties of mozzarella cheese such as meltability, flowability and stretchability were extracted from these results. Capillary flow and rolling experiments were also performed to determine their suitability as innovative post-production processing techniques for mozzarella cheese. Finally, a comparative study on the effect of frozen storage on the rheology of three different brands of mozzarella cheese was performed.

In general, it was found that mozzarella cheese can be classified as a pseudoplastic (shear thinning) semi-solid material possessing a yield stress at room temperature. Upon heating, the yield stress gradually diminishes and it can be considered as a viscoelastic fluid. The results obtained from the various rheometers indicate that the yield stress, duration of experiment, sample geometry and temperature greatly affect the consistency of the results. It was also shown that extrusion can be used as a processing technique for mozzarella cheese above a certain temperature where the cheese is in a melt state. Rolling was also found to be a potentially feasible processing method. Finally, in terms of the effect of frozen storage, in general, the dynamic moduli decrease with the period of storage due to the freezing of the proteins in the cheese.

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NOMENCLATURE

a_T	: horizontal shift factor for time-temperature superposition.
b	: Rabinowitsch correction.
G(t)	: relaxation modulus.
G'	: storage/elastic modulus.
G''	: loss/viscous modulus.
K, n	: consistency index and power-law index parameters for Herschel-Bulkley equation, respectively.
L/D	: length to diameter ratio of a capillary die.
N	: number of Maxwell elements.
RR	: defined as t_F/t_G in rolling experiments.
t_F	: thickness of feed samples in rolling experiments.
t_G	: gap between the SER rollers.
t_E	: thickness of exit samples in rolling experiments.
2α	: entrance angle of a capillary die.
δ	: phase shift in oscillatory shear experiments.
$\varepsilon_H, \dot{\varepsilon}_H$	: Hencky strain and strain rate, respectively.
γ_o	: strain amplitude in oscillatory shear experiments.
$\underline{\underline{\dot{\gamma}}}$	: rate of deformation tensor.
$\dot{\gamma}_A$	: apparent shear rate.
λ	: time constant (the relaxation time).
λ_i and $\eta_{o,i}$	: relaxation time and shear viscosity of the ith Maxwellian element respectively.
η_o	: zero shear viscosity.
η^*	: complex modulus.
η_E^+	: tensile stress growth coefficient.
η_s^+	: shear stress growth coefficient.
σ_o	: stress amplitude in oscillatory shear experiments.
σ_A	: apparent shear stress.
σ_E	: tensile stress.

σ_w : wall shear stress.

σ_y : the yield stress.

$\underline{\underline{\tau}}$: stress tensor.

ω : frequency of oscillations in oscillatory shear experiments.

CHAPTER 1:

FUNDAMENTALS

1.1 Introduction

A class of food that has attracted the attention of rheologists and scientists is the dairy products due to their structural dynamics and properties. One diary product that has showed tremendous growth commercially is cheese. For example, in the 1990s, the production of only Mozzarella cheese in Australia has increased more than 100% (Rowney et al., 1999) and in the United States, the total production of cheese is estimated to be around 3.5 million tonnes, with Cheddar and Mozzarella being the most dominant varieties (Gunasekaran and Ak, 2003).

In this chapter, the typical commercial production technique of cheese is presented. In addition, the morphology and physical properties of cheese will be examined and finally, the importance of understanding the rheology of cheese is discussed.

1.2 Commercial Production of Cheese

Milk is the raw material in the manufacture of cheese. Major constituents of milk are fat, water, protein (casein in colloidal form and albumen/whey in soluble form), sugar (lactose) and enzymes (Gunasekaran and Ak, 2003). Other minor constituents include vitamins and ash.

Pasteurization is usually the first step in cheese making (NEM Business Solutions, 2002). In this step, milk is heated (72°C) for a short period of time (~15 seconds) to destroy any harmful bacteria (Gunasekaran and Ak, 2003). While the milk is warm (20°C to 40°C), special starter cultures are added to breakdown a

small amount of the milk sugar into lactic acid. This acidifies the milk and prepares the milk for the next step; coagulation.

Rennet, a coagulant enzyme, is then added to the milk after which a curd is formed. During coagulation, the enzyme breaks down the K-casein present on the surface of the casein micelle. This destabilizes the casein micelles and causes them to gel. As they form gel, the coagulum tends to shrink and expel entrapped liquid. This liquid is called whey. To improve whey expulsion, the curd is usually cut into small cubes to increase its surface area to volume ratio (Gunasekaran and Ak, 2003). Throughout these stages, fat exists as globules and as the coagulum shrinks, the fat is entrapped within the casein matrix (Johnson, 2000). The void space within the casein is called serum. Coagulation period can vary from 30 minutes to 36 hours, depending on the cheese type (Gunasekaran and Ak, 2003).

The next step is to drain off the whey which contains water soluble substances such as lactose, whey proteins, salts, peptides, other non-protein nitrogeneous substances and fat which is released during cutting. The manner by which the whey is removed is important in determining the resulting texture and flavour of the cheese. For example, Cheddar and Swiss type cheeses require cooking and stirring during whey drainage, whereas soft cheese such as Camembert cheese does not require stirring.

After the whey is drained, the curd is shaped and salted. Shaping is also an important step at which the texture of cheese is determined. For example, Mozzarella cheese needs to be kneaded (heated and stretched) in warm water to give its unique texture. Hard cheeses, on the other hand, need just to be pressed to mat the coagulum into a large slab of cheese. Shaping is then followed by salting to improve the textural quality and flavour of the cheese.

The last step in cheese making is ripening. Ripening allows continued microbial and biochemical processes in the cheese which further develop its unique texture and taste as the proteins, lipids and carbohydrates are broken down. Ripening can vary from a few days (eg. Mozzarella) to a few months (eg. Cheddar) depending on the cheese types (Gunasekaran and Ak, 2003).

Variations to the basic steps described above are possible. For example, milk acidification can be achieved by addition of lactic acid or hydrochloric acid, instead of starter culture. Also, heating and lowering pH helps to facilitate more efficient whey expulsion.

1.3 Cheese Structure and Melting Behavior

A schematic of a typical structure of cheese is shown in Fig. 1.1 (Johnson, 2000). The major components in most varieties of cheese are casein, fat, and water (or an aqueous component). In most varieties of full fat cheese, these major components co-exist in approximately equal proportions by weight. However, since the specific gravity of casein is about twice that of water and slightly higher than that of the fat, approximately one-sixth of the cheese total volume is casein (Prentice, 1992).

Figure removed for copyright reasons. Original source Fig. 1, p.2 (Johnson, 2000).

Fig. 1.1 Schematic of casein micelle agglomeration and the entrapment of fat globules; structure of cheese (Johnson, 2000).

At normal room temperatures, the casein is solid and exists as micelles, having a molecular weight of about 10^4 g/mol to 10^5 g/mol and their sizes range from 0.05 μm to 1 μm. The casein gives a cheese its "solid" appearance and the

interactions within and among these casein micelles provide the elastic property of the cheese. In a cheese, the casein micelles actually agglomerates and form into chains (Prentice, 1992). At the minimum, these chains must occupy the space around the fat globules and this provides the rigidity of the cheese. The actual amount of casein in a cheese depends on the number, size, and size distribution of the fat globules and on the sizes of the casein micelles themselves. Once the minimum amount of casein has been exceeded, any further casein present in a cheese provides additional strength to the chains and their junctions, making the cheese more rigid (Prentice, 1992). In a study on the firmness of several cheese varieties, it is estimated that a minimum of about 25 wt. % casein must be present in order for a cheese to have a rigid framework (Chen et al., 1979).

At normal room temperatures, fat in the cheese exist as a mixture of liquid and solid fractions. The fat particles have a molecular weight in the range of 10^5 to 10^6 g/mol and diameter in the range of 0.5 μm to larger than 10 μm. The fat globules are normally held in place by entrapment within the casein network. These fat globules are relatively large in size and they do not interact with each other. The only interaction between the fat particles and the casein is through friction. Thus, it has been suggested that the fat globules are inert fillers as they do not contribute much to the elastic property of the cheese (Prentice, 1992). However, at sufficiently low temperatures, the fat globules are able to add rigidity of the casein matrix. Nevertheless, fat is an important component of a cheese because it provides a critical role in the sensory perception of consumers as the cheese is consumed.

The aqueous phase in the cheese is usually made up of the soluble constituents of the milk serum (eg. minerals, lactic acid, peptides, and amino acids) and any enzyme or salt (eg. residual rennet) that may have been added during the manufacturing process (Fox et al., 2000). Although, some of the aqueous phase is bound to the casein and therefore largely immobilized, most of

the aqueous phase is free and fills the interstices between the fat and the casein matrix (Prentice, 1992). The aqueous phase, thus, serves as a low viscosity lubricant between the surfaces of the fat and the casein. Consequently, the amount of aqueous phase in a cheese affects its firmness. For example, if a cheese has a relatively high content of aqueous phase, the space between the fat and the casein will also be relatively larger. This causes the flow of the water within this space easier and provides less restraint on the movement of the casein mesh around the enclosed fat. Consequently, the cheese exhibits less firmness.

Although different treatments and manufacturing processes result in different cheeses having different characteristics, in general, cheese has an open, meshlike structure of casein, composed of overlapping and cross-linked strands of partially fused casein aggregates (micelles) (Prentice, 1992; Fox et al., 2000). The integrity of the casein matrix is maintained by various intra- and inter-aggregate hydrophobic and electrostatic forces. The fat, which had its origin as the fat globules of the milk, and the aqueous phase are entrapped within the casein network. The casein network is essentially continuous, extending in all directions, although some discontinuities in the matrix exist due to the presence of curd granule junctions and/or curd chip junctions. These junctions are devoid of fat and exhibit different molecular attractions with the casein molecules mainly due to the differences in cheese composition between the junctions and the interior of the cheese particles (Fox et al., 2000).

The structure of the cheese is highly dependent on the temperature. As the cheese melts, the fat, together with the moisture in the cheese, can become important as they can alter the rheological properties of the cheese. Since cheese is composed of constituents that have significantly different properties, it is expected that the melting of cheese occurs at a range of temperature, depending on the casein to fat ratio. At room temperature, fat exists as solid and liquid. As the temperature is increased, the ratio of solid fat to liquid fat decreases

(Prentice, 1992). Significant changes in the structure of the cheese which alter the rheological properties of the cheese occur within the temperature range of 20°C to 45°C. Within this temperature range, the cheese undergoes heat induced softening which is mainly due to the melting of the fat and increase in casein salvation or hydration (Guinee et al, 2000). Total melting of the fat usually occurs at around 40°C (Muthukumarappan et al., 1999). Total protein mobilization, on the other hand, occurs at relatively higher temperature. For example, Wetton and Marsh (1990) and Guinee and Fox (2001) investigated the dynamic phase angle of mild Cheddar cheese as a function of temperature and they found a peak at approximately 75°C, which was attributed to the total mobilization of the protein matrix. However, a similar peak for a different type of cheese may occur at a different temperature, depending on the arrangement of the fat within the casein network and the presence of additives (eg. melting salts) (Gunasekaran and Ak, 2003).

As the temperature increases beyond 40°C, the protein network starts to disassociate as the electrostatic and van der Walls' interactions and hydrogen bonds are weakened (Gunasekaran and Ak, 2003). At the same time, there are greater hydrophobic interactions among the protein, which causes an increase in protein aggregates density and size (Pastorino et al., 2002) and viscosity of the cheese melt. The aggregation of the protein which leads to the constriction of the casein network causes the moisture to be squeezed out of the network. This results in larger gaps between the casein aggregates which makes it much easier for the fat to "leak" out and phase separate from the protein (Johnson, 2000). Fig. 1.2 shows confocal laser scanning micrographs of Cheddar cheese at room temperature and at 95°C (Guinee and Fox, 2001). The Figure clearly shows the phase separation between the fat and the proteins as the cheese is heated. It has also been suggested that as the fat coalescence, it forms a large oil pools which form a lubricating film between the protein layers and this facilitates the mobility of the protein phase. Physically, this causes an overall reduction in the rigidity of the cheese (Guinee and Fox, 2001).

Figure removed for copyright reasons. Original source Fig. 2, p. 8 (Guinee and Fox, 2001)

Fig. 1.2 Confocal laser scanning micrographs of 5 day-old full fat Cheddar cheese at a) room temperature and b) 95°C. The micrographs show protein, as red areas, and fat, as green areas (Guinee and Fox, 2001).

1.4 Importance of Rheology of Cheese

Research on cheese is currently concentrated on areas such as production of cheese, improvement of taste and texture in low fat cheese, and post-production processing and product development.

To efficiently produce and process cheese, one must understand its rheology. Understanding its rheology allows the design of optimized processes and cheese handling equipment. In addition, the rheology of the raw material; milk, intermediate product; cheese curd, and the final product; cheese, is highly dependent on the different variables associated with the different production stages of cheese. Thus, full understanding of the rheology during manufacture of cheese is essential.

In analyzing cheese texture, various empirical and subjective methods of characterization have been developed (Voisey, 1976; Bourne, 1982; Gunasekaran and Ak, 2003). The development in the area of material science and testing, however, has allowed more consistent measurements of rheological properties of materials in general. Thus, a logical way to develop non-subjective methods to characterize cheese texture is to correlate its rheological properties with its sensory data/properties. In this way, the rheological properties of a

cheese can be correlated to its textural attributes such as chewiness, cohesiveness, firmness, adhesiveness, stickness, etc. Besides utilizing the rheological properties to predict the textural behaviour of cheese, these properties can be useful in predicting the quality of the final product as cheese is sometimes used as raw material and processed into other food products.

Post-production processes of cheese can be done to increase the shelf life of the cheese or to add value to the cheese by improving its texture, shape and overall commercial attractiveness. Value added food products make them commercially attractive and allow manufacturers to obtain higher profit margins for their products. Again, understanding the rheology of cheese will aid in the development and improvement of practical post-production processing techniques such as extrusion or rolling. Application of such processing techniques that are widely used in the processing of commercial synthetic polymers to food materials allows the development of novel food products (for example, co-extruding different types of cheeses using an industrial extruder to manufacture a unique product; shaping cheese using an extruder and dies with unique profiles to create cheese products with commercially attractive profiles). In addition, understanding the performance of cheese during these operations may be beneficial to the dairy industry as they may identify alternative ways of more efficient and more economical ways of continuous processing. In fact, a recent US patent illustrates how extrusion process can be used to manufacture string cheese (Cortes-Martines, 2005).

It is clearly illustrated above that a common aspect in the aforementioned fields of interests and research areas is the study of the rheological behaviour of cheese. It is noted that rheology is the study of deformation and flow of materials when they are subjected to external forces and it plays a critical role in understanding the practical characteristics of the material and its processing behavior. Although empirical measurements on the rheological properties of cheese have been around for sometime (Bourne, 1982; Arnott et al., 1957; Fife et

al., 2002; Gunasekaran and Ak, 2003), these methods result in parameters that are not acceptable rheologically since they depend on the geometry of the equipment and/or the shape and size of the sample. Fundamental measurements, using well established methods yielding consistent and comparable material properties parameters, have gained more importance over the past decades. However, most of these have been restricted to dynamic oscillatory and uniaxial or biaxial extensional experiments; while other rheological characterization techniques such as capillary extrusion and rolling have not been widely utilized. A more detailed study of the rheology of cheese using rheologically acceptable measurement techniques is, therefore, necessary and will be the main focus of this thesis.

CHAPTER 2:

GENERAL REVIEW

2.1 Introduction

The importance of understanding the rheology of complex food material as a means for quality control has been realized since the early 1950s (see for example, Arnott et al., 1957; Olson and Price, 1958). As discussed earlier, this has led to the development of various rheological measurement techniques which were mostly empirical in nature during these early years. In the past decades, however, there has been a paradigm shift in how food manufacturers utilize their understanding of food rheology. Now, understanding the rheology of various food products (raw or otherwise) is critical as it does not only serve as a means for quality control, but also forms the basis for product development.

In this chapter, a general review of the experimental and theoretical aspects in the study of cheese rheology is presented. A brief summary of some of the empirical experimental techniques that have been developed to study the rheology of cheese will be presented first. This is followed by a discussion of the more fundamental rheological measurements using well-established methods. A simple model to describe linear viscoelasticity (the generalized Maxwell Model) will also be presented. This chapter ends with a review of the basic equations and the principles of operations of the experimental equipment utilized in this work.

2.2 Rheological Techniques

2.2.1 Empirical Measurements of Cheese Rheology

In empirical measurements, tests are usually done to obtain rheological properties that are poorly defined but which, from experience, are found to be

related to the physical property and textural quality of the sample. These tests are usually easy to perform, rapid and frequently use inexpensive equipment (Bourne, 1982).

Meltability is an attribute of cheese that is widely examined empirically. Traditional melt tests include one that was suggested by Arnott et al. (1957), and the Tube (Olson and Price, 1958) and Schreiber tests (Kosikowski, 1977). In each of these tests, a piece of cheese with specific dimensions is placed on a dish or in a tube and then into an oven. There, it is heated to a specific temperature for a specific period of time. The final dimensions (e.g. final height of sample or diameter of spread) of the cheese are measured to determine its meltability. Park et al. (1984), however, found that there is a significant lack of correlation between Arnott and Schreiber tests.

One notable modification was proposed by Muthukumarappan et al. (1999) who suggested a modified Schreiber test, where the cheese is placed onto an aluminum dish, instead of glass and subjected to a much lower temperature of 90°C, instead of 232°C. In addition, they recommended that the area covered by the melted specimen be used as an indicator of the meltability. It was found that these modifications result into a better correlation between the Schreiber and Arnott tests (Muthukumarappan et al., 1999).

Consistency (apparent yield stress) of cheese can be estimated using an empirical method that uses cone penetrometer (Gunasekaran and Ak, 2003). In this test, a cone assembly of specific mass and dimension is placed onto a cheese sample and allowed to sink into its smooth and flat surface. Variation of the penetrometer includes a spherical tip instead of a cone.

An empirical measurement to determine the stretchability of mozzarella cheese is the “fork” test (Gunasekaran and Ak, 2003). In this empirical test, a fork is used to vertically lift up a lump of melted cheese until the bulk of the cheese

strands break. The length at which these cheese strands breaks indicates the stretchability of the cheese. This test has low reproducibility, but it has been found useful in comparisons between samples manufactured within the same plant (Gunasekaran and Ak, 2003). Various modifications to the "fork" test have also been developed (Gunasekaran and Ak, 1997; Fife et al., 2002; Apostolopoulos, 1994). This includes the incorporation of a universal testing machine to ensure consistent drawing speed of the probe. Thus, this is also called the vertical elongation test.

In an empirical version of the horizontal uniaxial extension test, Guinee and O'Callaghan (1997), cut a pizza base in half, without separating them. Shredded cheese is sprinkled over the base at a density of 0.35g/cm^2 and heated for 4 minutes at 280°C. One half of the base is held constant, and the other is pulled away at a constant speed of 3.3 to 10 cm/s until the cheese strands fail. The distance between the pizza bases is used to indicate the stretchability of the cheese.

2.2.2 Fundamental Measurements of Cheese Rheology

In fundamental tests, well-defined rheological properties are quantified. However, the results from these tests do not necessarily reflect the feeling when the food is masticated (Bourne, 1982). Fundamental tests can be classified according to the type of deformations: shear, extension, shear/extension and compression.

<u>Shear Deformation</u>

The most common shear deforming tests is the small amplitude oscillatory shear. These dynamic oscillatory tests on cheese have been used extensively (Ak and Gunasekaran, 1996; Venugopal and Muthukumrappan, 2003; Taneya et al., 1979; Nolan et al., 1989; Subramanian and Gunasekaran, 1997a and 1997b). In performing dynamic oscillatory tests, it is important to determine first the region of linear viscoelasticity. In this region, materials are deformed at relatively small

scale and slow rate. In addition, in this region, the Boltzmann superposition principle applies to describe the behaviour of a linear viscoelastic material (see Section 2.3). Subramanian and Gunasekaran (1997a) determined the region of linear viscoelasticity of Mozzarella cheese at various conditions. In general, linear viscoelastic range decreases with an increase in temperature and age. From the tests (temperature range of 10°C to 70°C and age of 1 week to 12 weeks), it was determined that a range of 0.05% shear strain ensures that tests are within the linear viscoelastic limit. It was also found that the region of linear viscoelasticity decreases with an increase in test frequency. In addition, previous studies on the viscoelastic behaviour of various types of cheeses have been limited to a shear strain of less than 1% (Nolan et al., 1989; Wium and Qvist, 1997; Ak and Gunasekaran, 1996; Drake et al., 1996).

If cheese is compressed or heated, fat tends to be exuded from the cheese sample, a process called "oiling-off". This poses a unique challenge as the fat will induce significant slip. Using waveform analysis, Nolan et al. (1989) found that using pitted aluminum plates and bonding the cheese sample onto the plates with cyanoacrylate resin can prevent slippage and ensure that the test can be performed under constant temperature with relatively short equilibrium time (within 70°C $\pm$ 2°C within 30 seconds). Subramanian and Gunasekaran (1997a and 1997b) used coarse sand paper glued onto the plates to prevent slippage in their experiments.

With respect to storage, Subramanian and Gunasekaran (1997b) performed small amplitude oscillatory shear tests on Mozzarella cheese. They found that proteolysis during storage causes the cheese to soften, thus decreasing the dynamic moduli. The effect was found to be significant in the first four weeks of ripening. This finding is further supported by Joshi et al. (2004), Ak and Gunasekaran (1996), Tunick et al. (2000), Diefes et al. (1993), Yun et al. (1994), and Subramanian and Gunasekaran (1997a). The changes that occur during storage can be attributed to the break down of proteins which causes the

moisture from the fat channels to be absorbed into the protein matrix. As a result, the protein network becomes more hydrated and weakened, resulting in the decrease of the dynamic moduli (Joshi et al., 2004). Further, the elastic modulus decreases due to the softening of internal structure (Joshi et al., 2004). Tunick et al. (1997) suggested that the coalescence of fat globules causes the decrease of dynamic moduli and Ak and Gunasekaran (1996) suggested that the binding of water by ionic groups produced during storage (and proteolysis) causes the viscous modulus to decrease.

With increase in temperature, the dynamic moduli were noticed to decrease (Joshi et al., 2004; Hsieh et al., 1993; Venugopal and Muthukumarappan, 2003; Guinee et al., 2002; Karoui et al., 2003). Guinee et al. (2002) also noticed a steep reduction of the dynamic moduli in the temperature range of 20°C to 45°C, which was attributed to the melting of the fat phase. They further observed a decrease in elastic modulus up to a temperature of 80°C. Loss tangent, on the other hand, is expected to increase with temperature as observed by Karoui et al. (2003) who performed experiments with Comte and Emmental hard cheeses.

Subramanian and Gunasekaran (1997b) were able to perform time-temperature superposition on the dynamic rheological properties (G', G" and η^*) of Mozzarella cheese successfully over a temperature range of 10°C to 70°C. In the same work, the storage modulus was used to predict the generalized Maxwell model parameters such as Newtonian viscosity and relaxation time. It was found that generally, as the cheese matures, the viscosity of corresponding Maxwell elements shifts towards smaller values.

To investigate the effect of large and small scale deformations on various food products, including cream cheese, Bistany and Kokini (1983) utilized the Cox-Merz rule to determine the consistency of the viscosities obtained from small and large scale deformations. They found that the rheology of the food product is

dependent on the scale of deformations and suggested that a modified Cox-Merz rule with an experimentally determined constant to shift one of the viscosities be used to describe such systems. Yu and Gunasekaran (2001), on a similar work on other various food products, including mozzarella cheese, also made similar observations. They have provided further discussion and essentially have attributed the dependencies of the rheology of the cheese on the scale of deformations and the ability of the cheese to maintain its structure as a solid.

Extensional Deformation

Ak and Gunasekaran (1995) performed a vertical uniaxial extension of low moisture part skim Mozzarella cheese in an oil bath that was kept at 60°C by applying a constant force. It was found that strain rate and sample temperature increase simultaneously during the test and a sample extension of more than 400% was achieved. In addition, it was also observed that the transient elongational viscosity of the sample decreases during the test, with the authors attributing this effect to the increase in temperature. It was also found that aging the cheese up to 28 days does not significantly affect the transient elongational viscosity. However, this might be due to the low sensitivity of the apparatus used in their experiment (Ak and Gunasekaran, 1995).

Horizontal uniaxial extension tests on Mozzarella cheese were done by Ak et al. (1993). This was achieved using a universal testing machine and a set of pulleys that translate the downward crosshead motion of the universal testing machine to a horizontal movement of one of the clamps that held the cheese sample. The clamps and the cheese sample were held in a constant temperature-heated oil bath to allow testing at elevated temperature and to prevent sagging. It was found that fracture stress and deformability modulus decreases with an increase in temperature. On the other hand, the fracture strain increases with temperature.

Wang and co-workers (1998) developed a device (UW meltmeter) that is

capable of performing lubricated squeezing flow to subject the cheese sample to biaxial extensional. Using this device, Wang et al. (1998) generated the biaxial stress growth coefficient as a function of biaxial extensional strain rate to determine the meltability of Mozzarella and Cheddar cheeses under various conditions (temperature, fat level and compression force). The result suggested that at constant compression force, higher fat and higher temperature resulted in the Mozzarella and Cheddar cheeses to have lower biaxial stress growth coefficients, thus they flow more easily. Using a modified UW Melt Profiler, Gunasekaran et al. (2002) found that the softening points of various cheese samples compare reasonably well with the temperature at crossover modulus determined from temperature sweep under small amplitude oscillatory shear test.

A common problem that is faced most commonly in performing extension tests is the rapid localized build up of stress concentrations at the fixed ends of the sample (Pesenti and Luginbuhl, 1999). It was found that dumbbell sample shape, i.e. having smaller cross sectional area at the middle of the sample helps in ensuring that fracture does not occur near the clamps, without the need to apply a notch (Pesenti and Luginbuhl, 1999). In the present study, extensional tests will be performed using the Sentmanat Extensional Rheometer (SER) (see section 4). Its unique design prevents localized buildup of stresses at the fixed end of the sample, thus allowing true extensional deformations and fracture to occur in the middle of the fixed ends. Again, "oiling-off" will be a major challenge, especially since the clips that hold the sample in the SER are relatively small. However, tests have shown that the usage of sand paper helps in eliminating slip.

Shear/Extensional Deformations

Shear and extensional deforming tests can be achieved by using a capillary rheometer (Cogswell, 1977). Capillary rheometry has been widely used to characterize and analyze the processing behaviour of molten polymers (Dealy, 1982, Ferry, 1980). The basic equations utilized in the analysis of capillary flow

can be found in section 2.4.3. Several authors have also used a capillary rheometer to characterize viscoelastic food materials due to their similarities with molten polymer (Smith et al., 1980; Shukla and Rizvi, 1995; Taneya et al., 1992; Sharma et al., 1993). However, very few of these are done on cheese. Smith et al. (1980), have used a capillary rheometer, to test Mozzarella cheese. They have found that Mozzarella cheese is a Herschel-Bulkley fluid. It was also found that the drop in viscosity in the 55°C to 70°C temperature range is more pronounced than in the 40°C to 55°C range. It was reported that fat separation of Cheddar and American process cheeses induces a serious slippage problem during capillary flow (Smith et al., 1980).

Compression Deformation

Another common test that is usually carried out to characterize cheese is compression. Jaros and Rohms (1994) conducted compression tests of 136 Swiss cheese samples with an Instron testing machine under constant strain rate. They found that fracture stress and strain are significantly lower in constant strain rate compression than in constant speed compression. However, the modulus of deformability was found to be unaffected by the different test setups.

Compression tests have also been used to characterize Leicester cheese (Vernon Carter and Sherman, 1978), Cheddar cheese (Hort and Grys, 2000; Ak and Gunasekaran, 1992) and various kinds of cheeses (Shama and Sherman; 1973). It was shown that typically, initially compression force increases almost linearly with the degree of compression before it plateaus or decreases slightly followed by a sharp increase in the compression force. In these compression tests, it was shown that compression force varies enormously from sample to sample and that it depends on the compression rate (Shama and Sherman, 1973; Wium et al., 1997; Wium and Qvist, 1997; Ak and Gunasekaran, 1992). At higher deformation rates, stress achieved higher values because cheese has less time to relax (Wium et al., 1997).

Ak (1993) examined the effect of anisotropy of Mozzarella cheese on compression deformation. It was found that at relatively high deformations (50% and 75%), the associated force is higher when the fibers in the sample are perpendicular to the compression direction. This is also supported by previous finding by Cervantes et al. (1983). This anisotropy has also been attributed to a type of Swiss hard cheese; the Gruyere de Comte cheese (Grappin et al., 1993).

Compression tests have also been used to investigate the effect of water in the cheese. It was found that as moisture content decreases, the modulus of deformability and fracture stress increase (Tunick et al., 1993; Prentice, 1992; Visser, 1991; Rohm et al., 1992; Tunick et al., 1991). Prentice (1992) suggested that as moisture content increases, less protein is present in the cheese. In addition, water, having a low viscosity, provides a good lubrication between the fat and the protein. These and the fact that the diffusion of water into the protein creates swollen protein particles that causes cheese with higher moisture content to deform more easily (Prentice, 1992). The fracture strain, however, was found to show more dependence on the age of the cheese than on the moisture content (Visser, 1991; Rohm et al., 1992).

2.3 Generalized Maxwell Model

A very simple model of a linear viscoelastic material, a Maxwell element, consists of a spring in series with a dashpot containing a Newtonian fluid. If the spring constant is taken to be analogous to the modulus of the Hookean solid, and the dashpot constant analogous to the viscosity of the Newtonian fluid, then the Maxwell model is (Dealy, 1982):

$$\underline{\underline{\tau}} + \lambda \frac{d\underline{\underline{\tau}}}{dt} = \eta_o \underline{\underline{\dot{\gamma}}} \tag{2.1}$$

where $\underline{\underline{\tau}}$ is the stress tensor, λ is a time constant (the relaxation time), η_o is the

zero shear viscosity of the linear viscoelastic material, and $\dot{\underline{\underline{\gamma}}}$ is the rate of deformation tensor.

This equation can be solved for the stress tensor to result:

$$\underline{\underline{\tau}} = \int_{-\infty}^{t} \frac{\eta_o}{\lambda} e^{-\frac{t-t'}{\lambda}} \dot{\underline{\underline{\gamma}}}(t')dt' \tag{2.2}$$

When written in this form, the model states that the stress at the present time t depends on the rate of strain at all past times t' $(-\infty < t' \leq t)$, with a weighting factor that decays exponentially.

Actual relaxation processes cannot be described by a single exponential function. More flexibility can be obtained by the use of the generalized Maxwell model, which is achieved by connecting a number of Maxwell elements in parallel. Then the total stress is a superposition of the partial contributions of each element:

$$\underline{\underline{\tau}}_i + \lambda_i \frac{d\underline{\underline{\tau}}_i}{dt} = \eta_{o,i} \dot{\underline{\underline{\gamma}}} \text{ and } \underline{\underline{\tau}}_i = \sum_{i=1}^{N} \tau_i \tag{2.3}$$

or

$$\underline{\underline{\tau}} = \int_{-\infty}^{t} \sum_{i=1}^{N} \frac{\eta_{o,i}}{\lambda_i} e^{-\frac{t-t'}{\lambda_i}} \dot{\underline{\underline{\gamma}}}(t')dt' \tag{2.4}$$

where N is the number of Maxwell elements, and λ_i and $\eta_{o,i}$ are the relaxation time and shear viscosity of the ith Maxwellian element respectively.

2.4 Basic equations of the principles of operations of the experimental equipment

2.4.1 Parallel Plate Flow

Rotational rheometers equipped with parallel-plate or cone-and-plate geometries are commonly used to perform rheological measurements at low shear rates and small deformations (linear viscoelasticity). A simple schematic of a concentric parallel plate geometry is shown in Fig. 2.1. In this setting, the sample is placed in between the two concentric plates which are mounted on a common axis of symmetry.

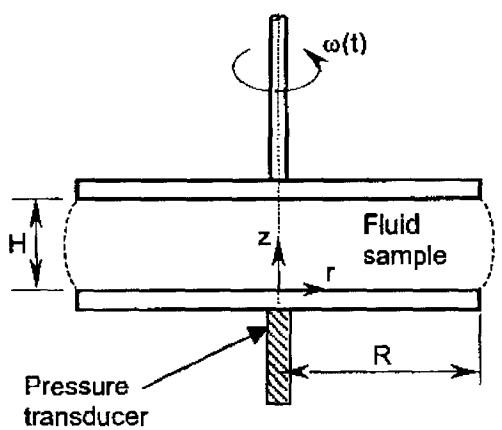


Fig. 2.1 Schematic diagram of a parallel plate rheometer.

Under steady shear mode, the upper plate is rotated at a specified steady angular velocity ω to impose a steady shear deformation to the sample. The resulting torque, M is measured which can then be converted to meaningful rheological parameters such as shear stress and shear viscosity. The shear rate in parallel plate rheometer experiments is given by the following expression (Dealy, 1982):

$$\dot{\gamma} = \frac{r \cdot \omega}{H} \tag{2.5}$$

where ω is a rotational speed, r is the distance from the center of the plate, and H is the gap size between plates. Rotational rheometer can also be operated in a stress-controlled mode, where the torque is fixed and the displacement is measured.

Since the shear rate is a function of the plate radius, the shear rate in the gap is not uniform. This makes it impossible to calculate values of material functions on the basis of a single experiment, and differentiation data is required as indicated by the following equations, obtained by performing a force balance (Dealy, 1982):

$$\frac{2F}{\pi R^2}\left[1+\frac{1}{2}\frac{d\ln F}{d\ln\dot{\gamma}_R}\right]=N_1(\dot{\gamma}_R)-N_2(\dot{\gamma}_R) \tag{2.6}$$

$$\eta(\dot{\gamma}_R)=\frac{3M}{2\pi R^3\dot{\gamma}_R}\left(1+\frac{1}{3}\frac{d\ln M}{d\ln\dot{\gamma}_R}\right) \tag{2.7}$$

where R is the radius of the plate, F and M are the force and the torque needed to rotate the plate, respectively, N_1 and N_2 are the forces exerted by the material perpendicular and along the plate, respectively, and $\eta(\dot{\gamma}_R)$is the viscosity at the shear rate value calculated at $r = R$.

Rotational rheometer can also be operated in a dynamic mode to obtain the linear viscoelastic properties (storage and loss moduli and dynamic viscosity) of the sample. In this mode, the sample is subjected to small amplitude oscillatory shear deformations given by:

$$\gamma(t)=\gamma_o\sin(\omega t) \tag{2.8}$$

where γ_o the strain amplitude and ω is the frequency. The stress is then

measured as a function of time. If the amplitude does not exceed its small linear viscoelastic limit, it can be shown that the shear stress is sinusoidal in time and independent of strain:

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \tag{2.9}$$

where σ_o is the stress amplitude and δ is a phase shift, or the mechanical loss angle.

Using a trigonometric identity, one can rewrite eqn. 2.9 in the following form:

$$\sigma(t) = \gamma_0 \left[G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t) \right] \tag{2.10}$$

where $G'(\omega)$ is the storage modulus and $G''(\omega)$ is the loss modulus. These two quantities can be calculated from the amplitude ratio, $G_d = \sigma_0 / \gamma_0$, and the phase shift, δ, as follows:

$$G' = G_d \cos(\delta) \text{ and } G'' = G_d \sin(\delta) \tag{2.11}$$

For a parallel plate rheometer, which was used in this work, the equations for calculating the storage and loss moduli in terms of the actual test variables are as follows:

$$G' = \frac{2M_0 h}{\pi R^4 \phi_0} \cos\delta \text{ and } G'' = \frac{2M_0 h}{\pi R^4 \phi_0} \sin\delta \tag{2.12}$$

where M_o is the torque amplitude, R is the plate radius, and ϕ_o is the angular amplitude.

The complex viscosity, η^*, which approximately equals the real viscosity under small deformation, can be calculated as:

$$\eta^* = \sqrt{\left(\frac{G'}{\omega}\right)^2 + \left(\frac{G''}{\omega}\right)^2} \tag{2.13}$$

To better understand the physical meaning of the storage and loss moduli, it is useful to examine two limiting cases: a Newtonian fluid, which is linear and purely viscous, and a Hookean solid, which is linear and purely elastic. In the case of a Newtonian fluid, *G'* is zero and *G"* equals to $\eta\omega$, where η is the fluid viscosity. The mechanical loss angle is at its maximum, 90°. This means that in a Newtonian fluid, the shear stress is in phase with the shear rate and out of phase with the strain. For a Hookean solid, *G'* equals to its shear modulus, *G"* is zero, and the mechanical loss angle is zero. This means that in a Hookean solid, the shear stress is in phase with the strain.

2.4.2 Extensional Flow

In this work, the Sentmanat Extensional Rheometer (SER) is used to investigate the extensional properties of the cheese sample. A schematic of the SER is shown in Fig. 2.2.

In an extensional flow, the Hencky strain, ε_H, is defined as:

$$\varepsilon_H = \ln\left(\frac{L}{L_o}\right) \tag{2.14}$$

where L is the length of the specimen at any time, and L_o is its initial sample length.

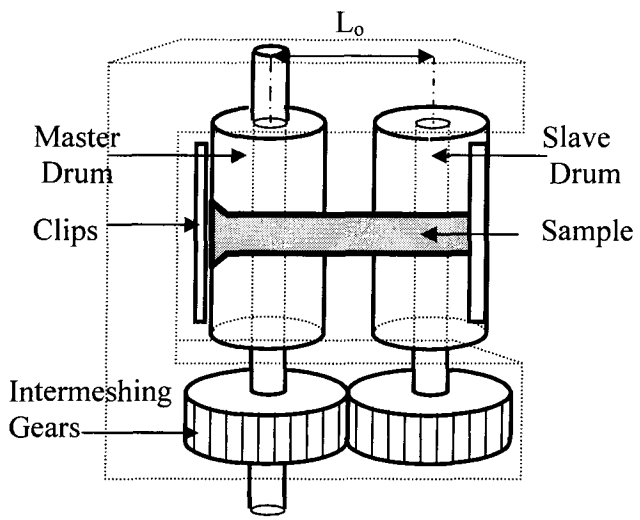


Fig. 2.2 Schematic diagram of Sentmanat Extensional Rheometer (SER).

The Hencky strain rate, $\dot{\varepsilon}_H$, is then obtained by taking the derivative of the Hencky strain with respect to time

$$\dot{\varepsilon}_H = \frac{d\varepsilon_H}{dt} = \frac{1}{L}\frac{dL}{dt} \tag{2.15}$$

For small deformations, the change of length with time can be approximated to the initial length and eqn. 2.15 becomes

$$\dot{\varepsilon}_H = \frac{1}{L_o}\frac{dL}{dt} \tag{2.16}$$

Since the change of length with respect to time is essentially the linear velocity at which the sample is been stretched, it can be converted into angular velocity taking into account the drive shaft rotation rate, Ω, and the radii of the drums, R (Sentmanat, 2003). Thus, eqn. 2.16 becomes

$$\dot{\varepsilon}_H = \frac{2\Omega R}{L_o} \tag{2.17}$$

The instantaneous torque reading, T(t), acquired from the instrument can be converted into instantaneous force, F(t), by:

$$T(t) = 2RF(t) \tag{2.18}$$

The instantaneous cross sectional area, *A(t)*, of the stretched specimen changes with respect to the initial cross sectional area, A_o, in an exponentially fashion as follows:

$$A(t) = A_o \exp(-\dot{\varepsilon}_H t) \tag{2.19}$$

The tensile stress, σ_E, can be then estimated as

$$\sigma_E = \frac{F(t)}{A(t)} = \frac{F(t)}{A_o \, exp(-\dot{\varepsilon}_H t)} \tag{2.20}$$

Finally, for a constant Hencky strain rate, the tensile stress growth function, $\eta_E^+(t)$, of the stretched sample can be expressed as

$$\eta_E^+(t) \equiv \frac{\sigma_E}{\dot{\varepsilon}_H} = \frac{F(t)}{A(t)\dot{\varepsilon}_H} = \frac{F(t)}{A_o \, exp(-\dot{\varepsilon}_H t)\dot{\varepsilon}_H} \tag{2.21}$$

2.4.3 Capillary Flow

The simplest and most popular industrial type of rheometer is the capillary rheometer shown in Fig. 2.3 (Dealy, 1982). In this partially controllable flow, a sample flows from a large reservoir into a capillary of small diameter. The flow can be imposed either by means of an imposed pressure or a piston moving at a fixed speed. Far from the capillary entrance where the flow is fully developed, the

streamlines are parallel to the channel axis, but the velocity profile depends on the rheological nature of the fluid. Unless a specific constitutive equation is known to be valid for the fluid, as in the case of a Newtonian fluid or a power-law fluid, special computational techniques are required to calculate the shear stress, shear rate and viscosity.

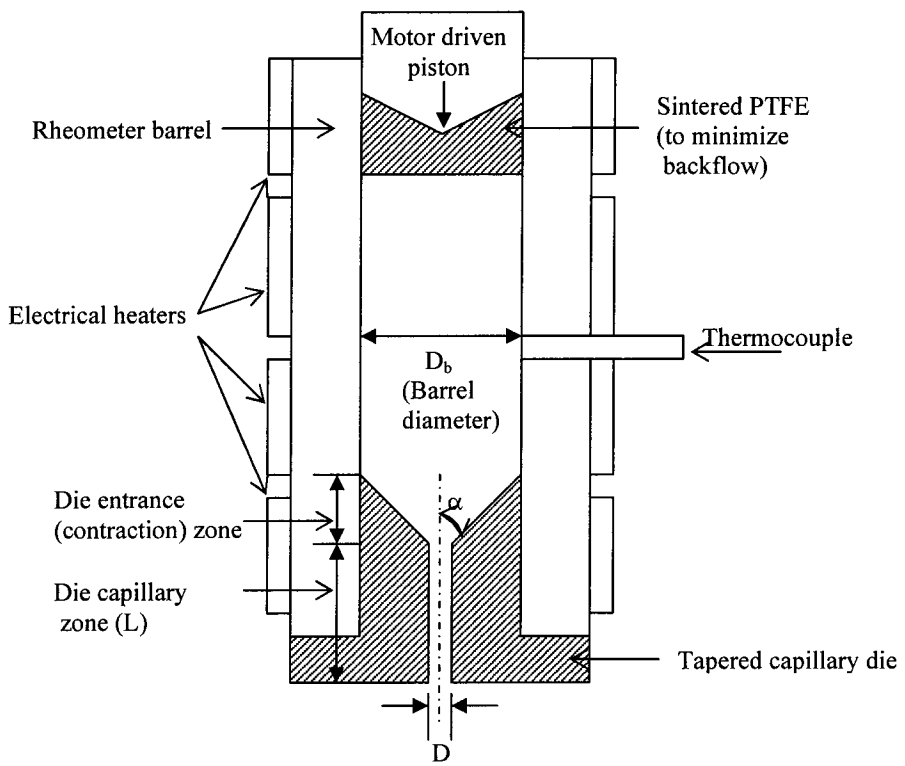


Fig. 2.3 Schematic diagram of capillary rheometer.

For the steady flow of an incompressible fluid in a tube of radius *R*, driven by a pressure gradient *dP/dz*, the Cauchy equation (momentum balance) on a cylindrical element of the fluid gives (Dealy and Wissbrun, 1990):

$$0 = -\frac{dP}{dz} + \frac{1}{r}\frac{\partial}{\partial r}(r\sigma_{rz}) \tag{2.22}$$

By integrating and assuming $P = P(z)$, and that stress is finite at the centerline,

$$\sigma_{rz}(r) = \frac{r}{2}\left(\frac{dP}{dz}\right) \tag{2.23}$$

When the flow is fully-developed over length L, the absolute value of the shear stress at the wall σ_W is:

$$\sigma_w \equiv -\sigma_{rz}\Big|_{r=R} = \frac{-\Delta P \cdot R}{2L} \tag{2.24}$$

where ΔP is the pressure drop over the length of tube. The pressure drop, ΔP, is always a negative quantity, because the flow is in the direction of the axial coordinate, z.

For a Newtonian fluid, the shear stress is proportional to the shear rate:

$$\sigma = \eta\dot{\gamma} \tag{2.25}$$

and the viscosity, η, does not change with $\dot{\gamma}$. Combining eqn. 2.22 with eqn. 2.25, using $\dot{\gamma} = du/dr$ and assuming that the velocity at the wall is zero, the velocity profile can be obtained as:

$$u(r) = \frac{2Q}{\pi R^2}\left[1 - \left(\frac{r}{R}\right)^2\right] \tag{2.26}$$

where Q is the volumetric flow rate. This is the velocity profile for "fully developed flow" in which the effects of the entrance and exit are assumed negligible and there is thus no velocity component in the radial direction. The velocity distribution is parabolic and the shear rate at the wall is given by:

$$\dot{\gamma}_w \equiv \left.\frac{du}{dr}\right|_{r=R} = \frac{4Q}{\pi R^3} \tag{2.27}$$

For non-Newtonian fluids, if a specific constitutive equation is assumed, one can derive equations analogous to those valid for Newtonian fluids. For example, if shear stress depends on shear rate according to the power law relationship

$$\sigma = K\dot{\gamma}^n \tag{2.28}$$

where K is the consistency index and n is the power-law exponent, it can be shown that the wall shear rate is (Dealy and Wissbrun, 1990):

$$\dot{\gamma}_w = \frac{3n+1}{4n}\left(\frac{4Q}{\pi R^3}\right) \tag{2.29}$$

and the velocity profile is given by:

$$u(r) = \frac{3n+1}{n+1}\frac{Q}{\pi R^2}\left[1-\left(\frac{r}{R}\right)^{\frac{1}{n}+1}\right] \tag{2.30}$$

The bracketed quantity in eqn. 2.29, which is equal to the wall shear rate in the case of a Newtonian fluid, no longer has this significance when the fluid is non-Newtonian. It is, however, referred to as the "apparent shear rate", $\dot{\gamma}_A$.

Using eqn. 2.27, eqn. 2.28 and eqn. 2.29, it can be shown that the wall shear rate, σ_W, is:

$$\sigma_w = K\left(\frac{3n+1}{4n}\right)^n \left(\frac{4Q}{\pi R^3}\right)^n = K\left(\frac{3n+1}{4n}\right)^n \dot{\gamma}_A^n \tag{2.31}$$

Therefore, a plot of log(σ_W) versus log($\dot{\gamma}_A$) will be a straight line for a power-law fluid, and the constants K and n can be determined from the slope and the intercept.

However, even if there is no constitutive equation relating the shear stress to the shear rate, a special technique can be used to determine the true wall shear rate and the viscosity for any non-Newtonian fluid. This technique requires pressure drop data for several different flow rates. It can be shown that these data should fall on a single curve when a plot of log(σ_W) versus log($\dot{\gamma}_A$) is made.

The shear rate at the wall is given by

$$\dot{\gamma}_w = \frac{3+\mathrm{b}}{4}\left(\frac{4Q}{\pi R^3}\right) = \frac{3+\mathrm{b}}{4}\dot{\gamma}_A \tag{2.32}$$

where b is the Rabinowitsch correction given by

$$\mathrm{b} = \frac{d(\log \dot{\gamma}_A)}{d(\log \sigma_w)} \tag{2.33}$$

This correction term is a measure of the deviation of a polymeric fluid from Newtonian behaviour. It equals unity for a Newtonian fluid and $1/n$ for a power-law fluid.

In a capillary rheometer, there is a large pressure drop associated with the flow in the entrance region (see Fig. 2.4), especially in the extrusions of pastes (Corfield et al., 1999; Halliday and Smith, 1995). This must be taken into account,

if the reservoir pressure is the quantity measured to determine the wall shear stress. There also appears to be a small residual pressure at the exit of the capillary. The total pressure drop for flow from the reservoir, through the capillary and out to the ambient pressure can be considered to consist of three components:

$$\Delta P = \Delta P_{ent} + \Delta P_{cap} + \Delta P_{exit} = \Delta P_{end} + \Delta P_{cap} \tag{2.34}$$

where ΔP_{ent} is the excess pressure drop due to entrance flow, ΔP_{cap} is the pressure drop for fully developed flow in a capillary, and ΔP_{exit} is the excess pressure drop due to exit flow. The end correction, ΔP_{end}, can be corrected by using a technique outlined by Bagley (1957). In this correction, the driving pressure, P_d, is measured for various values of the flow rate using a variety of dies with different length-to-diameter ratio. For each value of $\dot{\gamma}_A$, the driving pressure is plotted versus L/D and a straight line is drawn through the points. Extrapolating the lines corresponding to various values of $\dot{\gamma}_A$ to L/D=0, an end correction is obtained, which is often called "Bagley correction" (Fig. 2.5). Thus, the true wall shear stress which is obtained over most of the length of the capillary (except in the entrance) can be calculated as follows:

$$\sigma_W = (P_d - \Delta P_{end}) / (4L/D) \tag{2.35}$$

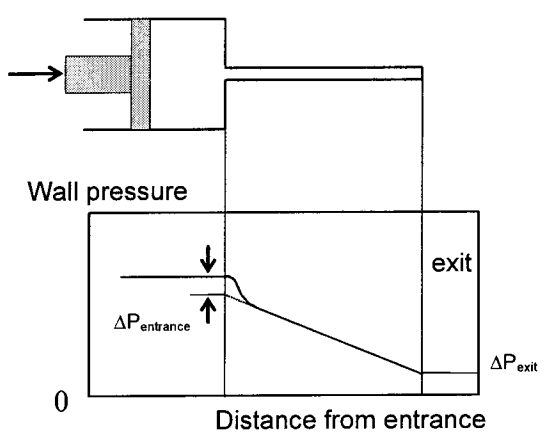


Fig. 2.4 Pressure distribution in a reservoir and capillary.

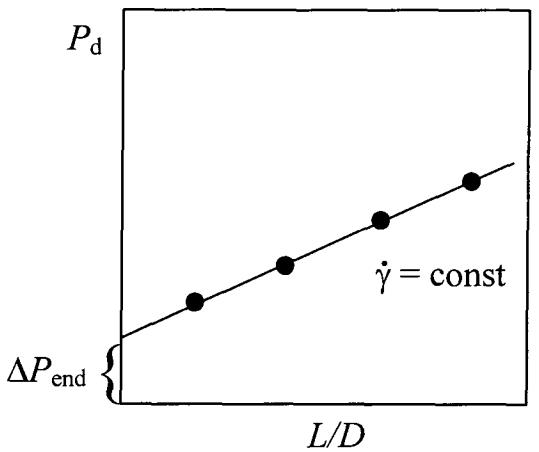


Fig. 2.5 Bagley plot (schematic).

2.4.4 Rolling

Roll forming experiments can be performed using the Sentmanat Extensional Rheometer (SER). A schematic of the set-up of the SER for rolling experiment is shown in Fig 2.6.

The shear force on each roller can be calculated from the total torque of the rheometer as follows:

$$F_S = T/2R \tag{2.36}$$

where F_S is the shear force, T is the torque, and R is the radius of the roller. However, since the area of contact between the sample and the rollers is usually different for each run, it is proper to normalize the shear force by the area of contact, A, to obtain an average shear stress, σ_S, according to:

$$\sigma_S = T/2 \cdot R \cdot A \tag{2.37}$$

The area of contact can be calculated based on the sample width and the arc formed by the angle θ as illustrated in Figs. 2.6 and 2.7.

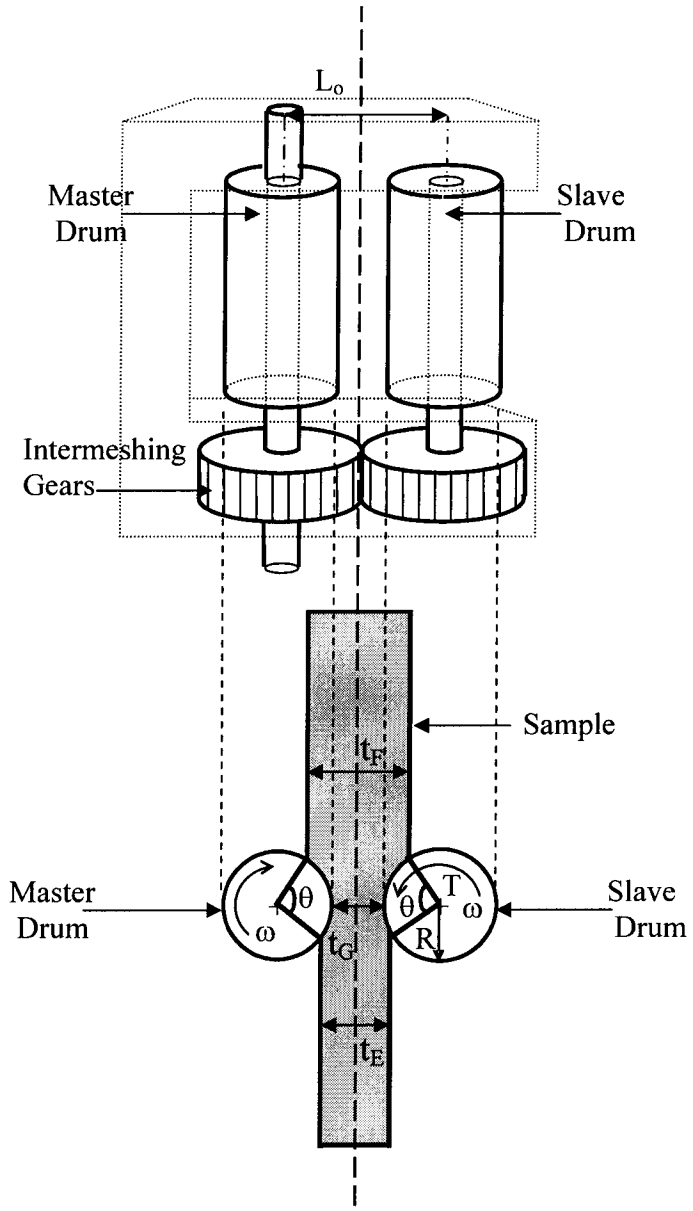


Fig. 2.6 A schematic of the set up of SER for rolling/calendaring experiments.

Referring to Fig 2.7, one can calculate the arc of contact of the sample and the drum as follows:

Arc of contact $= \theta R$

$= (\theta_1 + \theta_2)R$

$$= \left[\cos^{-1}\left(\frac{R_F}{R}\right) + \cos^{-1}\left(\frac{R_E}{R}\right)\right]R$$

where $R_F = \frac{t_G}{2} + R - \frac{t_F}{2} = \frac{2R + t_G - t_F}{2}$ and $R_E = \frac{t_G}{2} + R - \frac{t_E}{2} = \frac{2R + t_G - t_E}{2}$

thus,

Arc of contact $$= \left[\cos^{-1}\left(\frac{2R + t_G - t_F}{2R}\right) + \cos^{-1}\left(\frac{2R + t_G - t_E}{2R}\right)\right]R$$

$$= \left[\cos^{-1}\left(1 - \frac{(t_G - t_F)}{2R}\right) + \cos^{-1}\left(1 - \frac{(t_G - t_E)}{2R}\right)\right]R \qquad (2.38)$$

It must be noted, however, that the arc of contact defined above is half of the total arc of contact.

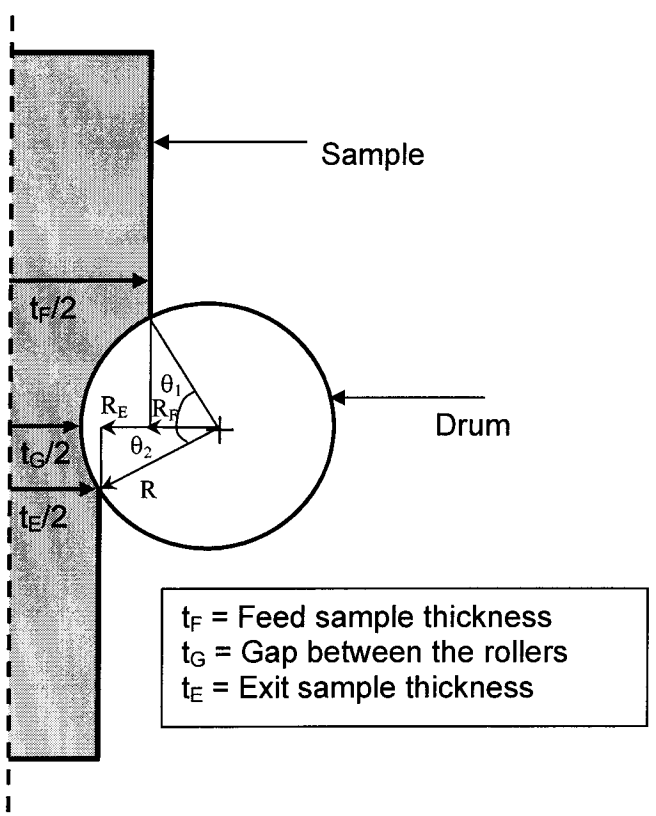


Fig. 2.7 Schematic of one of the SER drums in rolling.

CHAPTER 3:

SCOPE OF WORK

3.1 Introduction

Although many studies on the rheology of mozzarella cheese have been performed, they are mostly empirical in nature. This limits the leverage that can be accomplished based on these studies. Consequently, optimization on manufacturing and production processes is also limited.

Fundamental measurements, using well established methods yielding consistent and comparable material properties/parameters, have gained more importance over the past decades. However, most of these have been restricted to dynamic oscillatory and uniaxial or biaxial extensional experiments. Studies on other rheological characterization techniques such as capillary extrusion and rolling are scarce, even though these techniques have the potential for being used as a much more efficient post production processing method. Furthermore, to well-characterize a cheese, one must not only consider thoroughly the consistency of the measurements obtained from a rheometer, but also consistency of measurements obtained from a variety of rheometers. This allows characterization to span over a wide range of stress and time scales and capture the processing and post production behavior of the cheese.

3.2 Thesis Objectives

The research project is mainly experimental. The main focus of the project is to provide a clearer insight on the rheology of mozzarella cheese and its relations to practical processing possibilities.

The particular objectives of the project are summarized as follows:

1. To apply well-established fundamental rheological techniques to characterize mozzarella cheese. In specific, linear and non-linear viscoelastic measurements are performed in order to characterize the materials rheologically.

2. To understand the relationships between the rheological measurements obtained from different modes and scales of deformations. In other words, consistency of experimental results from different rheometers is sought.

3. To assess the processability of these materials in capillary flow and rolling. Important parameters to be studied are the surface texture and smoothness of the extrudates, wall slip of materials during flow and the effects of pressure and temperature on the flow curve of mozzarella cheese.

4. To identify the rheological properties which play a role in the processability and shapeability of mozzarella cheese, together with possible structural and texture changes that may take place during capillary flow and rolling.

5. To assess the effect of storage duration on the structure of mozzarella cheese by means of small amplitude linear oscillatory method.

3.3 Thesis Organization

The first chapter of the thesis provides fundamental information on manufacture, structure and properties of cheese. The motivation for the work is also discussed in Chapter 1. This is followed by some important literature review on cheese rheology, with particular emphasis to empirical and fundamental rheological measurements of cheese (Chapter 2). Chapter 2 includes a review of linear viscoelasitcity and the basic equations that are utilized in rheological analysis throughout the project. Chapter 3 is a summary of the detailed objectives of the work and the thesis organization. This is followed by a

description of the experimental apparatus, procedures and materials used in the present study (Chapter 4). A discussion of the linear viscoelastic behavior of the mozzarella cheese is presented in Chapter 5 (objective 1), while Chapter 6 focuses on the non-linear viscoelastic behavior and its consistency with linear viscoelasticity (objective 1). The extensional behavior of mozzarella cheese and its consistency with linear rheology is described in Chapter 7 (objective 1). Following this, the capillary extrusion of mozzarella cheese, with thorough discussion on end pressure corrections, wall slip, effect of die geometries and the comparison with linear rheology, is presented in Chapter 8 (objectives 2, 3, and 4). Chapter 9 provides results on the roll forming of mozzarella cheese (objectives 3 and 4) and Chapter 10 discusses the effect of frozen storage on the linear viscoelastic properties of different brands of mozzarella cheese (objective 5). Finally, the thesis is concluded in Chapter 11, with a general summary of the main findings of this work and their practical implications, contributions to knowledge, and some recommendations for future work.

CHAPTER 4:

EXPERIMENTAL WORK

4.1 Introduction

This chapter describes the mozzarella cheese used in this study and provides a description of the experimental equipment and procedures used to study the rheological behaviour of the mozzarella cheese. The three most basic rheometers; the concentric parallel plate rheometer to study the linear and non-linear viscoelastic behaviour, the extensional rheometer to carry out large scale extensional deformation measurements, and the capillary rheometer to study the post-production processing behaviour of mozzarella cheese, are the main pieces of equipment in this study. Hence, the bulk of this chapter is devoted to the description of these rheometers. It is noted that the basic equations associated with these rheometers are discussed in Chapter 2. The present chapter also describes other characterization technique such as the use of the extensional rheometer to perform rolling/calendaring experiments. Reproducibility of measurements is very important in working with a material such as mozzarella cheese. Some experimental techniques employed in addressing some of the challenges in generating consistent measurement are also described.

4.2 Material

Best Buy Mozzarella cheese manufactured by Lucerne Foods (Calgary, AB Canada) available at a local grocery store is used as the main material for this study. Table 4.1 summarizes the chemical composition of the mozzarella cheese (J.R. Laboratory, Burnaby, BC).

Since the cheese is obtained as a ready to eat consumer product, there is limited control on its quality. Hence, its gross structural uniformity and suitability as a testing material was investigated initially. The main purpose of assessing its gross uniformity was to ensure that any observations made in the rheological

measurements during the completion of the project were not due to experimental artifact arising from the heterogeneity of the samples. Sample gross structural uniformity was assessed by performing small amplitude oscillatory shear measurements periodically and before every major testing. On average, this type of measurement was performed on new batches of cheese about every two months.

Table 4.1 Compositional analysis of Best Buy mozzarella cheese.

Component	Content	Detection Limit	Method
Carbohydrate	6.08 wt.%	-	Calculated as (100 – wt.%moisture – wt.%protein – wt.%fat – wt.%ash)
Fat	25.29 wt.%	0.10%	Modification of AOAC 991.36 (extraction time at boiling was 3.5 hours instead of 25 minutes; drying oven temperature was 100°C instead of 125°C)
Moisture	42.44 wt.%	0.10%	AOAC 950.46
Protein-total	22.60 wt.%	0.50%	Modification of AOAC 981.10 (weight of sample was 1.0 g instead of 2.0 g; digestion time was 2.5 hours instead of 45 minutes; acid used for titration was sulfuric acid instead of hydrochloric acid)
Calcium	745.2 mg/100g	-	Modification of AOAC 985.35 (microwave digestion instead of ashing)

A summary of typical result from these periodic measurements are plotted in Fig 4.1. As can be seen, there are some variations in the dynamic viscoelastic properties of the different batches of the mozzarella cheese. The maximum and average standard deviations in the measurements from the average are about 13.7% and 7.3%, respectively. These values are in the range expected for this kind of material, where sample heterogeneity is prominent (Peck et al., 2006; Cheyne et al., 2005). In fact, these values can be considered relatively low and acceptable compared to other reported results in the literature (eg. about 10% variations in Bagley et al. 1998; 5%-10% variations in Cheyne et al., 2005).

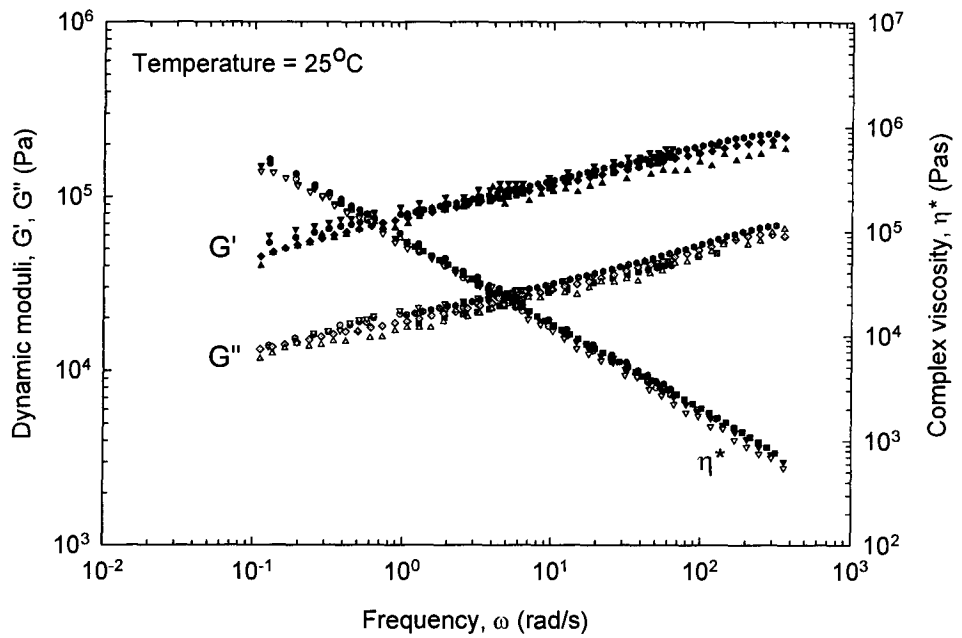


Fig. 4.1 Gross structural uniformity check of the different batches of mozzarella samples at 25°C. Different symbols and grey shades correspond to different experimental runs performed at different times throughout the completion of the project.

4.3 Experimental Equipment

4.3.1 Concentric Parallel-Plate Rheometer

A Bohlin C-VOR (Malvern Instruments, Worcestershire, UK), a stress-controlled concentric parallel-plate rheometer, was used to measure the linear and non-linear viscoelastic properties of mozzarella cheese. Since this is a stress-controlled rheometer, a constant stress is applied on the sample and the deformation is measured. This technique allows yield stress measurements to be carried out. The C-VOR is also equipped with a convective oven with PID temperature controller, which allows measurements at higher temperatures with accuracy $\pm$ 0.1°C.

4.3.2 Extensional Rheometer

The Sentmanat Extensional Rheometer (SER, Xpansion Instruments, Akron, OH, USA) was used to perform extensional experiments. A schematic of

this rheometer is shown in Fig. 4.2. This rheometer is designed to be fitted into a Bohlin VOR rheometer (strain-controlled rotational rheometer). Its unique design allows the rotational motion of the Bohlin VOR motor to wind up the two drums on which a sample is attached. As the drums wind, the sample is stretched uniformly from its two ends. This results in uniform extensional deformation and failure which occurs in the middle section of the sample.

The SER is also designed to fit into the chamber of the convective oven of the Bohlin VOR. Thus, experiments can be carried out at high temperatures. In addition, a separate data acquisition system that is capable of collecting data at a rate of up to 5000 Hz is connected to the SER. This allows torque data to be sampled every 0.005 second, which allows the measurement of transient extensional behavior of mozzarella cheese. Practically, however, a sampling time of 100 Hz was used.

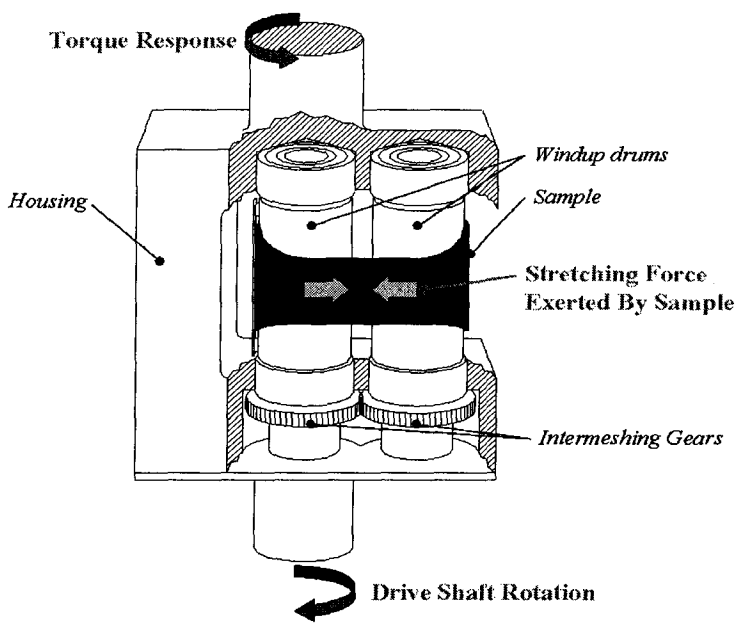


Fig. 4.2 A schematic of the Sentmanat Extensional Rheometer (SER).

The SER was also used to perform rolling experiments. The set-up for such an experiment using the SER is shown schematically in Fig. 2.6. The

cheese sample is fed into the gap between the drums (which act now as rollers) which are set to rotate at a specified speed. Although the rheometer does not have the capabilities to measure the roll separating force, it yields other equally important parameter such as the torque required to roll the sample.

4.3.3 Capillary Rheometer

A constant speed Instron capillary rheometer (Instron, Norwood, MA, USA) was used to simulate the process of ram extrusion, which is the most common processing technique in synthetic polymer processing. The cross head that drives the plunger is capable of traveling at a maximum speed of 51 cm/min (20"/min). A 890 N (200 lb) load cells is connected to the plunger and it is used to measure the extrusion load. The rheometer is connected to a computer that is able to control the rheometer and record force-deformation data. The barrel has a diameter of 0.9525 cm (0.375") and is equipped with PID-controlled heaters. The effective length of the barrel is approximately 30.5 cm (12").

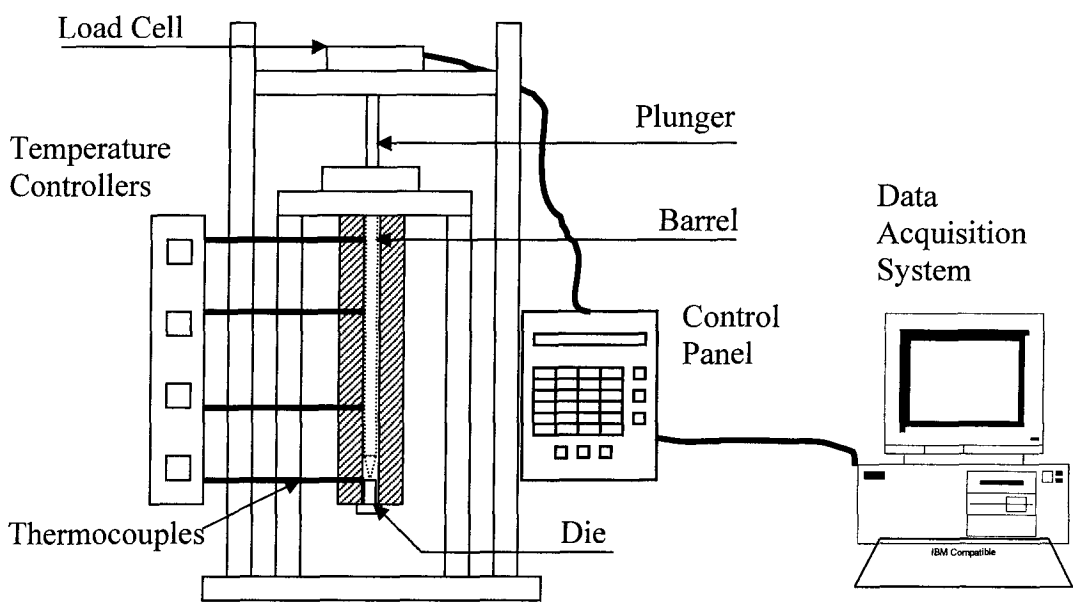


Fig. 4.3 A schematic of the computer-controlled capillary rheometer

Capillary dies with various length and diameters were used to correct the measurements for end pressures and to assess wall slip. All of these dies have

entrance angles of 180^0. In addition, capillary dies with different entrance angles were used to assess the effect of entrance angle on the extrusion pressure and the extrudate appearance.

4.4 EXPERIMENTAL PROCEDURES

4.4.1 Concentric Parallel Plate Rheometry

As already discussed, parallel-plate rheometry was one of the methods used to rheologically characterize mozzarella cheese. In using the rheometer, sample preparation was found to be very crucial because the cheese samples needed to be in contact with both the bottom and lower plates to ensure consistent results. At the same time, the samples cannot be over-compressed as liquid/fat migration will affect the measurement. Also over-compression may cause the material to be under a stressed state and this may cause experimental artifacts.

Thin slices (2 - 3 mm) were cut from a freshly procured block of cheese using a cheese slicer. Circular samples (25 mm in diameter) were then cut from these slices using a biscuit cutter. It was found that the best way to prepare the samples was when the material had been cooled at low temperature (~ 4°C). At this temperature, the cheese was firmer and this helped in producing good samples. The cheese samples were left to equilibrate at room temperature for about 2 hours in an air-tight container before experiments were carried out. Shear experiments were done at 25°C, 40°C, 50°C, and 60°C and in general, the experimental runs were repeated at least twice with fresh new samples as a mean to gauge the accuracy of the measurements.

In these experiments, slip and moisture loss was a major issue. Sand paper was found to be very practical in eliminating slip between the sample and the plates. In addition, mineral oil was used to coat the outer circumferential area of the sample to prevent moisture loss (Venugopal and Muthukumarappan,

2003). However, as will be discussed later, moisture loss cannot be completely prevented.

4.4.2 Extensional Rheometry

In extensional rheometry, thin samples (~ 0.8 mm thick) were used. For the mozzarella cheese, this was obtained by cutting the samples, using a cheese slicer, from a freshly procured cheese block which again had been cooled at low temperature (~4°C). These thin slices of cheese had different widths (~5 mm to ~12 mm), so that their cross sectional area could be controlled, and thus to ensure that the extensional experiments were operated within the acceptable range of operation of the torque transducer of the rheometer. The actual lengths of the samples were not critical, as long as the cheese samples could be clamped onto the SER drums. This is because the SER has a fixed sample deformable length (which is the axis to axis distance between the two windup drums of the SER). The cheese samples were again left to equilibrate to room temperature for about 2 hours in an air-tight container before they were used for the experiments.

In extensional tests, it is also important to ensure uniform width along the length of the sample. This was achieved by using a dual blade cutter with adjustable gap spacing. This allows preparation of cheese samples with different uniform widths. The thickness and widths of the samples were measured using a caliper and these dimensions were used to calculate the initial cross sectional area (and used in the subsequent data analysis). In using this rheometer, slip was also found to be a major challenge. It was found, however, that using sand paper glued to the clips that clamp the sample onto the drums was able to limit slippage. Moisture loss, especially, at relatively high temperatures were found to be significant as will be discussed later. However, there was no practical way to avoid this effect. Extensional experiments were done at 25°C, 40°C, 50°C, and 60°C. In general, extensional runs were repeated at least three times to assess the accuracy of the measurements.

4.4.3 Capillary Rheometry

Preliminary extrusion tests for the extrusion of cheese following the method typically used for polymers (chopped and loaded into the barrel) did not result into a steady state extrusion pressure. This was due to the air that was trapped in the barrel during loading. A loading method where a mold was initially used to cut a cylindrical cheese samples with diameter slightly less than the barrel was used. A typical cylindrical cheese sample had a diameter of about 9 mm and a length of about 50 mm. These cylindrical samples were cut from a freshly procured block of cheese at a low temperature (~4°C) and were left to equilibrate at room temperature for about 2 hours before being inserted into the capillary barrel. This method proved to be an excellent way of loading the rheometer reservoir and generating consistent measurements.

The actual extrusion process started first by heating the sample reservoir and the capillary die to the desired temperature. After thermal equilibrium was achieved, the cylindrical pieces of the cheese sample were loaded into the sample reservoir of the rheometer. The piston of the capillary rheometer was then driven into the capillary barrel at a constant speed to compress the cheese until a pressure of about 10 to 20 N (2 to 5 lb) was achieved. At this pressure, the piston was stopped and the cheese was allowed to rest for about 5 minutes. This compression squeezes some of the air out of the barrel and facilitates more efficient sample heating. The cheese sample was then extruded by driving the piston at a constant speed. Force-deformation data was recorded throughout the extrusion process and the steady state extrusion pressures were used to construct the flow curves. Experiments were done at temperatures of 25°C, 40°C, 50°C, and 60°C and the extrudates obtained during steady state extrusion were collected and analyzed visually and by means of an optical microscope. In general, extrusions were repeated at least twice.

4.4.4 Rolling/Calendaring

The gap between the drums/rollers of the SER is fixed at a distance of

0.241 cm, thus samples with different thickness were prepared in order to achieve different reduction ratios (the ratio of the sample thickness to the size of gap between the rollers) for rolling/calendaring experiments. Slabs of cheese with average thickness of 3.40, 4.20, 5.14, and 5.48 mm were used to achieve reduction ratios of 1.4, 1.7, 2.1, and 2.3 respectively. The slabs of cheese were cut from a freshly procured cheese block using a cheese slicer. Again, sample cutting were done at a sufficiently low temperature (at ~4°C) and the samples were left to equilibrate to room temperature in an air-tight container for about 2 hours. The slabs of cheese also had different widths (~5 mm to ~12 mm), so that the contact area between the sample and the rollers could be manipulated. This ensures that the rolling experiments were operated within the acceptable range of the torque transducer. The sample with the smallest thickness would be the widest and vice versa. Six different linear roller speeds (1.44E-01, 7.19E-02, 2.86E-02, 1.44E-02, 7.19E-03, and 3.61E-03 (all speeds in m/s)) were used in these experiments and rolling experiments were repeated at least three times. The steady thickness of each sample after it had passed the rollers was also measured using a caliper and recorded. Each value of thickness and width were based on three measurements at different locations on the cheese sample.

During a rolling experiment, the rollers of the SER were set to rotate at a specific speed and a slab of cheese was manually fed in between the rollers. The torque needed to roll the sample was measured and recorded. The transient response in the torque was discarded and the steady torque values were used to calculate the average shear force. Although, the SER is designed to fit into the convective heating oven of the rotational rheometer (Bohlin VOR, Malvern Instruments, Westborough, MA, USA), so that measurements can be performed at elevated temperatures, it was not practical to perform rolling experiments at elevated temperatures as the rolling experiment involves manually feeding the slab of cheese into the gap between the rollers. Rolling experiments were performed at ambient temperature (around 25°C) and no temperature control was utilized.

CHAPTER 5:

LINEAR VISCOELASTICITY

5.1 Introduction

Linear viscoelasticity is the most basic characterization technique for viscoelastic materials. Although techniques to perform linear viscoelastic measurements are well established, especially for polymer melts, this is not the case for mozzarella cheese. This is largely due to the fact that mozzarella cheese is made up of both solid and liquid phases that complicates matter further. Both these solid and liquid phases, their mixing and morphology are highly temperature dependent. Nevertheless, there have been several studies on the linear viscoelasticity of mozzarella cheese (for example those by Nolan et al., 1989; Hsieh et al., 1993; Diefes et al., 1993; Tunick et al., 1993; Yun et al., 1994; Ak and Gunasekaran, 1996; Subramanian and Gunasekaran, 1997a, 1997b; Joshi et al., 2004)

In this chapter, the linear viscoelastic properties of the mozzarella cheese under study are discussed. The linear viscoelastic properties were obtained from small amplitude oscillatory shear measurements and experiments were performed at 25°C, 40°C, 50°C, and 60°C. Applicability of time-temperature superposition is examined to provide an insight into the thermorheological property of mozzarella cheese. Finally, the linear viscoelasticity results are represented by a generalized Maxwell model.

5.2 Dynamic Time Sweep

Dynamic time sweep experiments were performed in order to check the stability of the materials at various temperatures. In a dynamic time sweep experiment, the frequency and temperature are kept constant and the dynamic properties are recorded as a function of time. Typical results are shown in Fig. 5.1 which depicts the complex modulus of the mozzarella cheese at different

temperatures as a function of time. At room temperature, it seems that the sample was quite stable up to 30 minutes. With increasing temperature, there is a gradual decrease in the sample stability which is indicated by the earlier onset of increase in the modulus. At 60°C, the complex modulus starts to increase quite sharply after about 100 seconds.

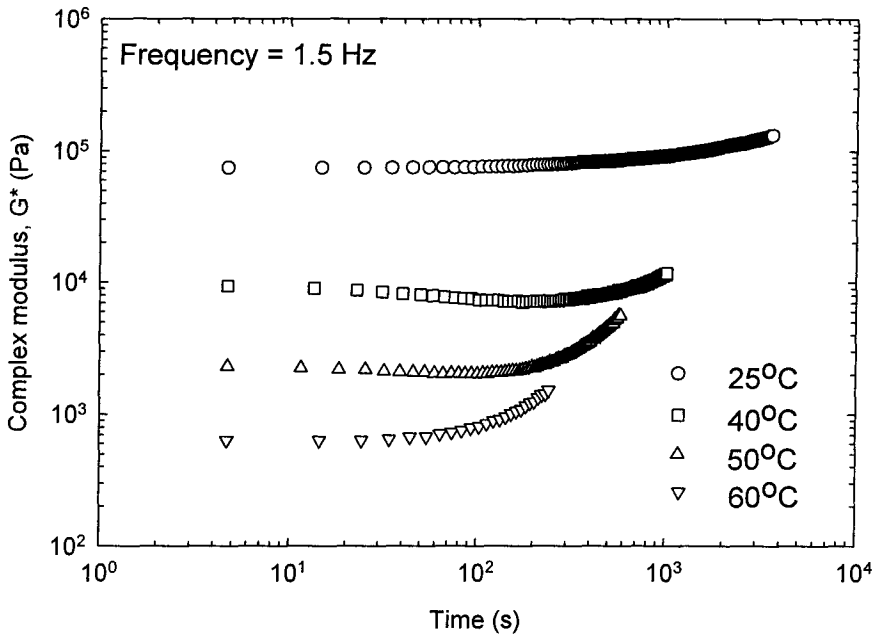


Fig. 5.1 Effect of time on the linear viscoelastic properties of mozzarella cheese at different temperatures.

In their work with bread dough, Ng et al. (2006) observed similar increase in the complex modulus with rest time and they attributed this increase to the gelation or crosslinking process that occurred continuously within the dough. This is, however, not a valid explanation for mozzarella cheese. Unlike bread dough which continuously develops its structure through hydrophobic and sulphide bonds even after mixing is completed, mozzarella cheese does not exhibit such dynamics. For mozzarella cheese to have this type of dynamics, the increase of modulus has to occur almost instantaneously (just like in bread dough), but this is not the case. At 25°C, for example, the mozzarella cheese needs about 30 minutes to exhibit significant sample hardening. Thus, the proteins micelles in the

mozzarella cheese can be considered as thermodynamically stable at a specific temperature. Thus, the increase of modulus can be mainly attributed to the loss of moisture and possibly due to loss of fat from within the sample, despite the fact that mineral oil was used to coat the exposed area of the sample (Muliawan and Hatzikiriakos, 2007a). The loss of moisture and/or fat causes the cheese to harden which increases both its dynamic moduli. To minimize the time effect on the linear viscoelastic measurements, all small amplitude oscillatory experiments were completed before significant increase (~10% increase) in the moduli was observed. For example, for the experiments performed at 60°C, tests were completed within 100 seconds.

5.3 Dynamic Stress Sweep

Dynamic stress amplitude sweeps at different temperatures were performed on the mozzarella cheese samples in order to determine the region of linear viscoelasticity. This is the region where the stress is proportional to the strain and the modulus is independent of the magnitude and rate of deformation. In a dynamic stress amplitude sweep test, the frequency of oscillation and the temperature are kept constant and the stress amplitude applied onto the sample is varied. The dynamic properties and the resulting strain are recorded as a function of the stress amplitude. The stress amplitude sweep results are plotted in Fig. 5.2 where the complex modulus, G* (left vertical axis) and the strain (right vertical axis) are plotted as functions of applied stress at a frequency of 1.5 Hz. The span of linear viscoelasticity is temperature dependent. The higher the temperature, the smaller should be the applied stress in order to be within the limits of linear viscoelasticity.

Typical results for the limits of linear viscoelasticity as a function of temperature are summarized in Table 5.1. It should be noted that these linear limits were identified visually from the stress sweep curves shown in Fig 5.2. From Table 5.1, one can see that the stress for the onset of non-linearity decreases from 1500 Pa to 100 Pa with an increase of temperature (from 25°C to

60°C). On, the other hand, the corresponding strain limit increases from 0.02 to 0.15. As the temperature increases, mozzarella cheese melts, becomes less elastic and flows rather easily. A decrease in applied stress does not necessarily result into a decrease of strain. In general, the observed trends in Table 5.1 are consistent with other reported results in the literature (Nolan et al., 1989; Ak and Gunasekaran, 1996; Subramanian and Gunasekaran, 1997a).

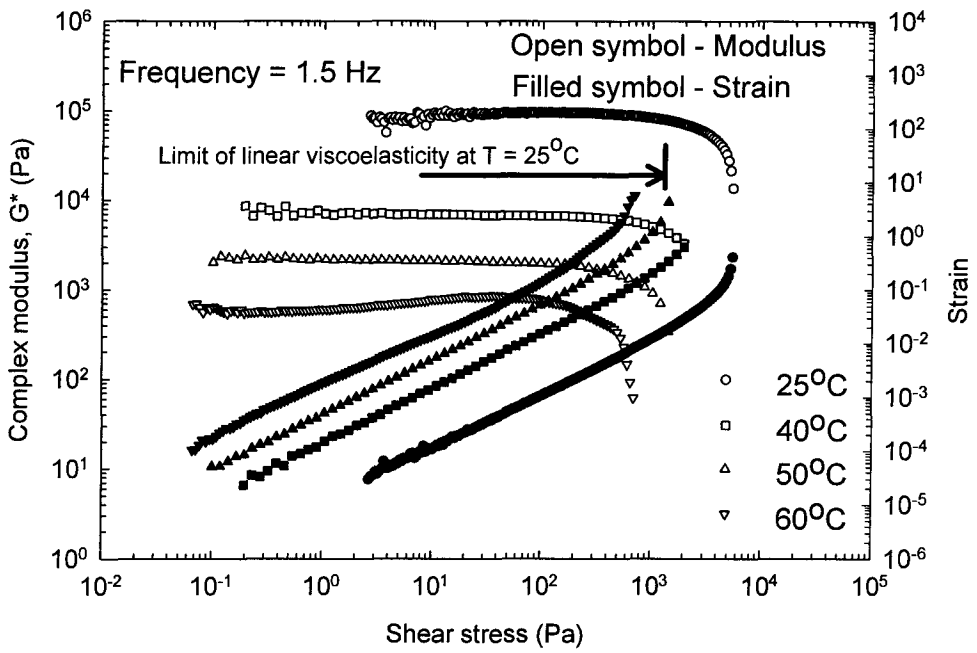


Fig. 5.2 Stress amplitude sweep of mozzarella cheese at different temperatures. Shown also are the corresponding strain values and the linear viscoelastic region at T = 25°C.

Table 5.1 Stress and strain limits of linear viscoelasticity of mozzarella cheese at different temperatures.

Temperature (°C)	Stress limit (Pa)	Strain limit (-)
25	1500	0.02
40	500	0.09
50	200	0.1
60	100	0.15

5.4 Dynamic Frequency Sweep

Dynamic frequency sweep experiments were performed at 25°C, 40°C, 50°C, and 60°C. At each temperature, the stress amplitude is maintained at a constant value and the dynamic viscoelastic properties are measured as a function of frequency. The results are plotted in Fig. 5.3.

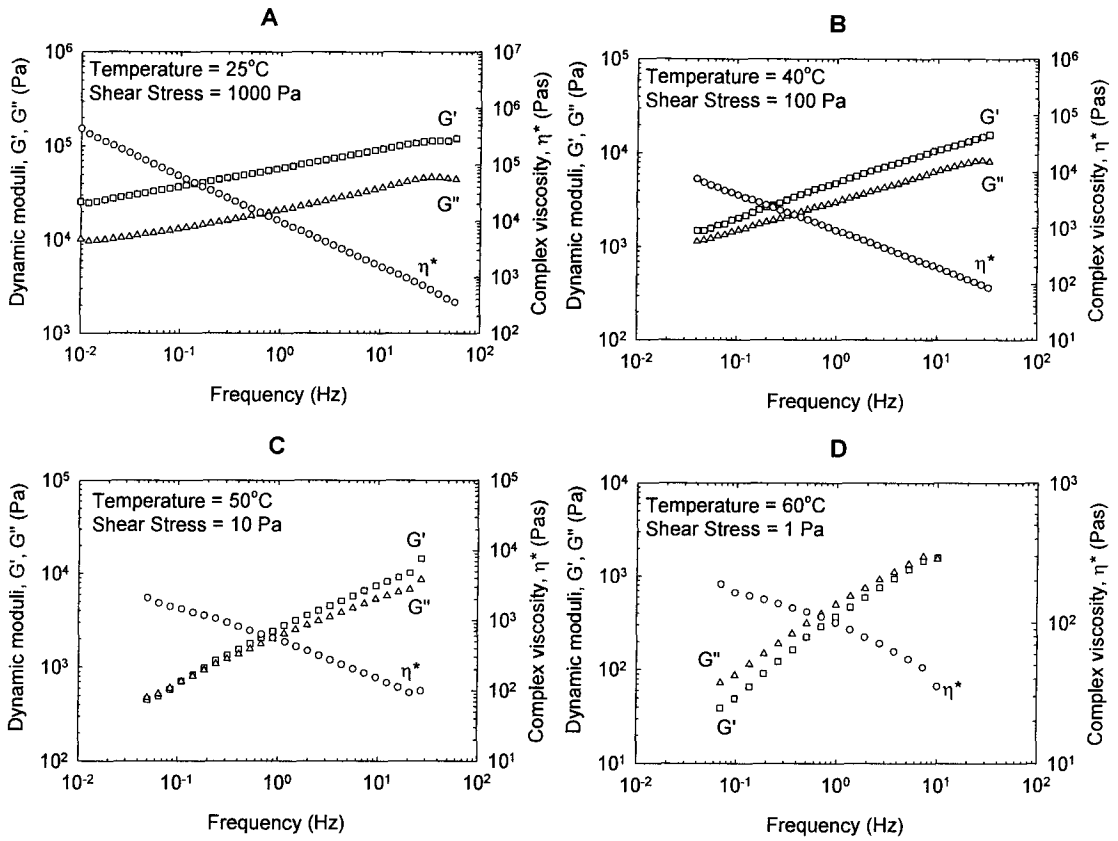


Fig. 5.3 Dynamic frequency sweeps of mozzarella cheese at A) 25°C, B) 40°C, C) 50°C, and D) 60°C.

At 25°C, G' is always higher than G" over the whole frequency range. The parallelism of G' and G" implies the typical behaviour of a viscoelastic solid, also reported by Subramanian and Gunasekaran (1997b), Nolan et al. (1989) and Diefes et al. (1993). The highly shear thinning behavior of mozzarella cheese is also clearly illustrated at 25°C. At 40°C, the cheese exhibits lower dynamic moduli and there is a change in the slopes of the dynamic moduli curves. The sample has started exhibiting liquid-like behaviour due to the melting of the fat and increase in protein mobilization. The constant change in the linear

viscoelastic properties of the mozzarella cheese continues at 50°C, where at the lower frequency range, G' and G" overlaps. Finally, at 60°C, the loss modulus starts to dominate the linear viscoelastic properties of the sample and the behaviour resembles that of a viscoelastic fluid i.e. similar to that of a molten polymer (Dealy and Wissbrun, 1990).

5.5 Dynamic Temperature Sweep

The transition (from a solidlike to a fluidlike behaviour) of mozzarella cheese can be seen more clearly from a dynamic temperature-sweep experiment, where the dynamic properties are measured as a function of temperature (see Fig. 5.4). As the temperature increases, there is initially a constant decrease of the complex modulus (~ -2.3 kPa/°C), followed by a more significant decrease (~ -6.7 kPa/°C) as the temperature increases to more than 45°C. The sudden significant decrease in the complex modulus is due to the mobilization of the protein matrix. The melting and transition from solid-like to liquid-like behavior is better illustrated by the phase angle, defined as $\delta \equiv \tan^{-1}\left(G''/G'\right)$. As can be seen from Fig. 5.4., δ is relatively constant at temperatures below 40°C (solid-like behaviour). There is perhaps a slight peak at around 34°C, which indicates the melting of the fat. As the temperature is increased beyond 45°C, δ increases sharply, indicating sudden transition to liquid-like behavior. This temperature region is dominated by both the continuous melting of the fat and the mobilization of the protein matrix which dramatically reduces the interactions between the casein micelles aggregates. Consequently, the viscous properties of the mozzarella cheese are enhanced. At 60°C, the mozzarella cheese melts completely and this is translated in a significant peak in the tan δ curve.

Mozzarella cheese also exhibits significant thermal hysteresis. As can be seen clearly from Fig. 5.5, the linear viscoelastic properties of mozzarella cheese exhibit dependence on heating or cooling. As mozzarella cheese is heated,

although there is a rather constant decrease in the viscous modulus, there is a significant decrease in the elastic modulus at around 45°C (as discussed earlier). As mozzarella cheese is cooled, the changes in both the elastic and viscous moduli seem to be constant throughout the temperature range. This is also reflected in the tan δ versus temperature curve. The thermal hysteresis of mozzarella cheese can be explained by the fact that the melt process of virgin mozzarella cheese occurs in 2 phases. The first phase involves the melting of fat at around 30°C. The second phase, which is more significant, occurs at around 55°C, where the proteins gain significant thermal energy to mobilize. As mozzarella cheese melts, there is a rearrangement of the fat and protein phases. As the temperature is increased, there is reduced moisture content in the cheese and this causes the protein aggregates to constrict due to hydrophobic interactions (Johnson, 2000). This constriction causes the fat to phase separate and forms much larger fat particles, most of which are still embedded in the protein matrix. Some of these fat particles, however, are able to escape from the protein matrix (Johnson, 2000). A combination of these processes; loss of moisture, formation of larger fat particles within the protein matrix, and simultaneous loss of some fat particles from the protein matrix, results in a formation of a more cohesive and a more thermally stable mass of cheese. Thus, when this mass of cheese is cooled, it exhibits a more constant change in its physical properties; a behavior that is significantly different than when it is heated.

The thermal hysteresis of the mozzarella cheese can be captured and illustrated from its microscopic images after heating. Fig. 5.6 shows the microscopic images of virgin mozzarella cheese (Fig. 5.6a) and cheese that has been heated to 60°C and cooled to room temperature (Fig 5.6b). These images are obtained from using a cryo-Scanning Electron Microscope (Hitachi S4700 SEM with Emitech K1250 Cryo System, Pleasonton, CA, USA). The samples collected for imaging were stored in an air tight container before their microscopic images were taken and all microscopic images were taken within 24 hours.

Before imaging, the samples were flash frozen using liquid nitrogen and they were fractured to expose the internal surface. The microscopic images are taken at random locations within the cheese samples and only representative images are shown.

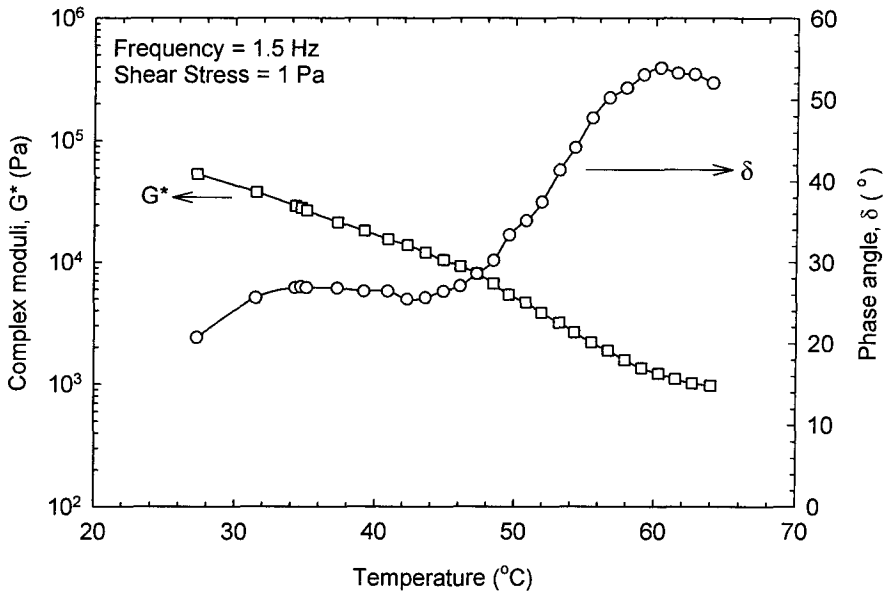


Fig. 5.4 Dynamic temperature sweep of mozzarella cheese at a frequency of 1.5Hz.

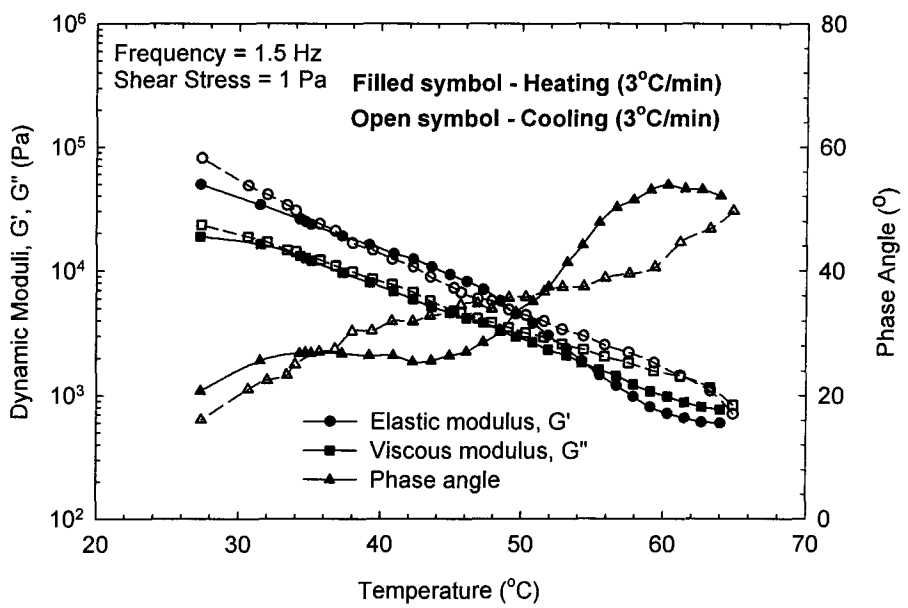
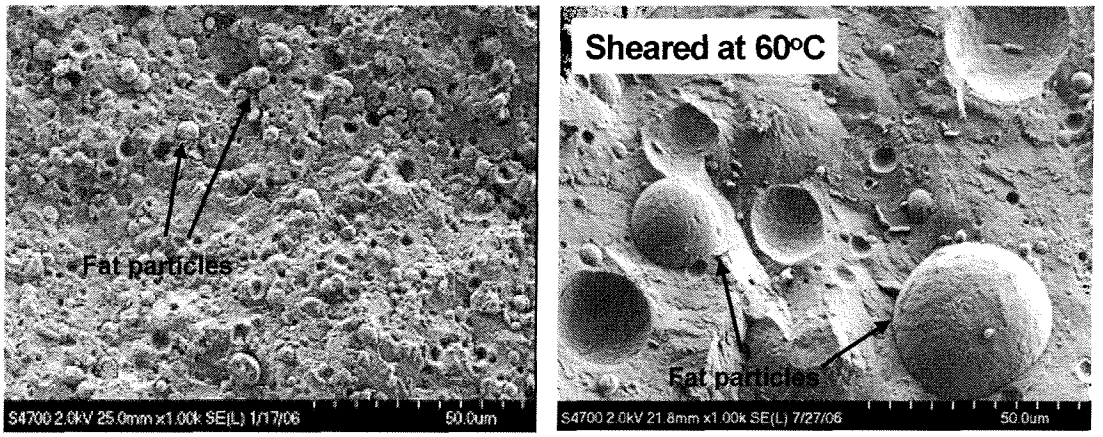


Fig. 5.5 Two-direction temperature sweep of mozzarella cheese, showing its thermal hysteresis behavior.

From Fig 5.6a, it can be seen that the unprocessed cheese has a structure which is mostly made up of protein matrix with dispersed fat globules, as described earlier. As the mozzarella cheese is heated to 60°C and cooled, one can see from Fig. 5.6b that the fat particles aggregate and form much larger fat particles (which is due to the constriction of the casein network). These large fat particles do not re-disperse themselves back when the mozzarella cheese is cooled. This results in the different rheological behavior of the mozzarella cheese during heating and cooling, as has been found by other researchers as well (for example, see Prentice, 1987; Gunasekaran and Ak, 2003; Venugopal and Muthukumarappan, 2003).



A B

Fig. 5.6 Cryo-scanning electron microscope of A) virgin mozzarella cheese at 25°C and B) mozzarella cheese heated to 60°C and cooled down to 25°C.

5.6 Time-Temperature Superposition

A thermorheologically simple polymer system is usually found to obey time-temperature superposition principle which simplifies the significant thermal dependence of its linear viscoelastic properties. Time-temperature superposition allows the shifting of linear viscoelastic data obtained at several temperatures to a single master curve at the selected reference temperature. The shift factors can be related with temperature according to either the Arrhenius or the Williams-Landel-Ferry equations, depending on the glass transition temperature of the

polymer system. Utilizing the shift factors, one can efficiently obtain linear viscoelastic data corresponding to very low frequency range (which can take hours) at a specific temperature by shifting the linear viscoelastic data gathered at relatively higher frequencies and high temperature.

The time-temperature superposition principle was applied on the linear viscoelastic data of the mozzarella cheese to obtain the master curve. This is plotted in Fig. 5.7. The reference temperature was selected to be 60°C. It is noted that the data obtained at 25°C were not able to be superposed satisfactorily to the data obtained at 40°C, 50°C, and 60°C. This agrees with the results from the dynamic temperature sweep, where it was found that at a temperature below 40°C, the cheese behaves as a solid. As the temperature exceeds 40°C, the cheese starts melting, undergoing structural changes. These (structural changes) include increased separation of fat from the protein matrix (Guinee and Fox, 2001), increased ratio of liquid to solid fat (Prentice, 1987), increased mobility of the protein phase (Wetton and Marsh, 1990), and loss of moisture. This means that, essentially, the data obtained at higher temperatures (> 40°C) corresponds to a physically different material. This is supported from the works done by Mavridis and Shroff (1992) and Van Gurp and Palmen (1998) who attribute the failure of time-temperature superposition as an indication of the presence of relaxation time (or moduli) having non-uniform temperature dependence such as those exhibited by multiphase systems or those that undergo physical changes during the rheological measurements. As illustrated earlier, cheese can be classified as a multiphase system that exhibits a solid-like behaviour, which gradually changes to a liquid-like behaviour as the temperature is increased. Thus, it is not surprising that only the data obtained at the melt state (> 40°C) can be superposed. This indicates that mozzarella cheese can be considered as a thermorheologically simple material for T > 40°C.

The horizontal shift factors, a_T were found to follow the Arrhenius equation

$$a_T = exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \tag{5.1}$$

where E_a is the energy of activation in cal·mol^{-1}, R is the gas constant (1.987 cal·mol^{-1}·K^{-1}), and T_{ref} is the reference temperature in K. A plot showing this relationship is shown in Fig. 5.8. From the equation of the fit, E_a can be determined and was found to be 4.21E04 kcal·kmol^{-1}.

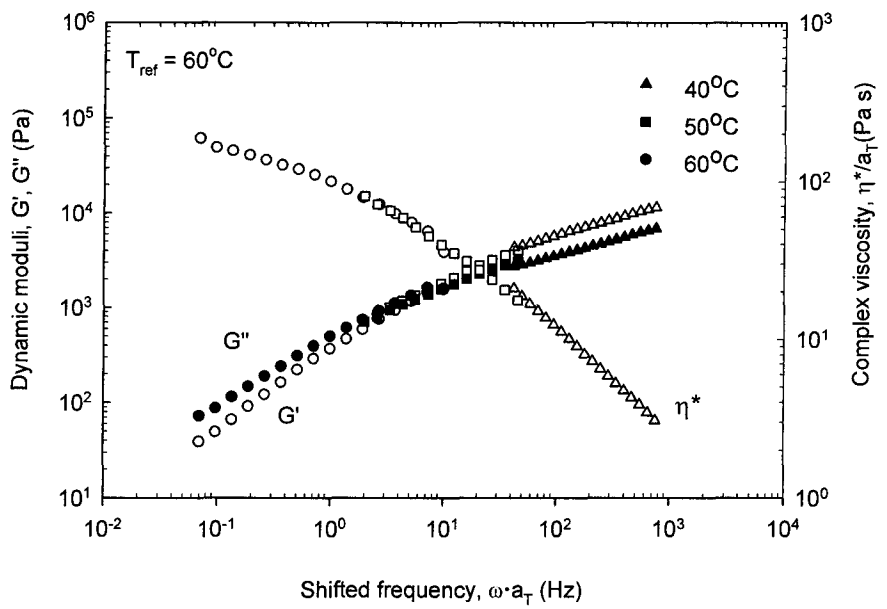


Fig. 5.7 Master curve of mozzarella cheese at a reference temperature of 60°C, obtained from shifting the linear viscoelastic data gathered at 40°C and 50°C.

5.7 Generalized Maxwell Model Fit

The generalized Maxwell model was used to describe the linear viscoelastic data of the mozzarella cheese. The linear viscoelastic moduli data is used to determine the relaxation spectrum in terms of a discrete spectrum of Maxwell relaxation times (Dealy and Wissbrun, 1990). The storage and loss moduli in terms of the discrete Maxwellian spectrum can be expressed as

$$G'(\omega)=\sum_i G_i \frac{(\omega\lambda_i)^2}{1+(\omega\lambda_i)^2} \tag{5.2}$$

$$G''(\omega)=\sum_i G_i \frac{\omega\lambda_i}{1+(\omega\lambda_i)^2} \tag{5.3}$$

where ω is the frequency of oscillations and G_i and λ_i are the generalized Maxwell model parameters. The parameters (G_i,λ_i) of equations 5.2 and 5.3 were determined using a nonlinear optimization program following the algorithm developed by Baumgartel and Winter (1989). The program results into the least number of (G_i,λ_i) parameters (Parsimonious spectra). Table 5.2 lists the values of these parameters for mozzarella cheese at different temperatures.

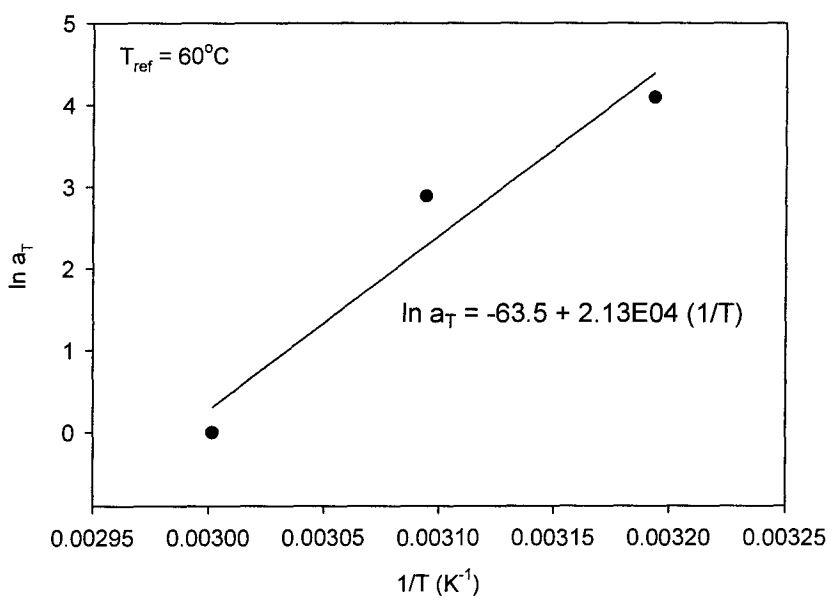


Fig. 5.8 Shift factors of mozzarella cheese as a function of temperature and its Arrhenius fit.

The predicted fits of the linear viscoelastic data are shown in Fig. 5.9. The fits obtained from these parameters are satisfactory. It should be noted that in

Fig. 5.9, the plot corresponding to the temperature of 60°C is shown as master curve (from Fig. 5.7).

Table 5.2 Generalized Maxwell model parameters for mozzarella cheese at different temperatures.

T = 25°C		T = 40°C		T = 50°C		T = 60°C	
λ_i	G_i	λ_i	G_i	λ_i	G_i	λ_i	G_i
1.00E-06	1.00E+08	1.00E-06	2.30E+07	-	-	1.00E-06	7.00E+05
9.43E-03	5.07E+04	9.77E-03	8.41E+03	4.87E-03	1.37E+04	4.37E-04	6.95E+03
6.73E-02	2.62E+04	5.48E-02	3.56E+03	3.09E-02	3.23E+03	4.64E-03	3.92E+03
4.19E-01	1.80E+04	2.41E-01	2.16E+03	1.39E-01	1.98E+03	4.62E-02	1.13E+03
2.82E+00	1.42E+04	1.04E+00	1.47E+03	7.64E-01	9.54E+02	3.22E-01	2.42E+02
4.83E+01	2.53E+04	8.73E+00	1.56E+03	1.12E+01	4.67E+02	4.90E+00	4.77E+01

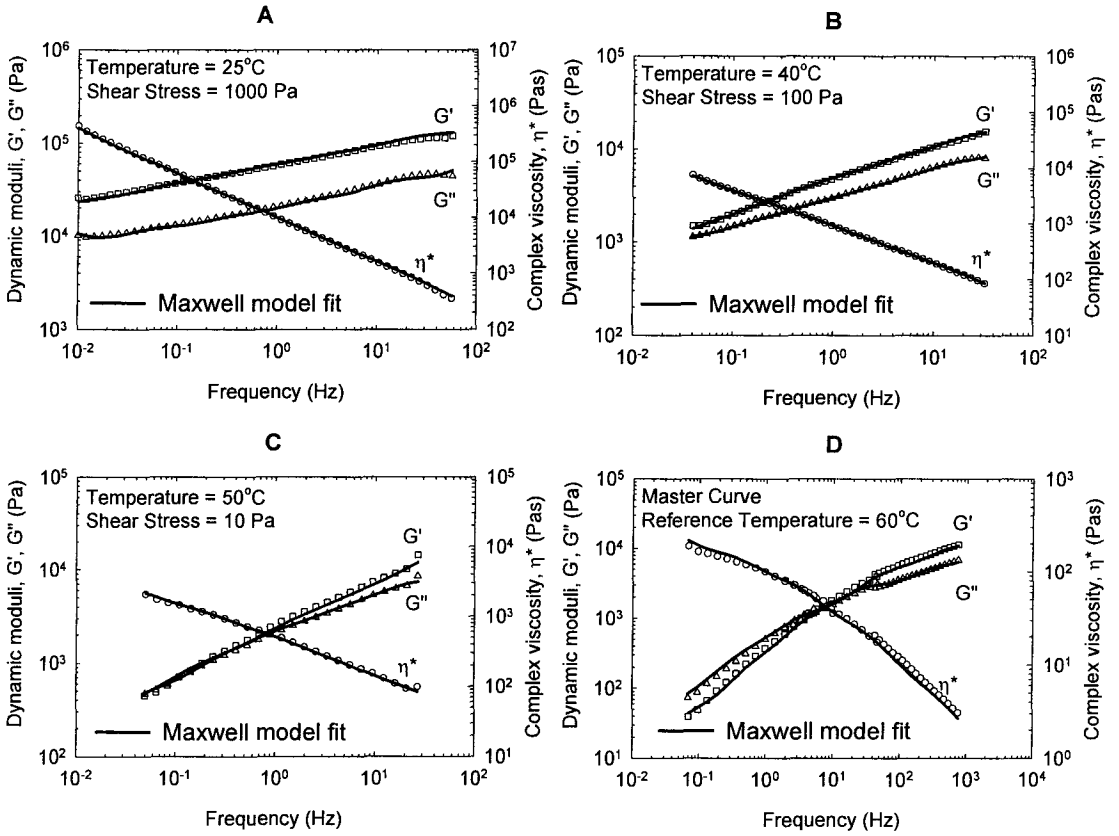


Fig. 5.9 Maxwell model fits of the dynamic linear viscoelastic data for mozzarella cheese at A) 25°C, B) 40°C, C) 50°C, and D) 60°C.

5.8 Summary

Linear viscoelasticity can be utilized to probe the microscopic behavior of mozzarella cheese. At room temperature, mozzarella cheese behaves like a semi-solid material. Upon heating, mozzarella cheese undergoes a gradual transition from a viscoelastic solid towards a viscoelastic fluid. It was also found that moisture loss which occurs prominently at relatively high temperatures has a significant effect on the stability of the sample. The irreversible thermal effect on the structure and rheological behavior of mozzarella cheese was also illustrated. As a result of this thermal effect, over the temperature range of 25°C to 40°C, mozzarella cheese can be considered as a thermorheologically complex material. Thus, time-temperature superposition was only applicable to data obtained at 40°C and above. It was also determined that the linear viscoelastic data can be described by a generalized Maxwell model with 6 relaxation modes.

CHAPTER 6:

NON-LINEAR VISCOELASTICITY

6.1 Introduction

In linear viscoelasticity, the Boltzmann superposition principle in the form of generalized Maxwell model provides a fairly detailed understanding of the material response. Thus, one can relate the molecular structure of mozzarella cheese with its linear viscoelasticity. However, the theory of linear viscoelasticity holds only if the deformation applied to the cheese is either very small or very slow. Practically, however, mozzarella cheese is subjected to deformations that are neither small nor slow. Processes such as masticating, cutting, shredding, and mixing impose large scale deformations and deformation rates. Non linear viscoelasticity, thus, is more important and relevant for practical purposes.

In this chapter, the non-linear viscoelastic behaviour of mozzarella cheese at different temperatures is studied using both small and large step shear strain relaxation experiments. The non-linear relaxation process of the mozzarella cheese is compared to that of linear relaxation and the damping is derived (Dealy and Wissbrun, 1990). Results from yield stress measurements are also presented in this chapter.

6.2 Step Strain Relaxation

Step strain relaxation measurements were carried out at temperatures of 25°C, 40°C, 50°C, and 60°C. In this test, a specific strain is applied to the cheese sample over a very short period of time and the stress relaxation behavior is monitored. The strain imposed in these experiments ranges from 0.005 to 0.1. The non-linear viscoelastic behavior of mozzarella cheese can be obtained from its non-linear relaxation modulus, shown in Fig. 6.1. The non-linear relaxation modulus is essentially the shear stress normalized by the corresponding values of strain. Beyond a certain strain, the non-linear relaxation modulus starts to

deviate from its linear relaxation modulus. For example, at 25°C (Fig. 6.1A), the deviation of the relaxation modulus from linearity occurs at a strain of 0.03. There is a systematic decrease of the relaxation modulus with increasing strain beyond the value of 0.03. This is valid at all other temperatures. An interpretation of the relaxation modulus is as follows. At very short times, the smaller agglomeration of protein micelles in the mozzarella cheese relaxes the fastest. This is reflected by the relatively sharper decrease of the modulus in this time scale. In the intermediate and terminal regions, the relaxation can be described by power law (with slopes of about 0.2, 0.25, 0.5, and 0.75 at 25°C, 40°C, 50°C and 60°C respectively)

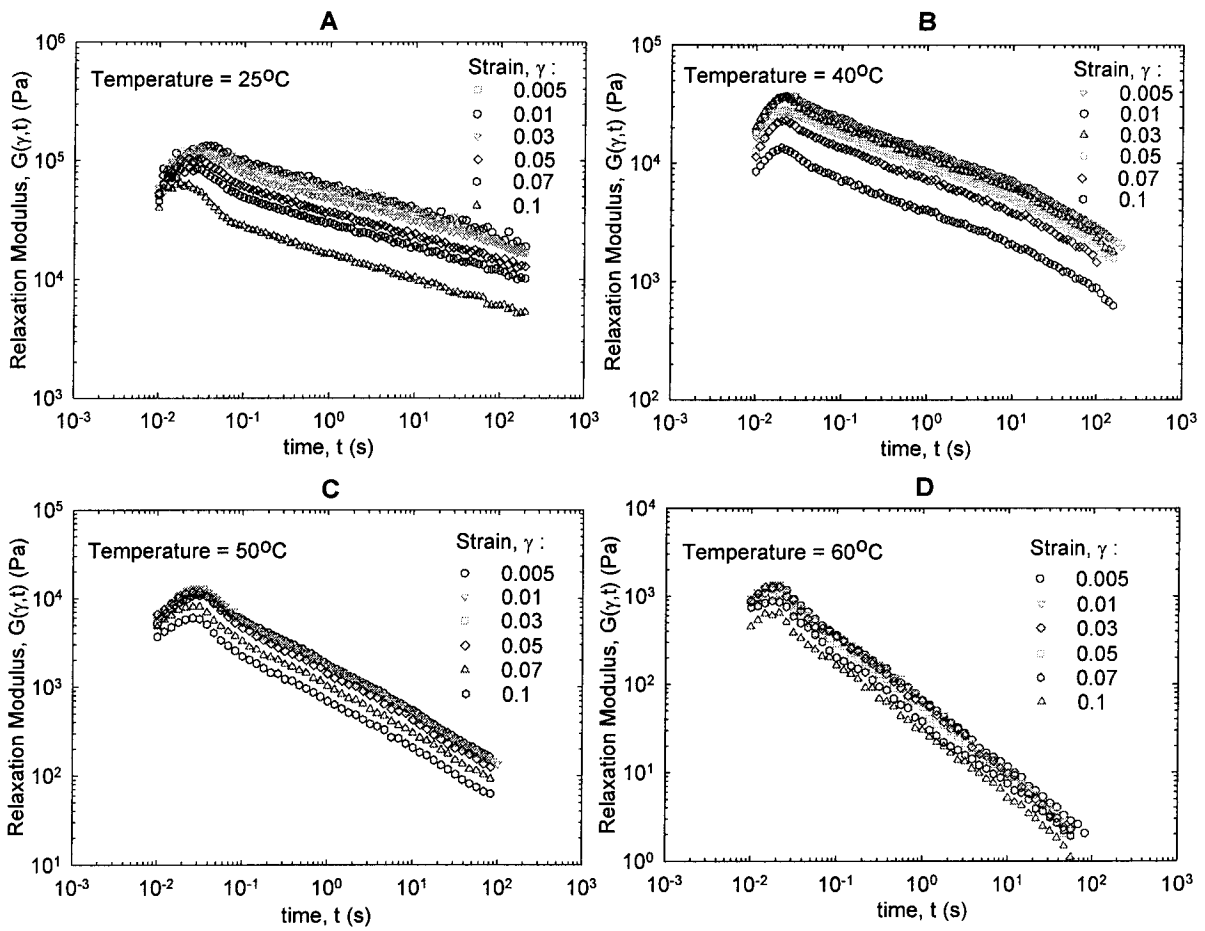


Fig. 6.1 Stress relaxation after imposition of step strains on mozzarella cheese at A) 25°C, B) 40°C, C) 50°C, and D) 60°C.

It should be noted that the initial increase in the shear stress at the early times is an experimental artifact due to the transient material response as the plate starts to rotate to achieve the desired strain as illustrated in Fig. 6.2. It takes about 0.05 seconds for the rheometer to achieve the desired strains. This corresponds to an increase in the shear stress at this short time scale. Similarly, the presence of slight overshoots in the applied strains, most noticeably at relatively higher strains, results in a small peak in the transient shear stress response.

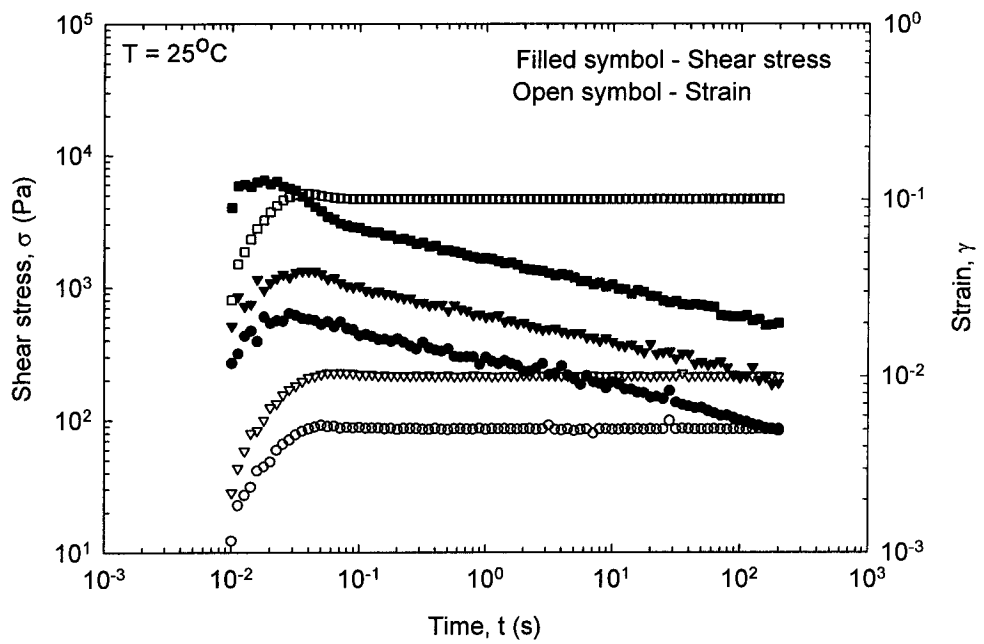


Fig. 6.2 Transient analysis of step strain relaxation of mozzarella cheese at 25°C.

The data in Fig. 6.1 can be shifted to superpose on the linear viscoelastic envelope in order to determine the damping function. The results are shown in Fig. 6.3. The shift factors which depend on the strain make up the damping functions. These factors are plotted as a function of strain, γ, in Fig. 6.4 at different temperatures. It can be seen that the damping function can be described accurately by the Zapas damping function (Dealy and Wissbrun, 1990):

$$h(\gamma) = \frac{1}{1+\alpha\gamma^2} \tag{6.1}$$

with α = 214, 159, 128, and 97 for temperatures of 25°C, 40°C, 50°C, and 60°C respectively.

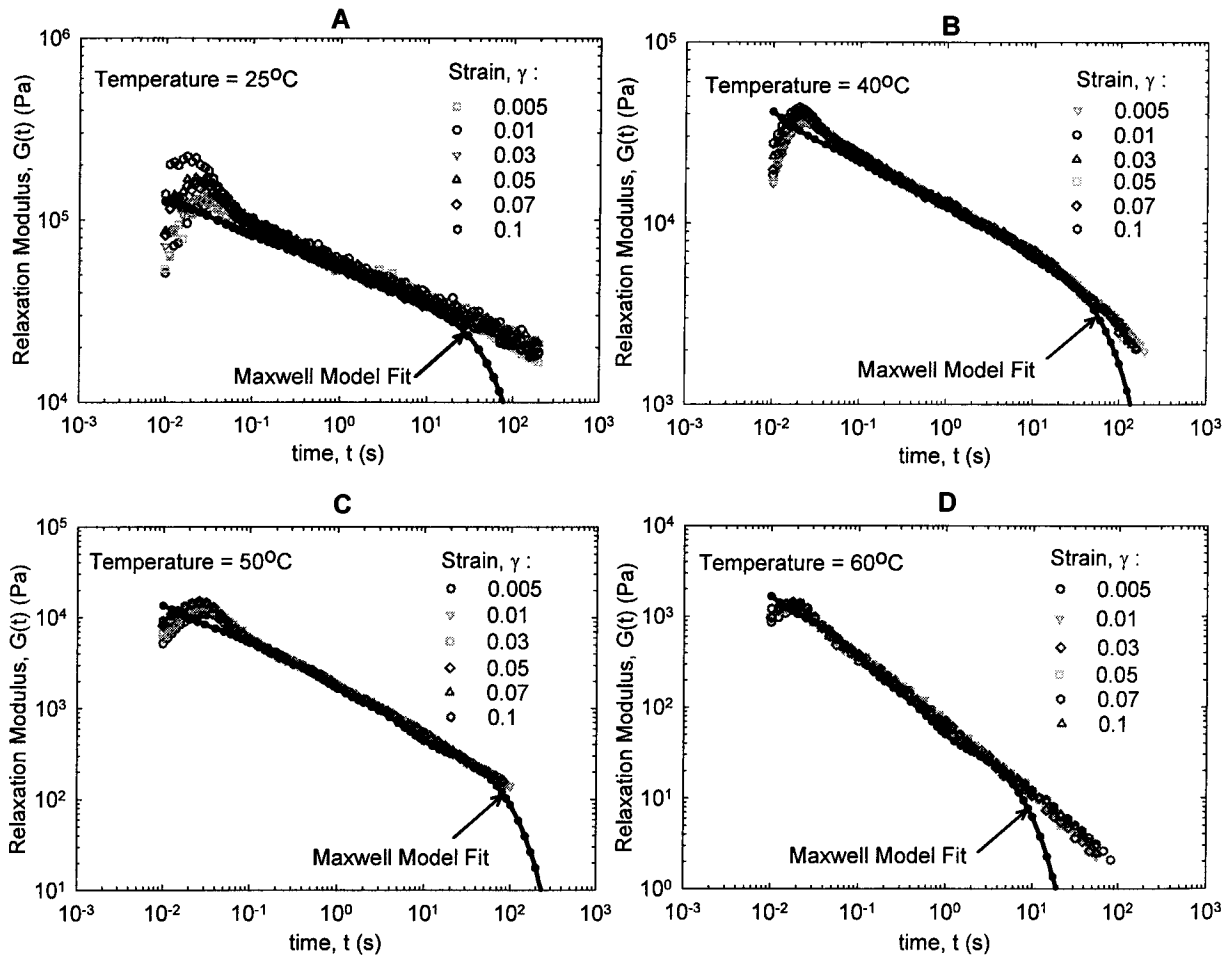


Fig. 6.3 Shift of the data plotted in Fig. 6.1 in order to determine the damping functions of mozzarella cheese at A) 25°C, B) 40°C, C) 50°C, and D) 60°C.

In addition, it can be seen from Fig. 6.4 that the damping function is a function of temperature. This indicates that the rheological behavior of mozzarella cheese comes closer to its linear viscoelastic counterpart with increase of temperature.

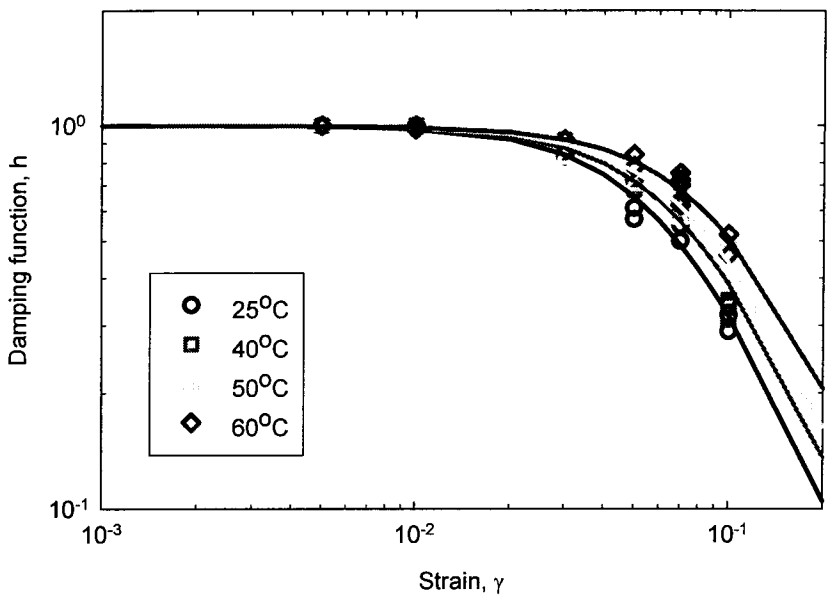


Fig. 6.4 Damping function of mozzarella cheese at different temperatures. Lines correspond to fitting of damping function with the Zapas generalized model.

From the Maxwell model parameters, one can also calculate the linear relaxation modulus from

$$G(t) = \sum_i G_i \exp\left(-\frac{t}{\lambda_i}\right) \tag{6.2}$$

where t is the time and G_i and λ_i are the generalized Maxwell model parameters.

The linear relaxation moduli as predicted from the Maxwell model fit for the different temperatures are also plotted on Fig. 6.3. The agreement between the linear relaxation moduli with those predicted by the Maxwell model fit is overall satisfactory in the intermediate region. At long times, the Maxwel model fit fails to predict the linear relaxation modulus. This is due to the fact that the Maxwell parameters are obtained from linear viscoelastic data determined over a limited frequency range. The linear viscoelastic experiments do not capture the response at very small and large frequencies.

6.3 Yield Stress Measurements

Cheese has been known to exhibit yield stress due to the presence of protein matrix that forms its structure. Thus, determining the yield stress can provide an insight on the structural changes that occur at high deformations. Initially, an attempt was made to determine the yield stress using creep tests. However, a disadvantage with creep tests is that a very long time (hours) is sometimes necessary to determine the steady creep compliance. This has been discussed by Cheng (1986) as one of the main problems. Structural changes on cheese within this period of time can affect the result significantly as demonstrated by the time sweep experiments. Hence, in this particular case, we used the stress ramp method. Although this method may not provide an accurate value of yield stress, it is a good alternative to the creep test.

Typical stress ramp test results used to determine the yield stress values at various temperatures are shown in Figs. 6.5 to 6.7. As can be seen, the peak of the curves, which corresponds to the yield stress, shifts towards smaller shear stress values as the temperature increases. This means that the yield stress value decreases with increase of temperature. Mozzarella cheese possesses yield stress because of the presence of solid protein phase which is able to support its own structure at small deformations. However, as the temperature is increased, the protein phase softens and the mozzarella cheese as a whole flows more readily; hence exhibiting lower yield stress. At the temperature of 60°C, the structure of the cheese has been broken completely due to the complete fat melting and protein mobilization. Consequently, it was not possible to determine a yield stress value at this temperature. At lower temperatures, however, the yield stress values were found to be 1620 $\pm$ 93 Pa (Fig. 6.5) at 25°C, 216 $\pm$ 19 Pa at 40°C (Fig. 6.6) and 1.4 $\pm$ 0.3 Pa 50°C (Fig. 6.7).

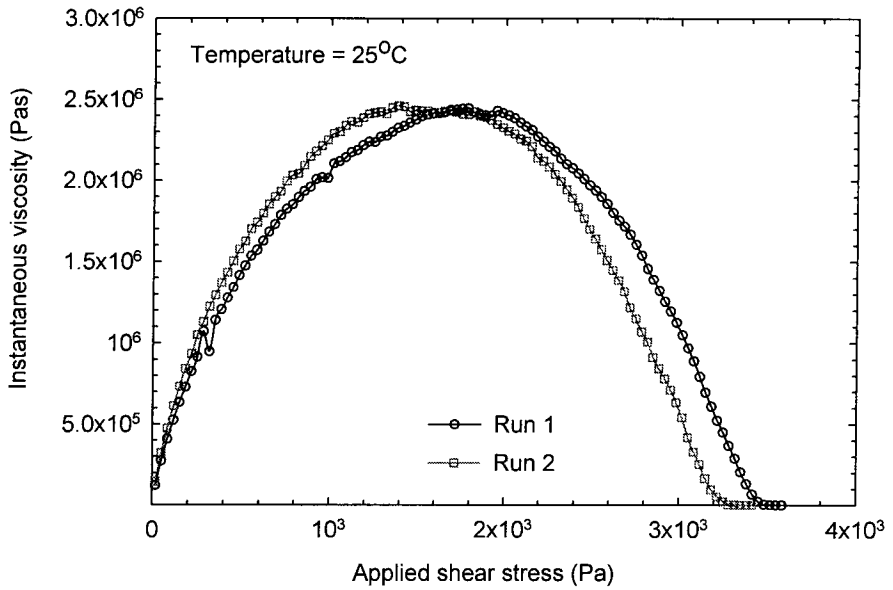


Fig. 6.5 Typical stress ramp test for mozzarella cheese at 25°C to determine its yield stress.

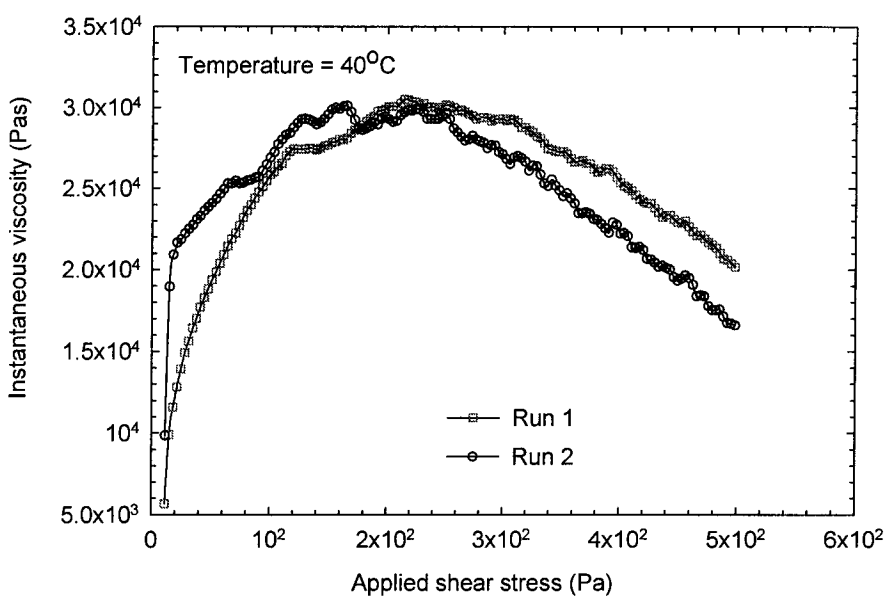


Fig. 6.6 Typical stress ramp test for mozzarella cheese at 40°C to determine its yield stress.

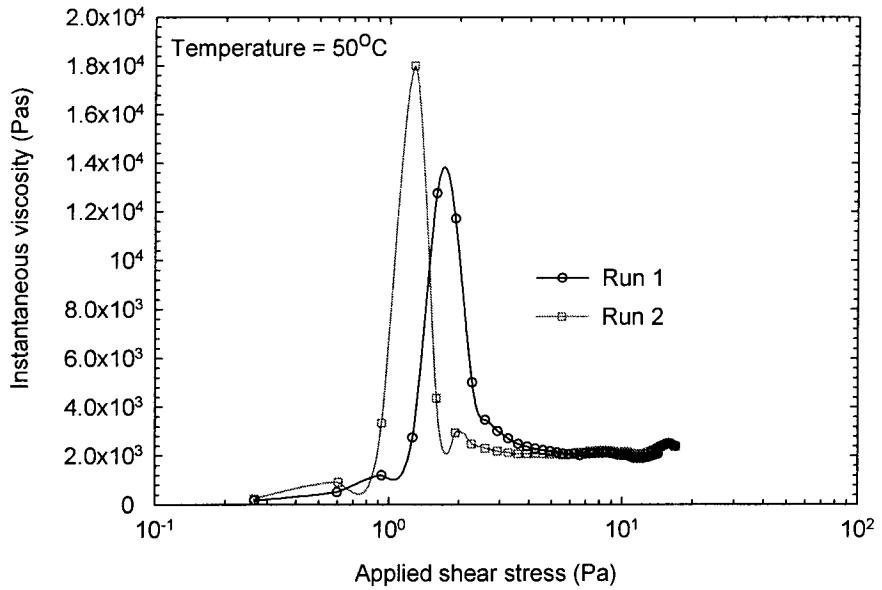


Fig. 6.7 Typical stress ramp test for mozzarella cheese at 50°C to determine its yield stress.

6.4 Summary

Understanding the non-linear rheology of mozzarella cheese is important because more often than not, mozzarella cheese is subjected to highly non-linear deformation during manufacturing, processing and consuming. It has been shown that the damping function of mozzarella cheese, which is a measure of the degree of non-linearity, can be described by a generalized Zapas model. In general, the linearity of the rheological behavior of mozzarella cheese increases with temperature because of the ability for the cheese to flow easier at higher temperatures. The generalized Maxwell model parameters obtained from the linear viscoelastic data were also found to describe the linear relaxation dynamics of the mozzarella cheese satisfactorily.

CHAPTER 7:

EXTENSIONAL RHEOLOGY

7.1 Introduction

A unique property of mozzarella cheese which makes it the most common pasta filata cheese is its flowability or stretchability. Consumers expect a high quality mozzarella cheese to exhibit significant stretchability. In stretching mozzarella cheese, one is applying an extensional deformation to the cheese. Although the stretchability of a mozzarella cheese depends on the control of its manufacturing process variables, such as pH and temperature, mechanical work (repeated kneading) on the mozzarella curd during manufacture is as important (Gunasekaran and Ak, 2003). Comprehending the extensional rheology of mozzarella cheese, hence, is an important aspect to the overall understanding of the rheology of mozzarella cheese.

In this chapter, the extensional rheology of mozzarella cheese at different temperatures is studied. Extensional measurements are carried out using the Sentmanat Extensional Rheometer (SER) described in section 2.4.2 and the extensional strain rates range from linear to non-linear. The extensional results are compared to linear rheology and discrepancies are discussed.

7.2 Transient Extensional Flow

The extensional properties of the mozzarella cheese sample were determined by using the SER at 25°C, 40°C, 50°C and 60°C. At 25°C, extensional tests were initially performed on samples cut in three different directions; perpendicular, parallel and in transverse directions to determine if the mozzarella cheese exhibit anisotropic behavior. This preliminary test was performed at a Hencky strain rate of 0.113 s^{-1}. As can be seen from Fig. 7.1, the samples being cut from the three different directions do not show significant differences with each other, which indicates that this mozzarella cheese (Best

Buy) is isotropic. This is in contrast to a result presented by Ak and Gunasekaran (1997), which reported anisotropic behavior in their mozzarella cheese. The reason for this difference is perhaps due to the different manufacturing techniques or the relatively small sample size that the SER uses (which can conceal the fiber orientation effects).

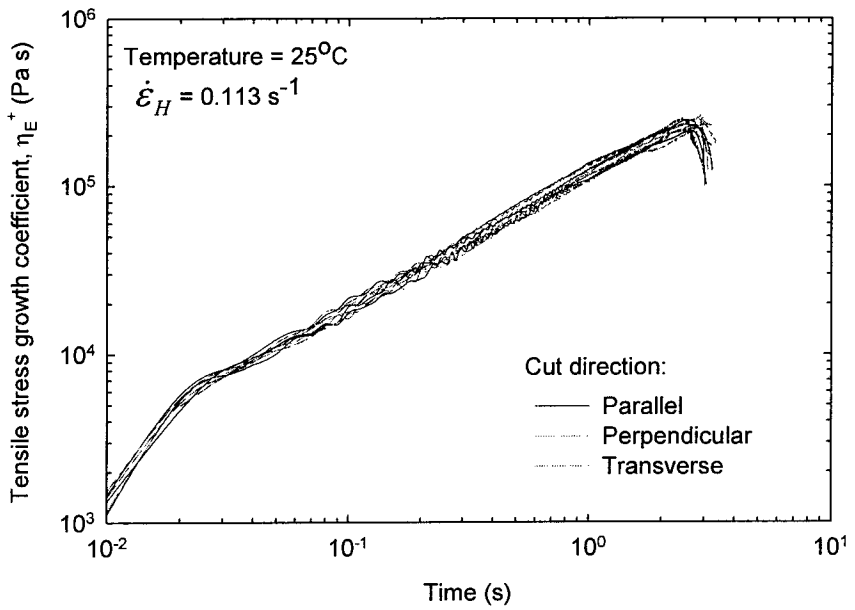


Fig. 7.1 Tensile stress growth coefficient of mozzarella cheese samples prepared by cutting in three different directions at a Hencky strain rate of 0.113 s^{-1} and temperature of 25°C.

Extensional results at different temperatures are shown in Fig. 7.2 in terms of tensile stress growth coefficient, $\eta_E^+ \equiv \sigma_E / \dot{\varepsilon}_H$ as a function of time for various Hencky strain rates, $\dot{\varepsilon}_H$, where σ_E is the tensile stress. In general, very good agreement between the tensile stress growth curves at the different temperatures are obtained. At 25°C (Fig. 7.2), a rapid increase can be observed that is followed by a sudden decrease in the tensile stress growth curves for the different Hencky strain rates. This sudden decrease is consistent with a brittle-type failure of a solid like material. As the temperature is increased, a gradual change in the type of cheese failure (from brittle to ductile) was observed. At

60°C, a plateau in the tensile stress growth was obtained as the cheese exhibited significant strain softening and ductile failure. Practically, this illustrates the unique stretchability property of mozzarella cheese, which makes it one of the most highly demanded pasta filata cheeses.

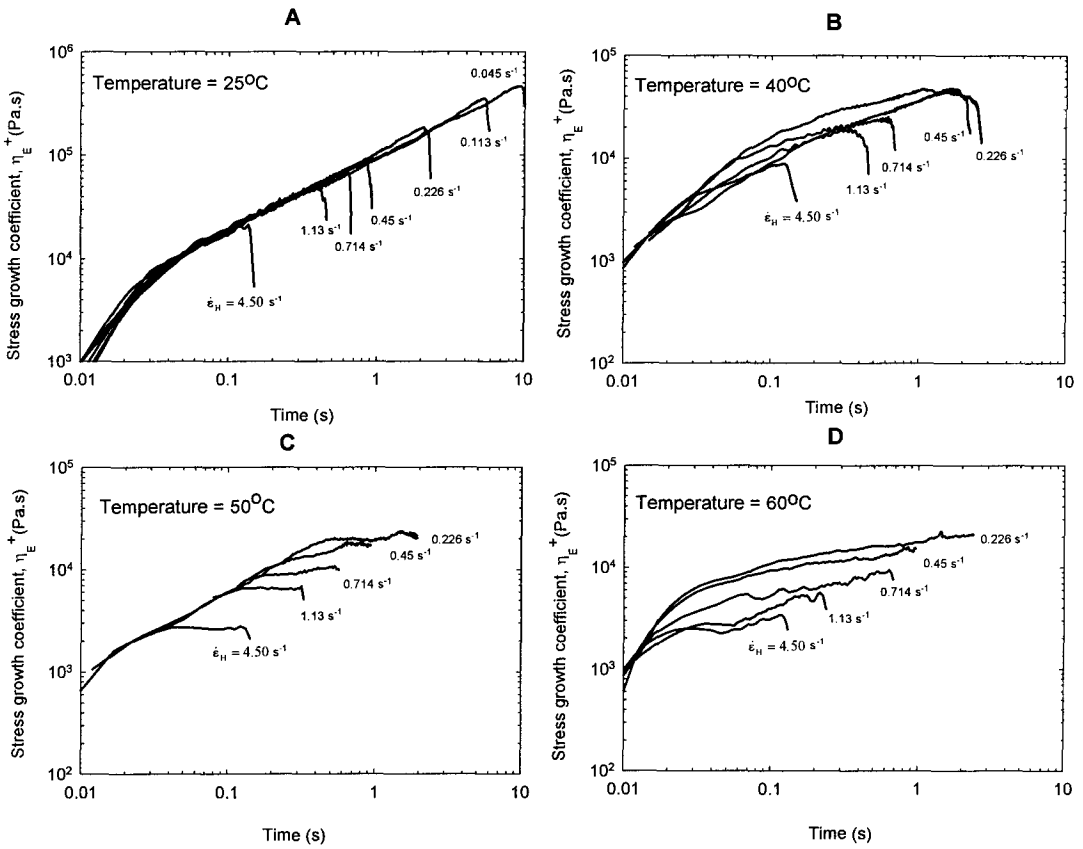


Fig. 7.2 Tensile stress growth coefficients of mozzarella cheese at A) 25°C, B) 40°C, C) 50°C, and D) 60°C.

This is also clearly illustrated in the typical stress-strain curves plotted in Fig. 7.3 at different temperatures. These curves are obtained at a Hencky strain rate of 4.5 s^{-1} shown earlier in Fig. 7.2. In general, as the temperature increases, the peak diminishes and transforms into a plateau. This transformation can be associated with the fact that at higher temperature the mozzarella cheese necks after yielding, before failing.

7.3 Comparison with Linear Shear Rheology

As described in section 2.3, the linear rheology of a viscoelastic material can be described adequately using the discrete relaxation spectrum obtained from the fitting of the generalized Maxwell model. Section 5.8 illustrates the fitting of the generalized Maxwell model to the linear viscoelastic properties of mozzarella cheese. The discrete relaxation spectrum obtained from the fitting of the generalized Maxwell model can be used to calculate the linear shear stress growth as follows

$$\eta_s^+(t) = \sum_i G_i \lambda_i \left[1 - \exp\left(-\frac{t}{\lambda_i} \right) \right] \tag{7.1}$$

where $\eta_s^+(t)$ is the shear stress growth as a function of time, t is the time and G_i and λ_i are the generalized Maxwell model parameters.

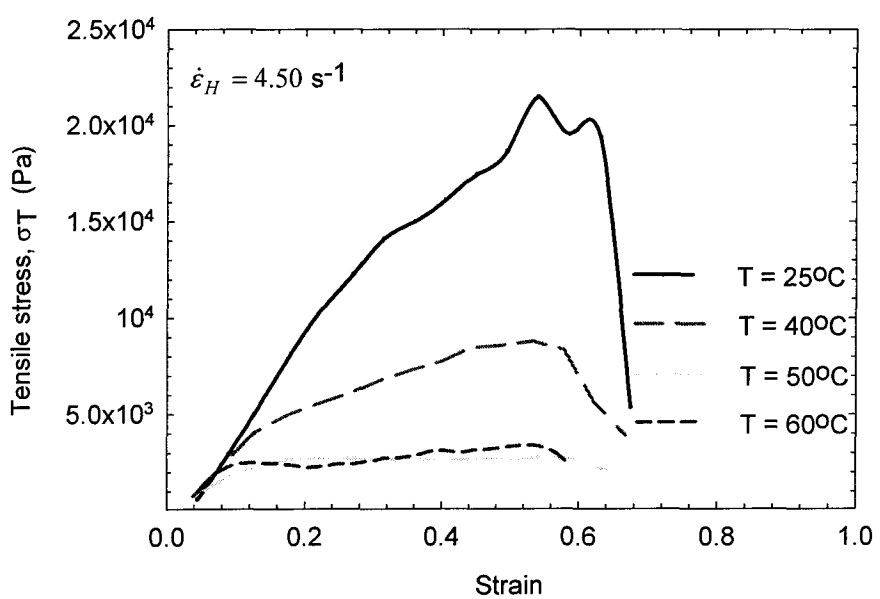


Fig. 7.3 Tensile stress-strain curves of mozzarella cheese at a Hencky strain rate of 4.5 s^{-1} at different temperatures.

The linear extensional stress growth can then be determined according to the following expression,

$$\eta_E^+ = T \cdot \eta_S^+ = T \cdot \sum_i G_i \lambda_i \left[1 - \exp\left(-t / \lambda_i\right)\right] \tag{7.2}$$

where T is the Trouton's ratio taken equal to 3 for incompressible homogeneous materials (Bird et al., 1977). This linear extensional stress growth forms the linear viscoelastic envelope. Alternatively, the linear viscoelastic envelope can also be obtained from a start-up of steady shear test at a very low shear rate i.e., typically 0.05 s^{-1}, using a rotational or a sliding plate rheometer. However, this method is more appropriate for more viscous materials such as polymer melts.

Consequently, the comparison of the extensional rheology with the linear shear rheology is done by comparing the linear viscoelastic envelope (equation 7.2) with the extensional stress growth curves, η_E^+ obtained from the SER. The comparison of the various curves is shown in Fig. 7.4. It can be seen that there is lack of agreement between the two sets of shear and extensional data as noticed before. At the temperature higher than 25°C, the Maxwell model fits are well below extensional ones. As the temperature increases, the disagreement between the two sets of data (shear vs. extensional) seems to be more pronounced.

The discrepancy between the tensile stress growth and the linear viscoelastic envelope is mainly due to moisture loss that is more pronounced at elevated temperatures (Muliawan and Hatzikiriakos, 2007). In performing the extensional tests, a very small amount (~ 1 g) of sample having a relatively high surface-to-volume ratio (~ 1600 m^{-1}) was used. For comparison, an oscillatory test sample in the rotational rheometer usually has a surface area to volume ratio of approximately 0.16 m^{-1}. Although the extensional tests typically lasted less than 2 minutes including equilibration time, the minute amount of sample used

(notably thin) was significantly affected within this period of time. As the sample is heated up in the oven prior to and during testing, significant loss of moisture occurs, which definitely affects the extensional measurements. For comparison, it was presented earlier that even for samples used in dynamic oscillatory tests, significant changes can occur in as little as 100 seconds at the temperature of 60°C. At 25°C where moisture loss is insignificant as can be seen from the time sweep experiment, there is a very good agreement between the shear data obtained from the sliding plate rheometer and the extensional data.

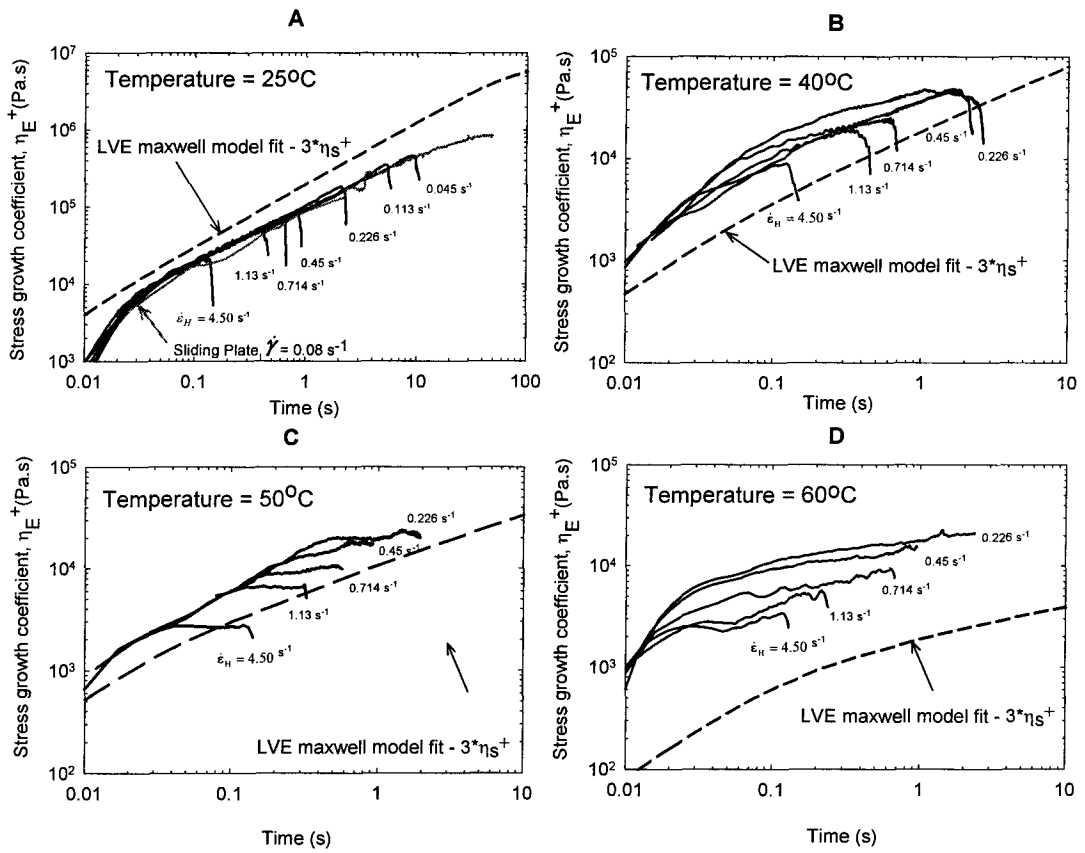


Fig. 7.4 Comparison of tensile stress growth coefficients of mozzarella cheese with the linear viscoelastic envelope predicted from the generalized Maxwell model fit of linear viscoelastic data at A) 25°C, B) 40°C, C) 50°C, and D) 60°C.

To quantify the moisture loss, a simple mass balance experiment was conducted. Mozzarella cheese samples were cut into typical testing dimensions

and they were placed into the oven for a certain period of time at a temperature of 50°C. The mass of the sample before and after being placed into the oven was measured. The difference in mass was taken to be the moisture loss from the cheese. A plot that summarizes the result is shown in Fig. 7.5. It can be seen that during the extensional tests (SER), moisture loss is significant. For example, for the extensional sample to achieve a 5 % loss of moisture is only 0.6 minutes compared to about 20 minutes for the oscillatory test sample. This ratio of about 33 is quite high.

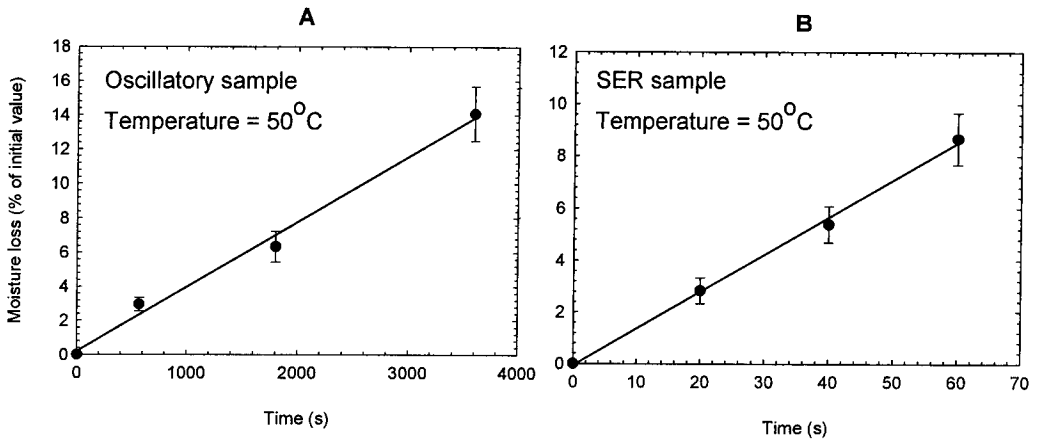


Fig. 7.5 Moisture loss in the mozzarella cheese as a function of time at 50°C for A) oscillatory sample and B) SER sample.

Samples which have been placed into the oven at 50°C for various rest times before testing were tested for their linear viscoelastic properties. The obtained data were subsequently analyzed in terms of the relaxation spectrum and eqn. 7.2 was used to predict the transient shear stress growth as explained earlier. The results are plotted in Fig. 7.6. Satisfactory agreement between shear and extensional data is achieved if the oscillatory sample is left in the oven for about 30 minutes. Referring back to Fig. 7.5, it can be seen that after this period of time, there is about a 6% loss of moisture in the sample used for the oscillatory test. This corresponds to about 42 seconds in the extensional test. This value compares very well with the equilibration time of the sample loaded into the SER in extensional tests. This experiment demonstrates that moisture loss (due to increased temperature) is a crucial factor that can significantly affect the

rheological properties of cheese, especially for samples having a relatively high surface-to-volume ratio. Obviously other structural changes such as degradation, increased separation of fat from the protein matrix, increased ratio of liquid to solid fat and increased mobility of the protein phase with exposure time cannot be excluded (Muliawan and Hatzikiriakos, 2007).

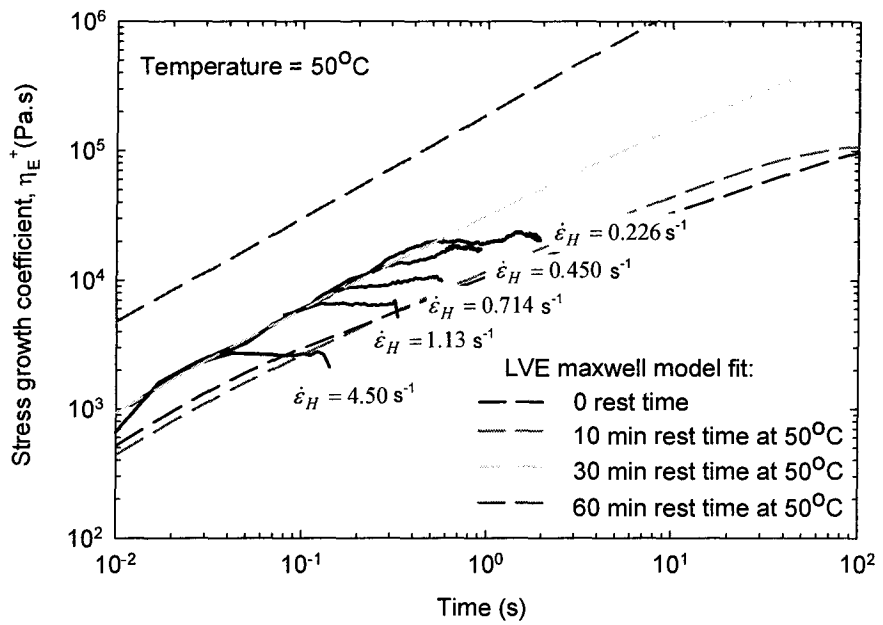


Fig. 7.6 Tensile stress growth coefficient of mozzarella cheese at 50°C and the linear viscoelastic envelope predicted from the fitting of the generalized Maxwell model fit of the linear viscoelastic data obtained from mozzarella cheese samples which have been dried in the oven at 50°C for a certain period of time.

7.4 Summary

Extensional rheology can be used to gain an understanding on the extensional property of mozzarella cheese. It has been shown that under extensional deformation, mozzarella cheese exhibit brittle type of fracture at room temperature. This is indicative of its solid like structure. Upon heating, mozzarella cheese exhibits significant strain softening and ductile type of fracture. Comparison between extensional and linear viscoelastic data was done by generating the extensional stress growth using the generalized Maxwell model

parameters. It was found that there is significant disagreement between the two set of data, especially at higher temperatures. This is due to moisture loss, which is more pronounced in the extensional sample. The extensional sample has a much higher surface area to volume ratio and it was not possible to coat the sample with heavy oil to minimize moisture loss.

CHAPTER 8:

CAPILLARY FLOW

8.1 Introduction

Pressure driven flow through tubes, slits and other types of channels are commonly used to assess the rheology and processability of many polymers. The most commonly used equipment to imitate such a flow is capillary rheometer. Besides typically being used to study flow behaviour of synthetic polymer melts, capillary extrusion has also been widely used in the study of starch-based food products such as cereals, doughs, and potatoes, as it mimics the flow of some food processing technique such as extrusion cooking. Despite this, work done on cheese using capillary rheometer is scarce.

In this chapter, the suitability of capillary rheometry to characterize mozzarella cheese is studied. The rheological data obtained from the capillary rheometer are compared to the linear viscoelasticy to assess the consistency of the measurements. This chapter also provides an assessment of pressure driven flows as a potential post-processing technique for mozzarella cheese.

8.2 Flow Curves

Capillary extrusion experiments were performed at 25°C, 40°C, 50°C, and 60°C. Typical pressure transients obtained from the capillary rheometer are shown in Fig. 8.1. The variance of the steady state extrusion pressure was significant in some cases, as typically expected in the testing of food materials such as cheese (Cheyne et al., 2005). In the present case, the standard deviation of the steady state value for most cases was about $\pm$ 8 %. The variation was due to the heterogeneity of the sample and to the way the sample was extruded. It was observed that the sample did not extrude smoothly, but rather exhibited a stick-slip type of extrusion, particularly at the lower and higher ends of the experimental range of shear rates. This behaviour was also persistent at low

temperatures where the cheese exhibits a certain degree of solid like behaviour. Smith et al. (1980), in their extrusion study on cheddar cheese, associated the variations in the extrusion pressure with fat separation in the cheddar cheese. In the same study, however, they found that the extent of fat separation in mozzarella cheese was not as significant and they were able to gather meaningful extrusion results. In the current work, similar observations were made. Although the extrudates were to some degree "oily" (which indicated some degree of fat separation), it was found that the extrusion data was not significantly affected by the fat separation.

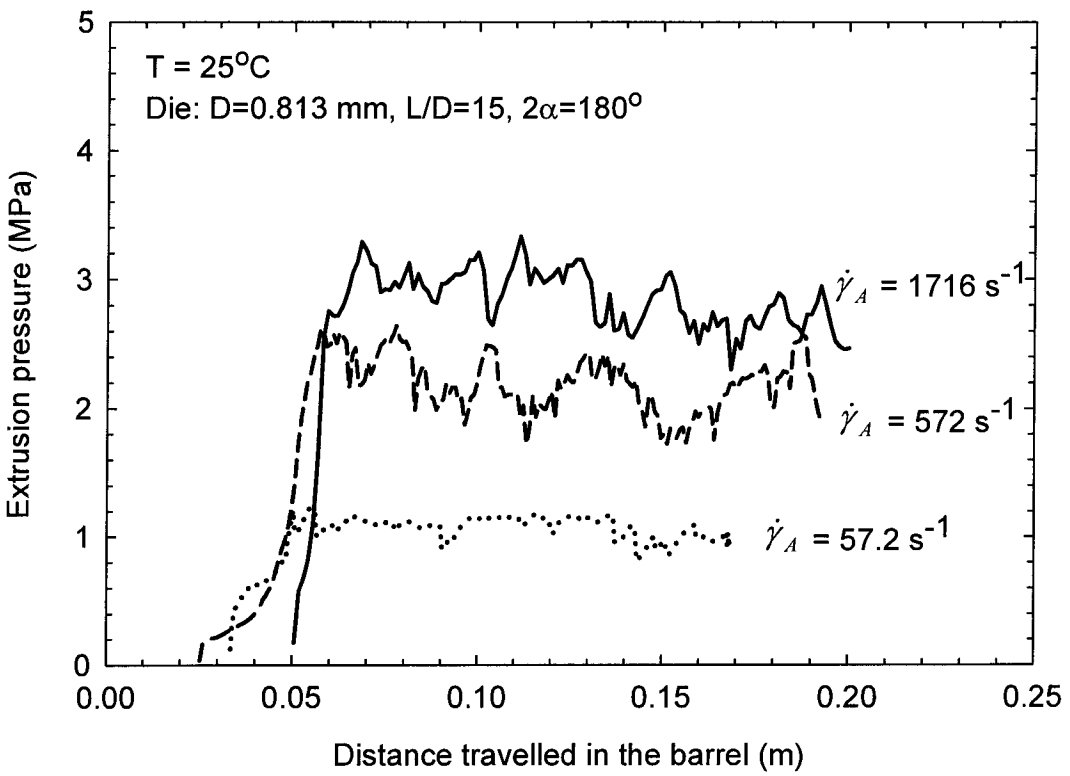


Fig. 8.1 Pressure transients in capillary extrusion of mozzarella cheese obtained by using a capillary die with a diameter of 0.813 mm, L/D of 15 and entrance angle of 180° at shear rates of 57.2 s^{-1} (dotted line), 572 s^{-1} (dashed line), and 1716 s^{-1} (solid line), at 25°C.

Fig. 8.2 depicts the apparent flow curves of cheese obtained from dies having different geometries. As the length of the die decreases, there is a

corresponding increase in the apparent shear stress. This is because a shorter die has a higher end pressure contribution, compared to that of a longer capillary die. In other words, the end pressure correction in shorter dies are more significant than that in longer capillary dies and this observation is true at all temperatures.

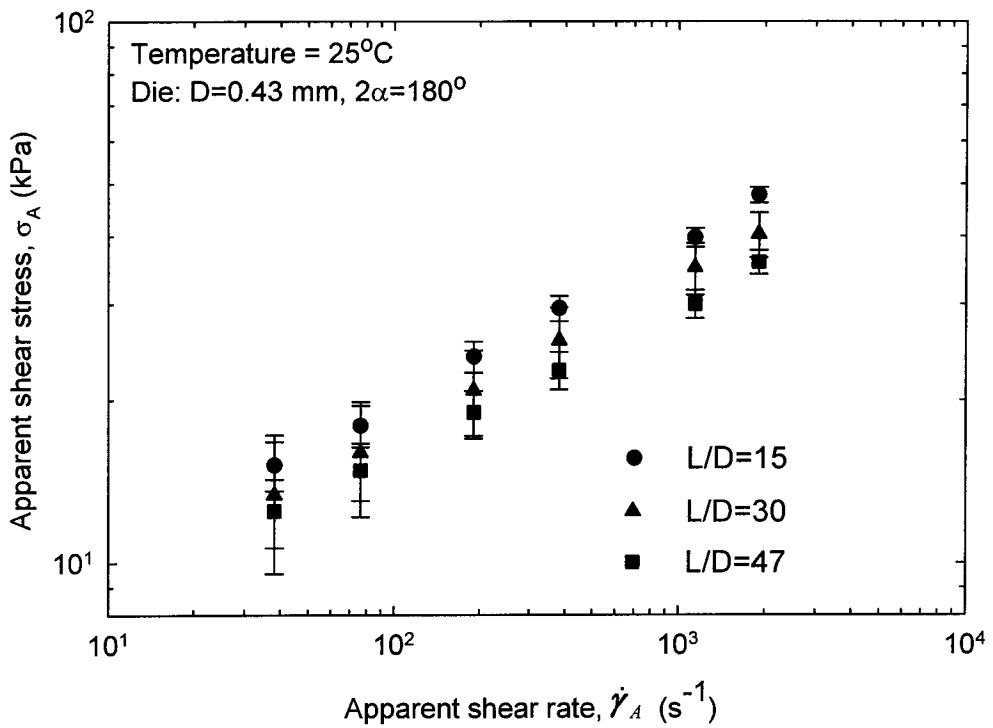


Fig. 8.2 The apparent flow curve of mozzarella cheese obtained from capillary extrusions using capillary dies having a diameter of 0.43 mm, L/D ratios of 15, 30, and 47, and an entrance angle of 180° at 25°C.

To determine the end pressure corrections at the different temperatures, the Bagley method is used, where the extrusion pressure is plotted as a function of L/D for several apparent shear rate values. A typical Bagley plot is shown in Fig. 8.3, where the data at 25°C are presented. As can be noticed in Fig. 8.3, a linear relationship exists between the extrusion pressure and the L/D. This is valid at each temperature. This shows that pressure and viscous heating have no significant effect on the viscosity of the sample, although these have opposite effects in a Bagley plot and can eliminate each other (Rosenbaum and Hatzikiriakos, 1997). Extrapolation of the straight lines to zero L/D, results in the

end pressure, ΔP_{ends} for the specific apparent shear rates. The true shear stress can then be obtained from eqn. 2.35. It is noted that the Bagley correction can be significant and should always be taken into account. For example, at 25°C and at the shear rate of 38 s^{-1}, the end correction accounts for as much as 26 % of the total extrusion pressure. The significance of end pressure in this type of semi solid material has also been reported elsewhere (Smith et al., 1980: Senouci and Smith, 1988; Bagley et al., 1998).

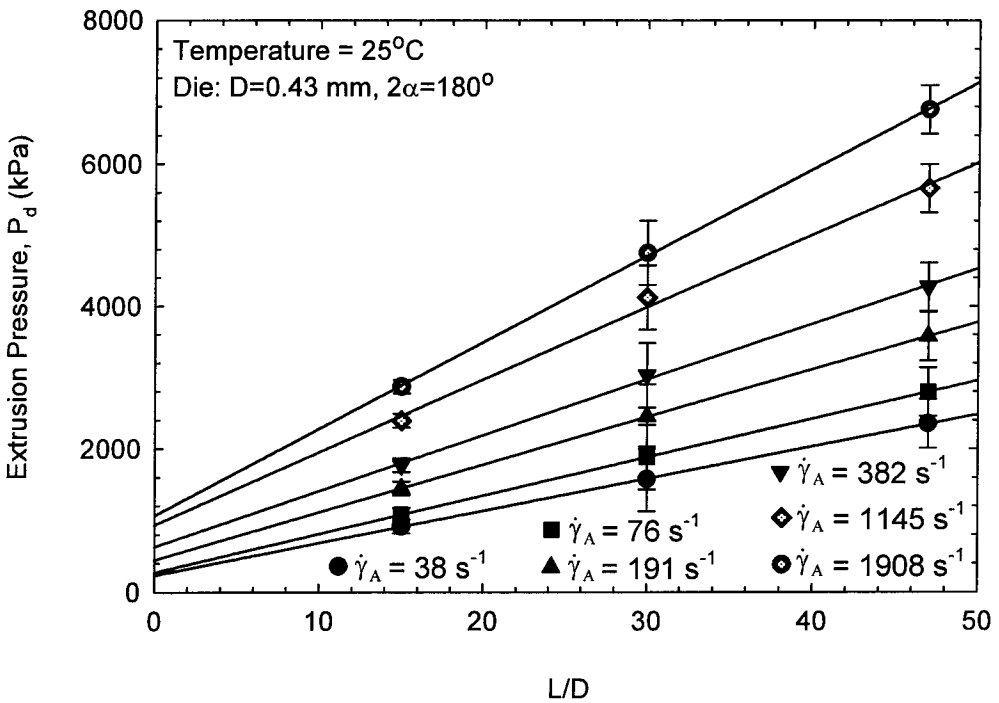


Fig. 8.3 End pressure corrections (Bagley plot) of mozzarella cheese for different shear rates and for a capillary die with a diameter of 0.43 mm and an entrance angle of 180° at 25°C. The straight lines are obtained by linear regression analysis of the data (R^2 = 0.99 for all curves).

A summary of the end pressures at the different temperatures, die diameters and shear rates are tabulated in Table 8.1. Generally, it can be concluded that the end pressures decrease with an increase in temperature. Again, this can be attributed to the fact that mozzarella cheese softens and deforms easily with an increase in temperature.

Table 8.1 A summary of end pressure corrections for the extrusion of mozzarella cheese for dies having different diameters, different apparent shear rate values and at various temperatures.

T = 25°C						T = 40°C	
Die diameter D = 0.43 mm		Die diameter D = 0.81 mm		Die diameter D = 2.18 mm		Die diameter D = 0.97 mm	
Apparent shear rate (s^{-1})	ΔP_{ends} (kPa)	Apparent shear rate (s^{-1})	ΔP_{ends} (kPa)	Apparent shear rate (s^{-1})	ΔP_{ends} (kPa)	Apparent shear rate (s^{-1})	ΔP_{ends} (kPa)
38.2	232.8	5.72	240.5	0.590	218	102.5	317
76.3	273.0	11.4	262.5	1.47	232	138.4	317
190.8	446.5	28.6	351.3	2.94	287	256.3	318
381.6	629.0	57.2	446.6	8.84	362	416.9	314
1144.9	938	171.6	611.0	14.7	364	696.1	314
1908.2	1065	286.1	676.6	29.5	418		
		572.2	865.5	59.0	492		
		1144.4	1076	88.4	547		
		1716.6	1158	147.4	592		

T = 50°C		T = 60°C	
Die diameter D = 0.97 mm		Die diameter D = 0.97 mm	
Apparent shear rate (s^{-1})	ΔP_{ends} (kPa)	Apparent shear rate (s^{-1})	ΔP_{ends} (kPa)
102.5	153	138.4	125
138.4	136	256.3	165
256.3	141	416.9	171
416.9	195	696.1	183
696.1	180	1390.7	242

The Bagley corrected flow curves of Mozzarella cheese at different temperatures are shown in Fig. 8.4. At each temperature, the flow curves corresponding to the dies with different L/D ratios now falls on a single line, defining uniquely the apparent flow curve of the mozzarella cheese. In addition, as the temperature increases, the wall shear stress decreases. The flow curve at 25°C has a slope of about 0.24 which is significantly different from those at the higher temperatures (~ 0.40). This is obviously due to the different nature (structure) of cheese at low temperature (solid-like) compared to that at higher temperatures (liquid-like), as previously illustrated in temperature sweep linear viscoelastic measurements.

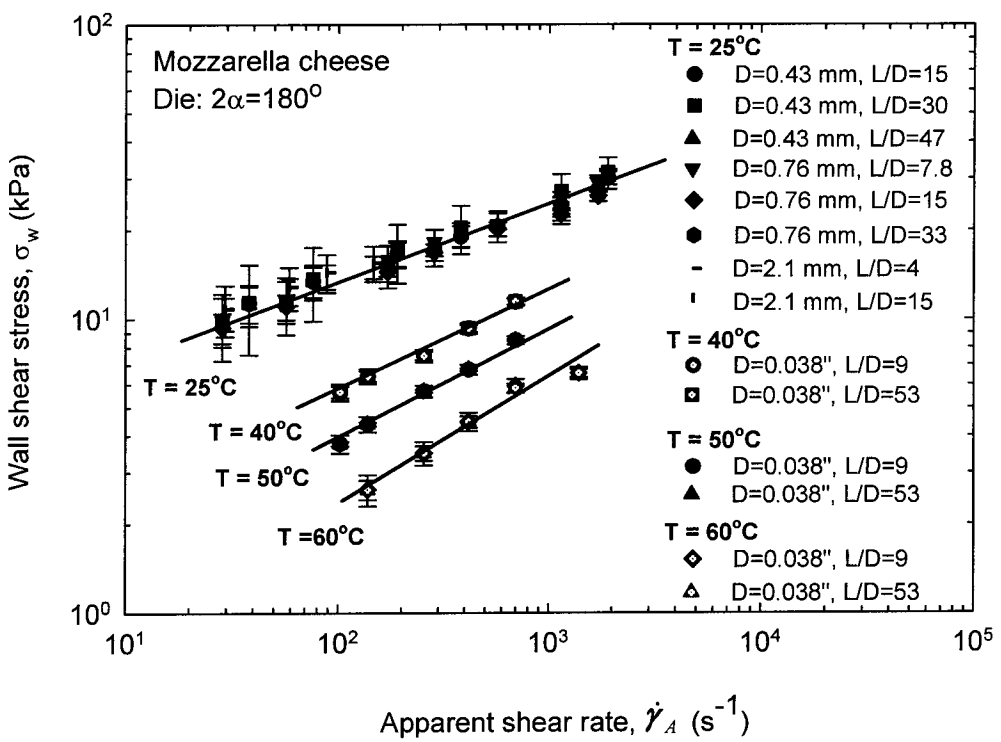


Fig. 8.4 The Bagley corrected flow curves of mozzarella cheese at the temperatures of 25°C, 40°C, 50°C, and 60°C obtained using capillary dies with various diameters, L/D ratios and an entrance angle of 180°. The straight lines shown are obtained by linear regression analysis of the data (R^2 = 0.97, 0.98, 0.99, and 0.93 for 25°C, 40°C, 50°C and 60°C respectively).

The slopes of these Bagley corrected flow curves are used to determine the Rabinowitch correction for each temperature as discussed in section 2.4.3. Table 8.2 summarizes the Rabinowitch correction at each temperature. Table 8.2 lists the decrease of Rabinowitch correction with an increase in temperature. The Rabinowitch correction is then used to calculate the true wall shear rate at the different temperatures following equation (2.32). The true flow curves of mozzarella cheese for the different temperatures can then be constructed, and these are shown in Fig. 8.5. Comparing to Fig. 8.4, these flow curves are essentially shifted along the shear rate axis according to the value of the Rabinowitch corrections.

Table 8.2 Rabinowitch correction for the capillary extrusion of mozzarella at different temperatures.

Temperature (°C)	Rabinowitch correction
25	4.1
40	2.7
50	2.4
60	2.4

8.3 Wall Slip

Possible wall slip effects can be observed from the flow curves of the material obtained using dies of different diameters. As can be seen clearly from Fig. 8.5, at 25°C, the flow curve of mozzarella cheese is independent of the die diameter and therefore no slip effects are present in capillary extrusion up to wall shear stress values of about 30 KPa. This value is perhaps too low to observe wall slip. In fact, reports by Corfield et al. (1999) and Halliday and Smith (1995) on the extrusion of potato pastes show that the critical shear stress for the onset of wall slip is in the range of 40 to 60 KPa, which is outside the wall shear stress window encountered in this study (Muliawan and Hatzikiriakos, 2007b).

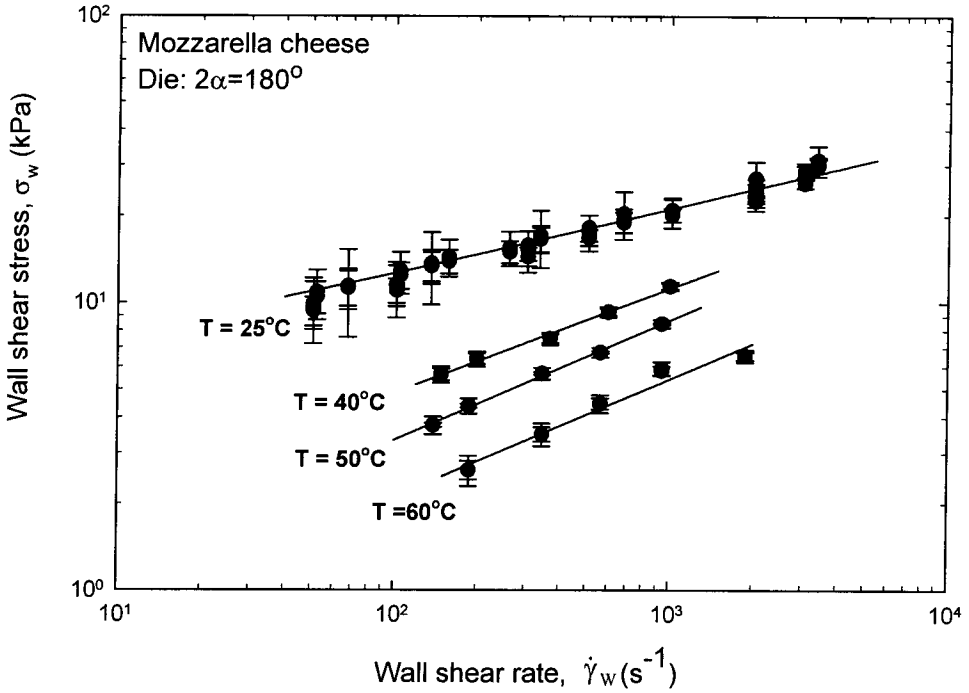


Fig. 8.5 The true flow curves of mozzarella cheese at temperatures of 25°C, 40°C, 50°C, and 60°C obtained using capillary dies with various diameters, L/D ratios and an entrance angle of 180°. The straight lines shown are obtained by linear regression analysis of the data (R^2 = 0.97, 0.98, 0.99, and 0.93 for 25°C, 40°C, 50°C and 60°C respectively).

8.4 Effects of Die Geometry

Dies of different entrance angles were also used to extrude the mozzarella cheese. The apparent shear stress, σ_A, is depicted as a function of the contraction angle, 2α for several values of the apparent shear rate, $\dot{\gamma}_A$ in Fig. 8.6. There seems to be an optimum value of entrance angle at which the wall shear stress is minimized. This trend has also been observed in the extrusion of polytetrafluoroethylene (PTFE) paste where it was found that at sufficiently small entrance angle, the flow of the material in the die conical section follows a plug flow type of pattern known as "radial flow" (Ariawan et al., 2002). The decrease of the apparent shear stress at small entrance angles is consistent with the lubrication approximation for flow of molten polymer and other materials (Dealy and Wissburn, 1990). The slight increase in the apparent shear stress beyond a certain entrance angle (30°) is also consistent with the trends observed in the

extrusion of elastic solids (Horrobin and Nedderman, 1998; Ariawan et al., 2002). Although this set of experiment was performed only at a temperature of 25°C, it is expected that at higher temperatures, where the flow properties of the mozzarella cheese are similar to those of molten polymer, the effect of die geometry on the flow curve will exhibit similar trend.

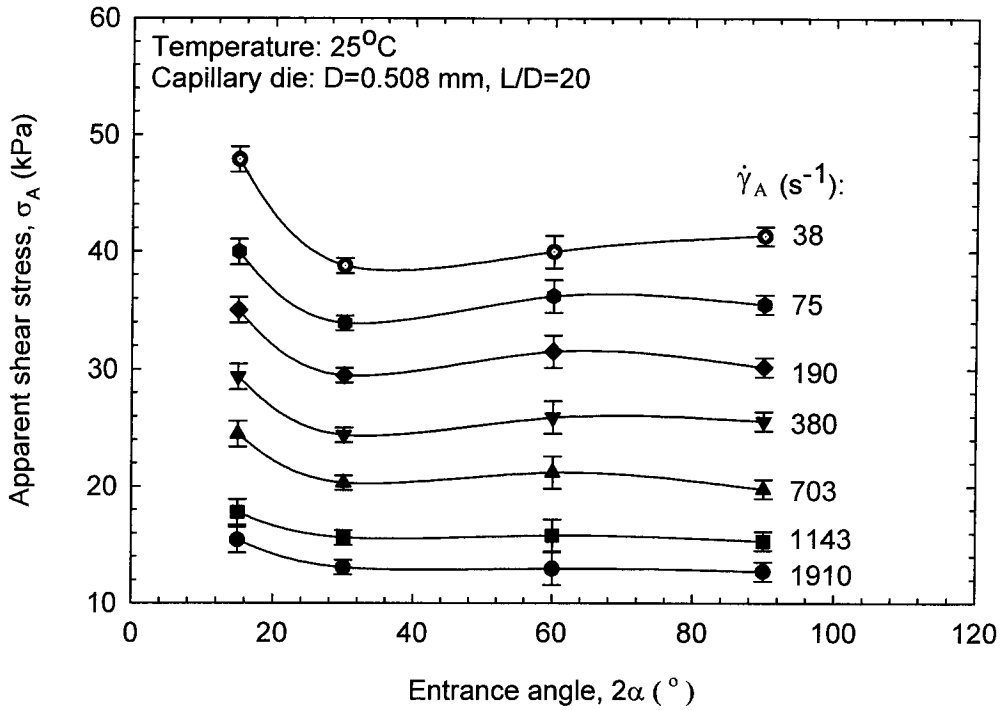


Fig. 8.6 The effect of entrance angle, 2α, on the apparent shear stress in the extrusion of mozzarella cheese at 25°C and several apparent shear stress values.

8.5 Extrudate Appearance

Typical extrudates collected from the extrusion experiments are shown in Fig. 8.7. The extrudates were obtained from the extrusion of the cheese sample at 25°C using a die with a diameter of 0.813 mm, L/D of 15 and entrance angle of 180°. These pictures were taken using an optical microscope (Olympus Mic-D, Olympus, Center Valley, PA, USA). Surface defects appear even at very small shear rate values. At such relatively low temperature, the mozzarella cheese retains its solid like behavior and tends to fracture as it is extruded. Surprisingly, the surface of the extrudates improves as the shear rate increases. A possible

explanation is that the extrusions at relatively high shear rates may generate sufficient shear heating which causes the cheese in contact with the die wall to melt locally and thus flow easily. At 60°C (Fig. 8.7b), the extrudates all show relatively smooth surface (even for shear rate as low as 27 s^{-1}). At 60°C, cheese is in a melt state and it flows through the contraction instead of fracturing. This results in a defect free extrudate surface. Furthermore, it has also been reported that at 60°C, there is an absence of yield stress which should induce capillary flow readily, even at relatively low shear rates (Muliawan and Hatzikiriakos, 2007b).

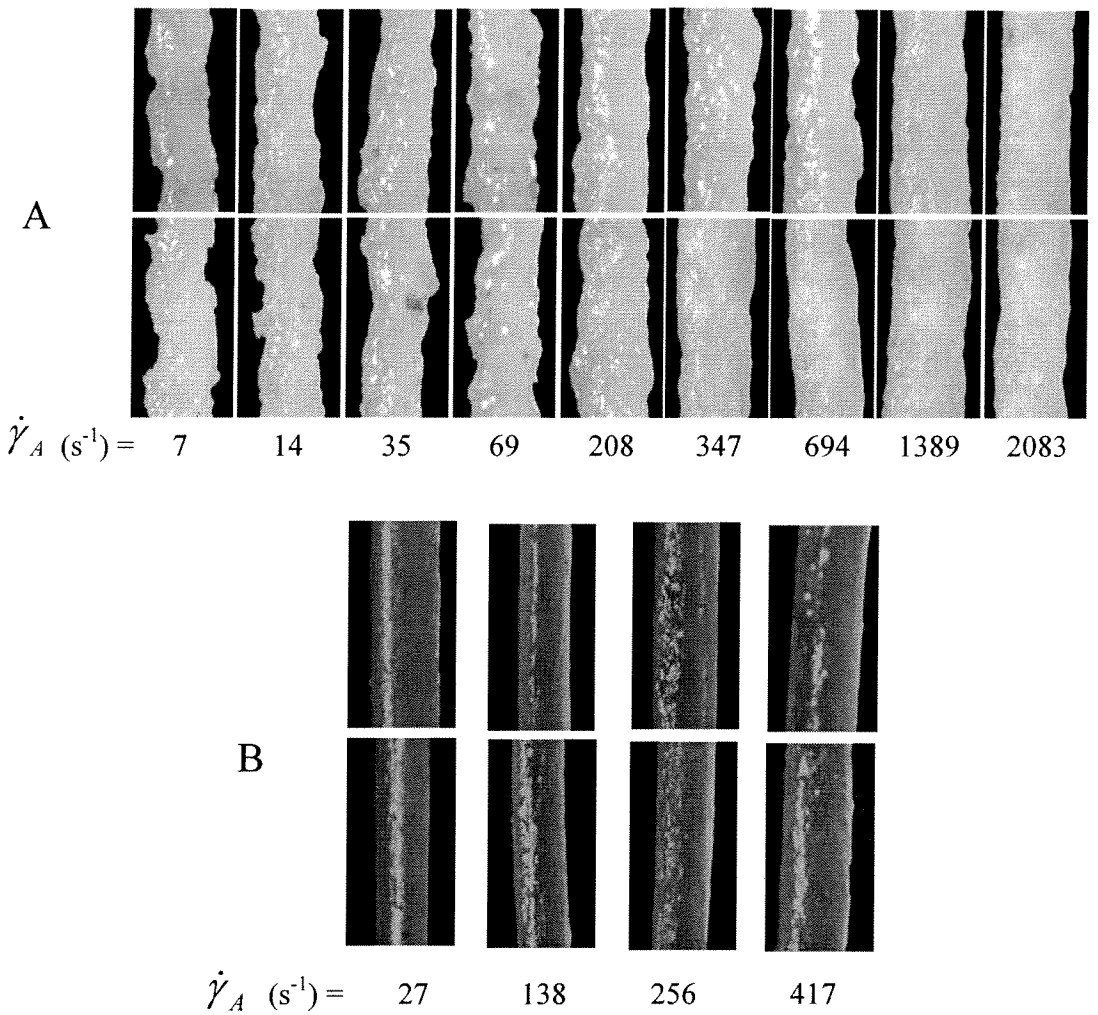
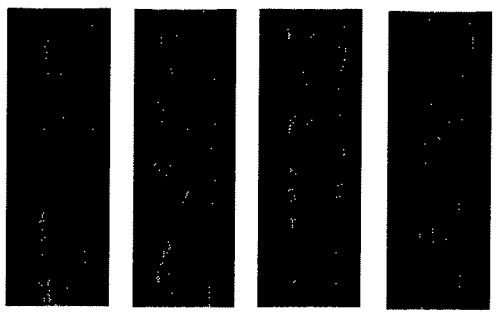


Fig. 8.7 Extrudate appearance of mozzarella cheese obtained from capillary extrusion at different shear rates at A) 25°C, and B) 60°C.

It appears that the entrance angle of the die does not have any significant effect on the extrudate appearance as can be seen from Fig. 8.8. Furthermore, extrusions using dies with different lengths and diameters have shown that these geometrical characteristics have no significant effect on the extrudate appearance.



$2\alpha =$ 15° 30° 60° 90°

Fig. 8.8 Extrudate appearance of mozzarella cheese obtained from capillary extrusion using capillary dies with a length of 10.2 mm (0.4"), diameter of 0.508 mm (0.02") and different entrance angles at a shear rate value of 38 s^{-1} at 25°C.

8.6 A Viscoplastic Model for Capillary Flow of Mozzarella Cheese

In Fig. 8.9, the true flow curve is given for mozzarella cheese as derived from capillary experiment at 25°C. The flow curve obtained from the sliding plate is also shown. At sufficiently low shear rates, the data obtained from the sliding plate rheometer is more reliable because the sliding pate rheometer has a smaller force transducer capacity. It can be seen from Fig.8.9 that there is generally a very good agreement between the two sets of data. The experimental data were successfully fitted with the Herschel-Bulkley viscoplastic model:

$$\sigma = \sigma_y + K\dot{\gamma}^n \qquad \text{for} |\sigma| > \sigma_y \qquad (8.1a)$$

$$\dot{\gamma} = 0 \qquad \text{for } |\sigma| \le \sigma_y \qquad (8.1b)$$

where σ is the shear stress, $\dot{\gamma}$ is the shear rate, σ_y is the yield stress, K is the consistency index, and n is the power-law index. In this case, $\tau_y = 1.93$ KPa, $K = 3.34$ kPa·s, and $n = 0.25$. Note that when $n = 1$ and $K = \mu$ (a constant), the

Herschel-Bulkley model reduces to the Bingham model. When $\tau_y = 0$, the power-law model is recovered, and when $\tau_y = 0$ and $n = 1$, the Newtonian model is obtained.

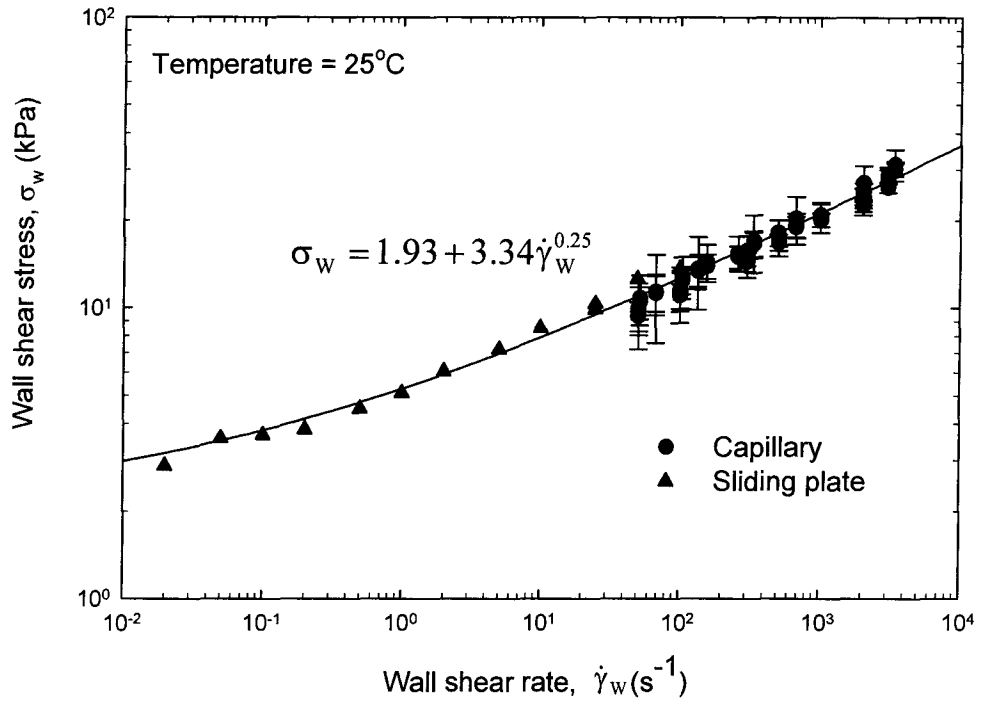


Fig. 8.9 True flow curve of mozzarella cheese obtained from capillary and sliding plate rheometers at 25°C. Solid line is a Herschel-Bulkley viscoplastic model fit of the experimental data.

As was presented earlier in chapter 6, the yield stress value acquired from the shear-ramp viscometry test for mozzarella cheese at 25°C was 1620 ± 93 Pa. This agrees reasonably well with the yield stress value derived from the fitting of capillary data, i.e., τ_y = 1930 kPa. An interesting point to note is also the fact that this stress value is in close proximity of the limit of linear viscoelasticity which is about 1500 Pa (see Fig. 5.2). Thus, it is clearly illustrated here that at 25°C, yield stress exists for mozzarella cheese and that to impose a flow under this condition, the structure of the mozzarella cheese has to be broken. As will be presented below, this will form the basis to explain the consistencies (or inconsistencies) between the result obtained from linear rheology and capillary flow.

8.7 Comparison with Linear Rheology

Plots that depict a comparison between the dynamic and absolute viscosity in shear are shown in Fig. 8.10. Viscosity data obtained from the sliding plate rheometer at 25°C are also plotted (Muliawan and Hatzikiriakos, 2007). Very good agreement can be seen between the viscosity determined from the sliding plate and capillary rheometers. On the other hand, the dynamic and steady viscosities are different at 25°C, 40°C and 50°C. First of all, it should be stressed that this disagreement is not due to moisture loss as the samples in these tests were exposed minimally and structural changes occurred much slower compared to those in extensional tests. The lack of agreement shows that cheese does not follow the classical Cox-Merz rule that typically applies to simple polymer melts at least over a range of shear rates. Bistany and Kokini (1983) reported similar result for various types of food materials such as butter, ketchup, margarine and cream cheese. They suggested that the dynamic and steady shear data can be superposed by shifting the dynamic data; no scientific reason was given for the necessity to this shift. Similar observation has also been reported by Doraiswamy et al. (1991) for concentrated suspension systems and Yu and Gunasekaran (2001) for different types of food such as ketchup, yogurt, mayonnaise, and mozzarella cheese. These systems including mozzarella cheese possess structure and therefore exhibit a yield stress at relatively low temperatures.

As presented in chapter 6, the yield stress of cheese found using the shear ramp viscometry method were 1620 $\pm$ 93 Pa at 25°C, 216 $\pm$ 19 Pa at 40°C and 1.4 $\pm$ 0.3 Pa 50°C. At 60°C, however, it was not possible to determine a yield stress value as the cheese loses its structure due to melting. Based on these observations, it can be presumed that at 25°C, 40°C and 50°C, the cheese sample is viscoplastic, possessing a structure, whereas at 60°C, the structure breaks and as a result the cheese behaves like a viscoelastic fluid.

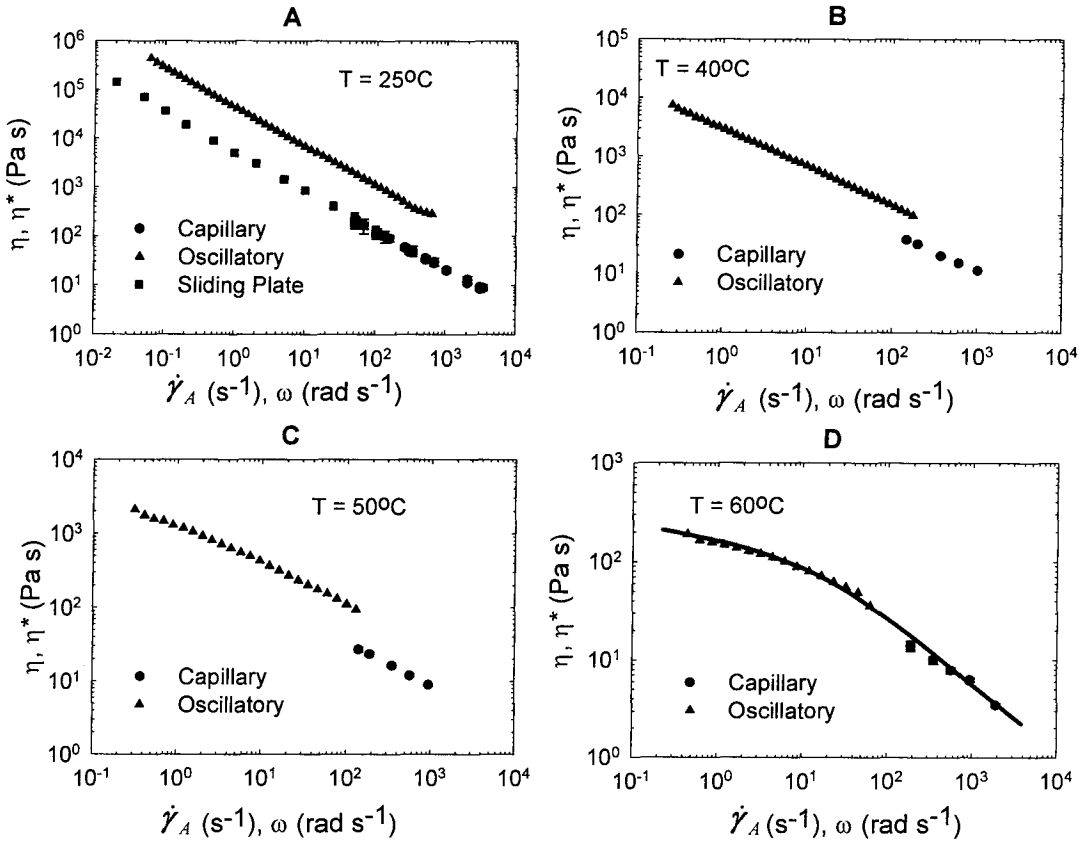


Fig. 8.10 Comparison of viscosities of mozzarella cheese obtained from linear oscillatory shear and capillary extrusion experiments at A)25°C, B)40°C, C)50°C, and D)60°C.

Based on this yield stress analysis, the discrepancy between the dynamic and steady shear viscosity data plotted in Fig. 8.10 can be explained. At 25°C, the dynamic oscillatory data are collected using a very small stress well below the yield stress. This causes no destruction of the structure. On the other hand, in extrusion and sliding plate experiments, the deformations are non-linear and result in stresses that are well beyond the yield stress. These essentially break any existing structure in the material and the material exhibits its fluid-like character (Muliawan and Hatzikiriakos, 2007). This observation has also been reported by Yu and Gunasekaran (2001) on their work on yogurt. They attribute the discrepancy to the presence of a weak gel structure that is broken in the large scale deformation but stays intact during small amplitude oscillatory shear experiments. Similarly, at 40°C and 50°C, the fact that yield stress exists at these

temperatures show that the cheese still maintains the structure of the protein matrix to a certain extent as the protein has not been totally mobilized. Again, extrusions at these temperatures involve large strain deformations that essentially break the structure of the cheese. Small amplitude oscillatory shear experiments at these temperatures are again performed at deformations which are small enough that the structures are preserved. This causes the disagreement between the capillary and oscillatory rheological data.

At 60°C, the mozzarella cheese loses its structure as most of the protein is highly mobile. This is reflected in its insignificant yield stress. Thus, at 60°C, dynamic oscillatory tests were performed at a deformation which causes the cheese sample to actually flow; consistent with the large scale deformation imposed during capillary flow. This explains the agreement between the dynamic and steady shear data at 60°C.

8.8 Summary

In this chapter, capillary extrusions were used to characterize mozzarella cheese rheologically. Bagley or end-pressure corrections were found to be significant, especially at lower temperatures. Surprisingly, wall slip was found to be insignificant in this specific study due to small shear rates attained. In general, the flow of mozzarella cheese can be described by a Herschel-Bulkley model. The extrudates collected during the extrusions were analyzed visually and it was found that at 25°C, the extrudates obtained were highly distorted. On the other hand, at 60°C, the extrudates have smooth profile. This indicates that extrusion can be used as processing method for mozzarella cheese at relatively high temperatures. In comparing with linear rheology, it was found that at lower temperatures, there is a significant disagreement between capillary and linear viscoelastic data. This was attributed to the presence of yield stress. This discrepancy disappears at 60°C due to the absence of yield stress.

CHAPTER 9:

ROLL FORMING

9.1 Introduction

Forming using rollers are commonly used in the forming of metals and sheeting of synthetic polymers; processes known as cold or hot rolling and calendaring respectively. In the food industry, rolling is mostly performed to sheet dough for bread and cookie production. Consequently, roll forming experiments to characterize dough and to model the sheeting process have been done by several authors (Levine, 1996; Engmann et al., 2005; Peck et al., 2006). Rolling of cheese, however, has not been used before as an alternative method of cheese processing.

In this chapter, the results obtained from roll forming experiments of mozzarella cheese at 25°C are presented. Rolling experiments were performed for the different reduction ratios and the shear stress on the rollers is calculated (according to Eqn. 2.37). The results presented here also include the initial and exit thickness of the mozzarella cheese samples at the different reduction ratios. Finally, several images of the rolled samples are presented.

9.2 Roll Forming of Mozzarella Cheese

Roll forming experiments were performed at 25°C. Similar to the extrusion experiments, the variance of the steady state rolling force is significant in some cases. Typical transient rolling curves are plotted in Fig. 9.1. In this case, the standard deviation of the steady state value for most cases can be as high as ± 20 %. Peck et al. (2006), on their rolling experiments on flour dough, observed data variation of about 17%. Thus, it appears that such variation is typical in food materials where sample heterogeneity can be significant. To minimize the effect of these variations, replicates of at least four runs were performed to generate the rolling curves. The measurement data presented is an average of these

different runs, with pooled standard deviations taken as an indication for error of these data.

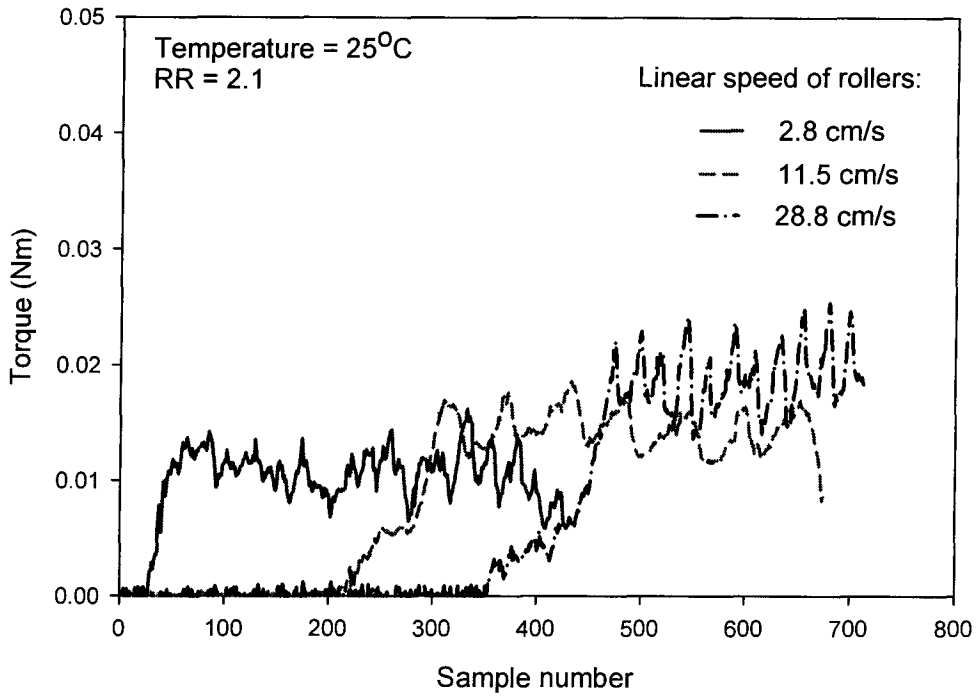


Fig. 9.1 Typical transient rolling curves of mozzarella cheese at a reduction ratio of 2.1 and at 25°C for various roller speed.

The rolling shear stress as a function of the roller linear speed for the different reduction ratio (RR) is shown in Fig. 9.2. The rolling shear stress and the linear speed of the roller follow a power law relationship for a given reduction ratio value. An increase in roller speed results in an increase in shear stress. The rate dependence can be represented with a power law index of 0.26, 0.27, 0.28, and 0.25 for the reduction ratios of 1.4, 1.7, 2.1, and 2.3 respectively. These values compare well with the slope of the flow curve obtained from the capillary extrusion experiments at 25°C (see Fig. 8.5). Roughly speaking, dividing the roller speed by the distance between the rollers results in a characteristic shear rate and thus such agreement is not surprising. Furthermore, these values appear to be in good agreement with those observed in the rolling of bread dough (Engmann et al., 2005). A higher reduction ratio also results in a higher rolling shear stress due to the higher extensional strain rate required to roll the

cheese into the gap. The shear stress appears to increase with the reduction ratio exponentially (see Fig. 9.3) which is in agreement with the rolling of soft and hard flour doughs at comparable reduction ratios (Peck et al., 2006).

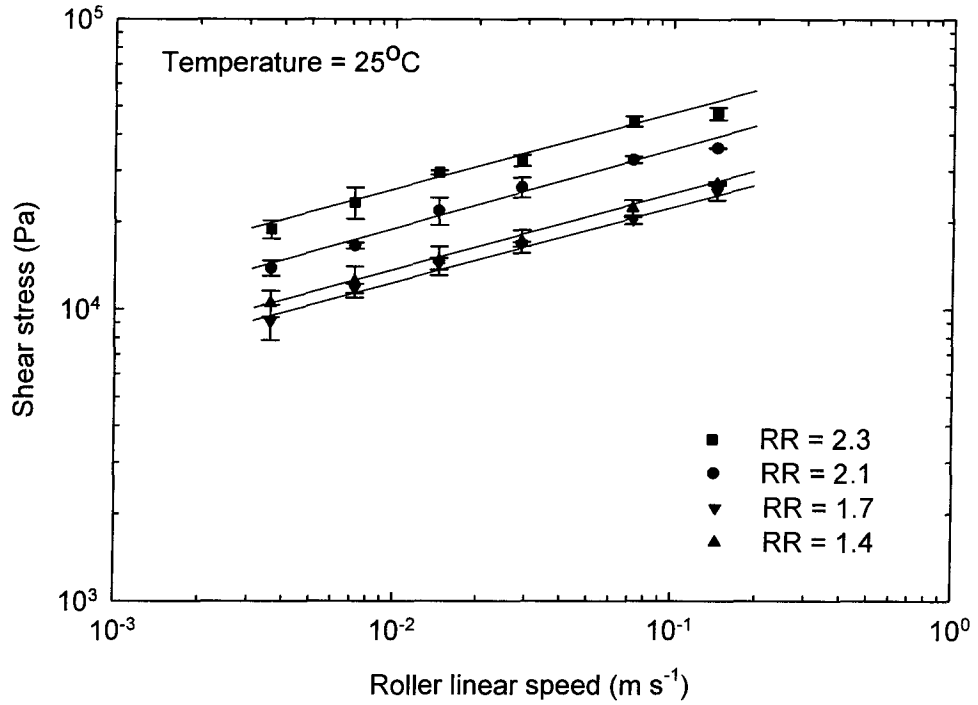


Fig. 9.2 Rolling curves of mozzarella cheese for different reduction ratios at 25°C.

The thickness of the sample as it exits the rollers was also measured in order to determine the elastic recovery of the material. The recovery in thickness can be used as a measure of elasticity i.e. the ability of the material to store energy when it passes through the rolls which is being released after and manifests itself as recovery in thickness (Muliawan and Hatzikiriakos, 2007b).

The rolled samples were allowed to relax fully before the thickness were measured using a caliper. Fig. 9.4 shows the recovery of thickness (exit thickness/roller gap) as a function of the roller speed for different reduction ratios. For a constant reduction ratio, the thickness recovery of the sample increases with roller speed. Thus, samples that are rolled at higher roller speed experience higher degree of swelling. It can also be seen that for a reduction ratio of 2.3, the

reduction in the thickness of the samples can be quite significant (as high as 22% of the initial sample thickness). It must also be noted that the standard deviation of the measurements at the reduction ratio of 2.3 is relatively higher than those corresponding to lower reduction ratios. This is because the deformation at such reduction ratio is quite significant which causes the sample to fracture.

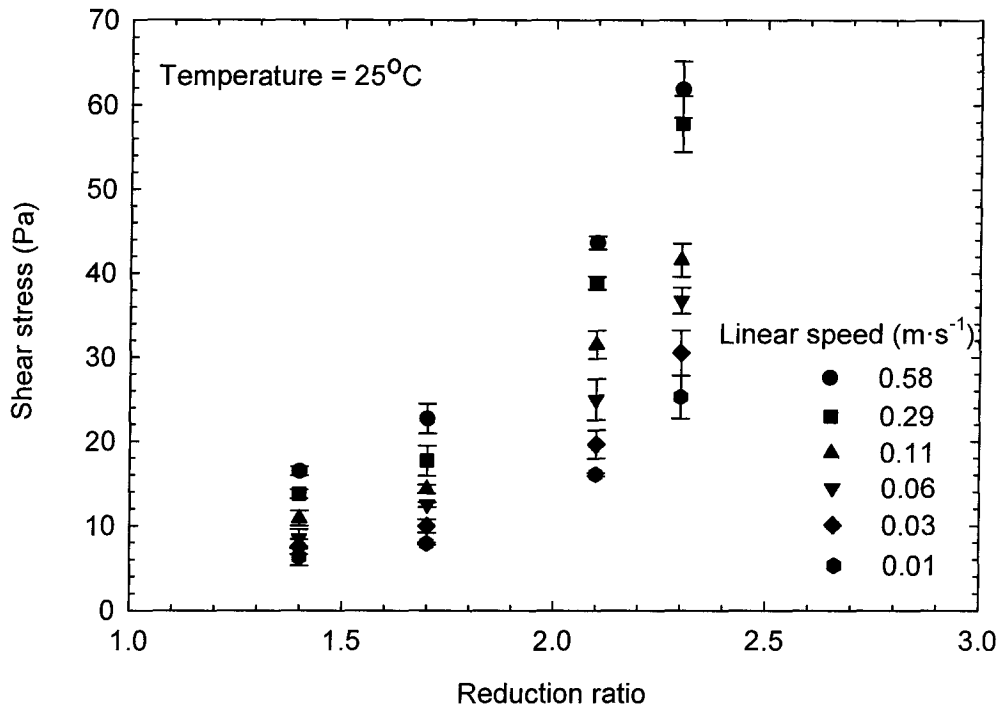


Fig. 9.3 Rolling shear stress as a function of reduction ratio for different linear speed for mozzarella cheese at 25°C.

Fig. 9.5 shows pictures of typical rolled samples. In general, at relatively low reduction ratios (<2.1), the cheese was able to be rolled cleanly, without any significant adherence of the cheese on the rollers. Significant sample deformation occurs at reduction ratios of 2.3 and 2.7 which causes some cheese samples to stick to the rolling drums as rolling occurs. In any case, rolling seems to be a viable option to shape mozzarella cheese as long as the reduction is kept relatively small (< 2.1) to maintain the structure of the cheese (Muliawan and Hatzikiriakos, 2007b).

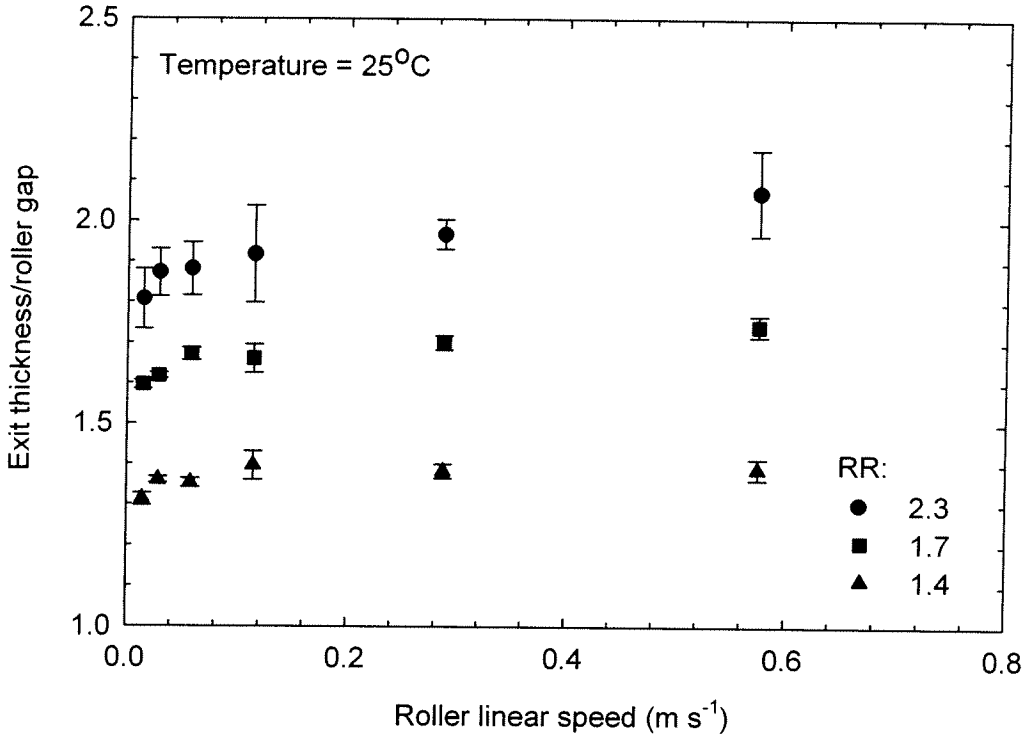


Fig. 9.4 The effect of roller speed on the exit thickness of the samples for reduction ratios of 1.4, 1.7. and 2.3 at 25°C. The exit thickness is normalized by the gap between the rollers (0.241 cm).

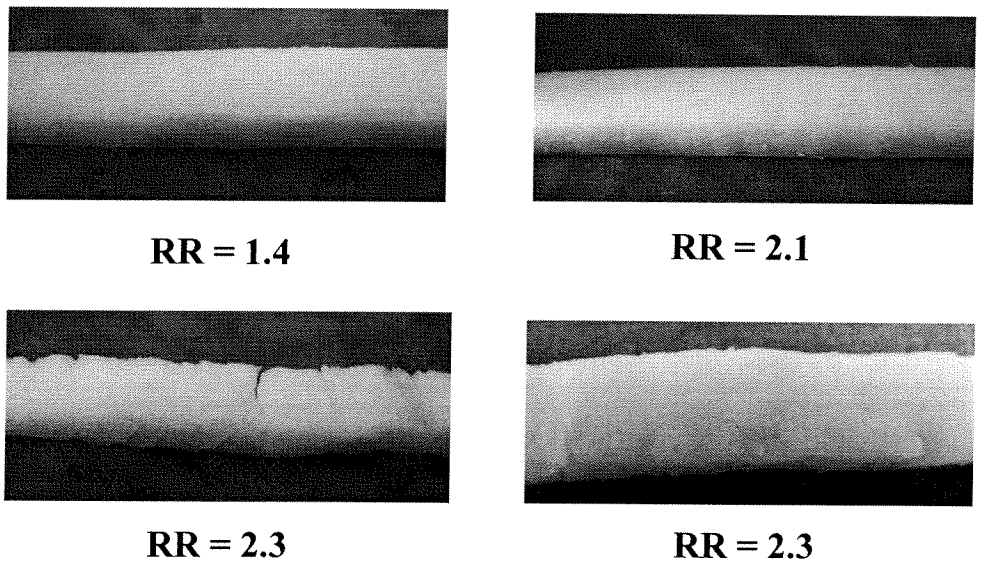


Fig. 9.5 Typical images of rolled mozzarella cheese samples at 25°C.

9.3 Summary

In the food industry, rolling is a technique which is widely used in the processing of dough. It has been shown that rolling can be used to process mozzarella cheese. In general, the rolling curves are consistent with the flow curves obtained from capillary extrusions. Based on the rolled samples, rolling has the potential to be a feasible technique for cheese processing, as long as the reduction ratio is kept to minimum.

CHAPTER 10:

COMPARATIVE STUDY OF FREEZING AND RHEOLOGY OF DIFFERENT BRANDS OF MOZZARELLA CHEESE

10.1 Introduction

In the last few years, the emergence of frozen foods has prompted the food industry to investigate the effect of storage on their products. In products such as frozen pizzas and lasagnas, the stability of cheese is very crucial because it is usually the only cooked ingredient in these products. Consequently, several studies on the effect of frozen storage on the viscoelastic properties of mozzarella cheese have been done (Ak and Gunasekaran, 1996; Bertola et al., 1996; Chaves et al., 1999; Cervantes et al., 1983). They have concluded that, in general, ripened mozzarella cheese can be stored frozen (sub zero temperature) for several weeks without significant effects. Storage at cold temperatures (0°C to 10°C), however, results in refrigerated aging, which causes the mozzarella cheese to have reduced dynamic moduli (Ak and Gunasekaran, 1996).

In this chapter, the extensional and linear viscoelastic properties of different brands of mozzarella cheese are studied and compared. The three different brands are namely Best Buy mozzarella cheese (Lucerne, Canada), which has already been studied extensively in the previous chapters, Kraft processed mozzarella cheese (Kraft Foods, Canada) and Ziggy's mozzarella cheese (President's Choice, Canada). The linear viscoelastic properties of the mozzarella cheese after sub-zero refrigerated storage are also determined. Several blocks of these different brands of cheese were purchased from a local grocery store and they were stored in a freezer at approximately -10°C. Before testing, the cheese was thawed at room temperature for about 12 hours.

Table 10.1 summarizes the chemical composition of these mozzarella cheeses (J.R. Laboratory, Burnaby, BC). The Table shows that the three different

brands of mozzarella cheese do not exhibit significant differences in terms of their compositions. However, as will be illustrated later, these different mozzarella cheeses exhibit quite different linear viscoelastic properties.

Table 10.1 Compositional analysis of the different brands of mozzarella cheese.

Component	Best Buy	Kraft	Ziggy's	Detection Limit	Method
Carbohydrate	6.08 wt.%	4.34 wt.%	6.97 wt.%	-	Calculated as (100 – wt.%moisture – wt.%protein – wt.%fat – wt.%ash)
Fat	25.29 wt.%	23.05 wt.%	24.45 wt.%	0.10%	Modification of AOAC 991.36 (extraction time at boiling was 3.5 hours instead of 25 minutes; drying oven temperature was 100oC instead of 125°C)
Moisture	42.44 wt.%	43.69 wt.%	40.77 wt.%	0.10%	AOAC 950.46
Protein-total	22.60 wt.%	24.92 wt.%	24.31 wt.%	0.50%	Modification of AOAC 981.10 (weight of sample was 1.0 g instead of 2.0 g; digestion time was 2.5 hours instead of 45 minutes; acid used for titration was sulfuric acid instead of hydrochloric acid)
Calcium	745.2 mg/100g	752.5 mg/100g	715.5 mg/100g	-	Modification of AOAC 985.35 (microwave digestion instead of ashing)

10.2 Extensional Properties

Samples cut in three different directions; perpendicular, parallel and in transverse directions were tested under extensional deformation at 25°C to determine if the mozzarella cheese exhibit anisotropic behavior. Figs 10.1 and 10.2 summarize the results for Kraft and Ziggy's mozzarella cheese respectively. As can be seen from Fig. 10.1, the Kraft processed mozzarella cheese exhibits some degree of anisotropic behavior. This anisotropic behavior is shown as an increase of extensional stress growth for a specific sample cut, which indicates

that the specific cut is along the direction of the protein fiber orientation (Ak and Gunasekaran, 1997). Ziggy's mozzarella cheese, on the other hand, does not seem to exhibit such anisotropy (Fig. 10.2). This is similar to the behaviour found in Best Buy mozzarella cheese (see section 7.2). Thus, most probably, the anisotropic behavior in the Kraft processed mozzarella cheese arises due to the different technique used to manufacture the processed cheese. Unfortunately, the details of the technique is unavailable, thus it is not possible to further assess this behavior.

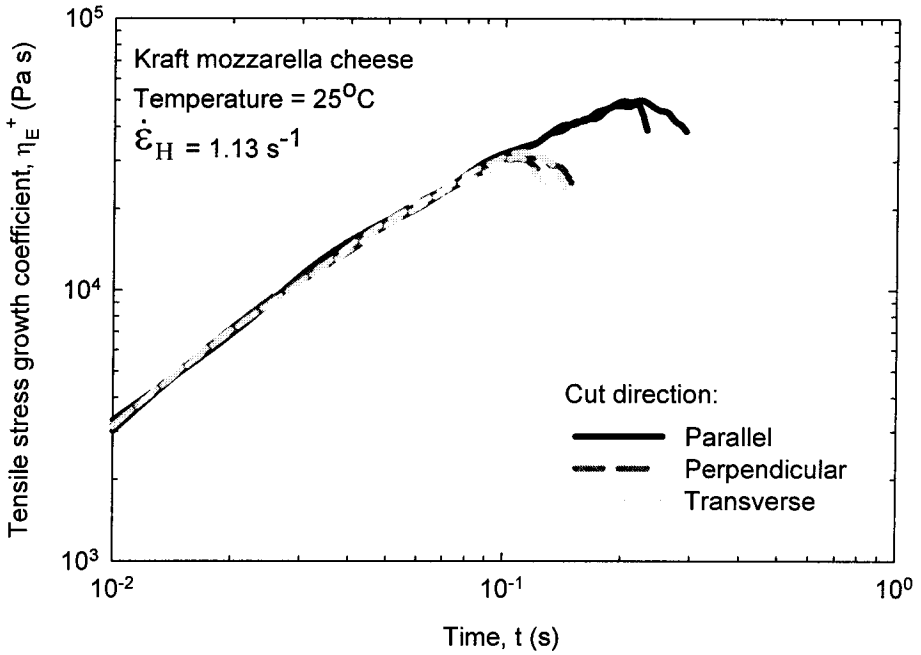


Fig. 10.1 Tensile stress growth coefficient of Kraft mozzarella cheese samples prepared by cutting in three different directions at a Hencky strain rate of 1.13 s^{-1} and temperature of 25°C.

Stress growth extensional curves for the two different brands of cheese are shown in Figs 10.3 and 10.4. In general, the extensional behavior of these cheeses are very similar to that exhibited by Best Buy mozzarella cheese (see Fig 7.2). In all cases, for the different Hencky strain rates, a rapid increase in the extensional stress growth can be observed which is followed by a sudden decrease in the tensile stress growth curves. This is, as explained earlier, an indication of the solid like behavior of the mozzarella cheese.

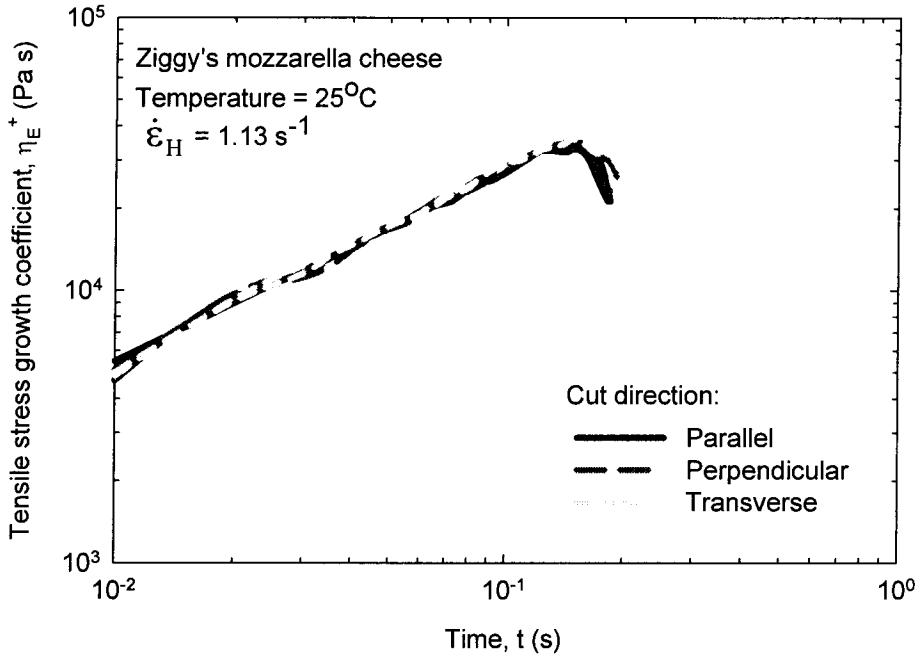


Fig. 10.2 Tensile stress growth coefficient of Ziggy's mozzarella cheese samples prepared by cutting in three different directions at a Hencky strain rate of 1.13 s^{-1} and temperature of 25°C.

10.3 Limit of Linear Viscoelasticity and Sample Stability

Dynamic stress amplitude sweeps at 25°C, 40°C, 50°C and 60°C were performed for the different brands of cheese. It was found that for up to eight weeks of frozen storage, there was no significant difference. The limits for the onset of non-linearity for Kraft and Ziggy's mozzarella cheese are very similar to Best Buy's (see Table 5.1).

Time sweep experiments were also performed on the different brands of cheese to determine the stability of the cheese during experiment. Again, the result is very similar to that exhibited by Best Buy (see Section 5.1). This observation is consistent for all of the samples which were frozen stored for up to eight weeks. Thus, in parallel with was done in the testing of Best Buy mozzarella cheese, all dynamic measurements were conducted within the time before the moduli increase sharply, as explained in section 5.1.

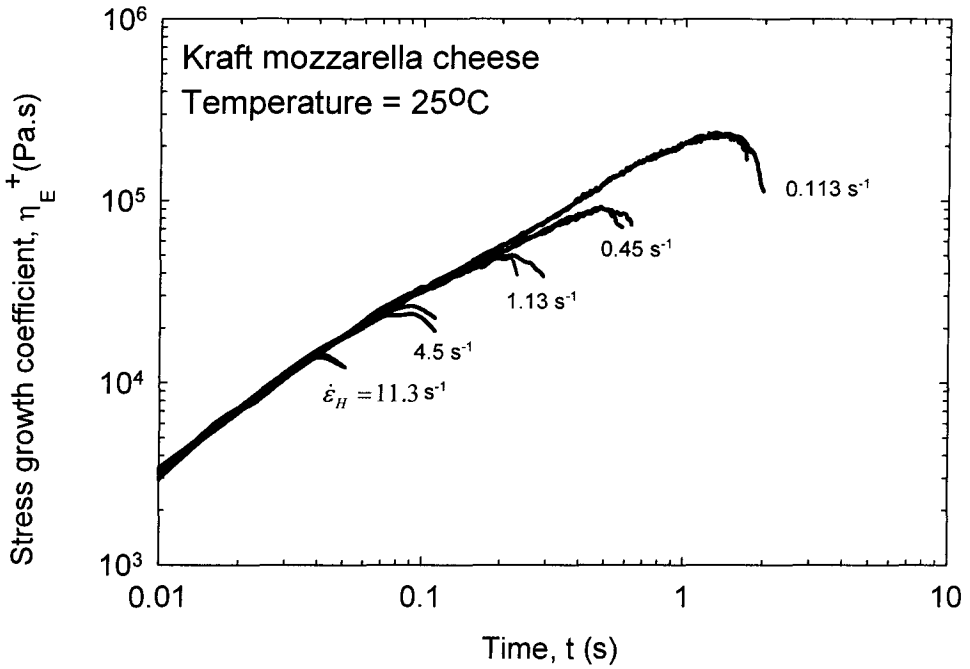


Fig. 10.3 Tensile stress growth coefficients of Kraft mozzarella cheese at 25°C.

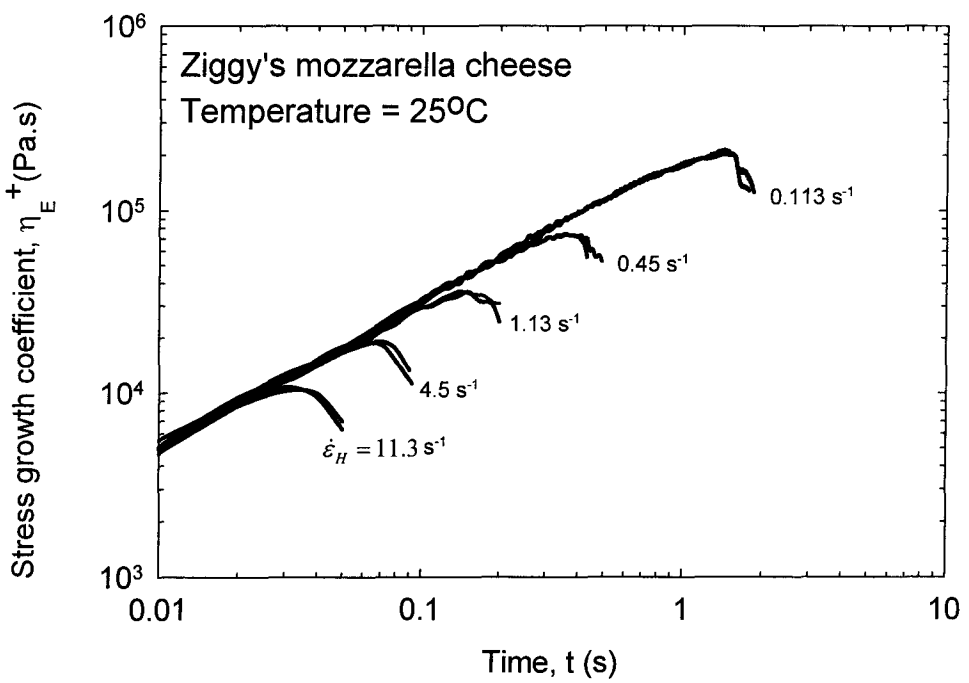


Fig. 10.4 Tensile stress growth coefficients of Ziggy's mozzarella cheese at 25°C.

10.4 Dynamic Frequency Sweep: Effects of Frozen Storage

Dynamic frequency sweep experiments were performed at 25°C, 40°C, 50°C, and 60°C for the different brands of cheese and for the different frozen storage periods. Figs 10.5 and 10.6 summarize the linear viscoleastic properties for the different brands of cheese. It can be seen that at 25°C (Fig 10.5), the different brands of cheese exhibit strikingly similar viscoelastic behaviour. Differences in their viscoelasticity are observed at an elevated temperature of 60°C (Fig 10.6; the curves are obtained from time-temperature superposition of data obtained at 40°C, 50°C, and 60°C to a reference temperature of 60°C). It must be noted that for clarity, the viscous modulus data has been multiplied by a factor of 0.1. At 60°C, Kraft and Ziggy's mozzarella cheeses exhibit the highest and lowest dynamic moduli respectively. The phenomenon that causes the different levels of moduli decrease for the different brands of cheese is most likely due to the way the cheeses were manufactured, which dictates the molecular arrangements of the protein matrix. It is expected that the Kraft mozzarella cheese, being a processed cheese, has a much tighter and more uniform protein matrix. In this configuration, upon heating, the interactions among the casein molecules are still maintained to a considerable degree. This results in Kraft cheese to exhibit less reduced dynamic moduli compared to the other brands of cheese. The other mozzarella cheeses are not processed cheese and they have more liberated casein particles which make these cheeses more sensitive to temperature changes.

The effect of long term frozen storage of the different brands of cheese up to 60 weeks on their linear viscoelasticity is determined. The results are summarized in Figs 10.7, 10.8 and 10.9 for Best Buy, Kraft, and Ziggy's mozzarella cheese respectively. It should be noted that some of the viscous modulus data in these plots have been multiplied by a factor of 0.1 or 0.01 for the sake of clarity.

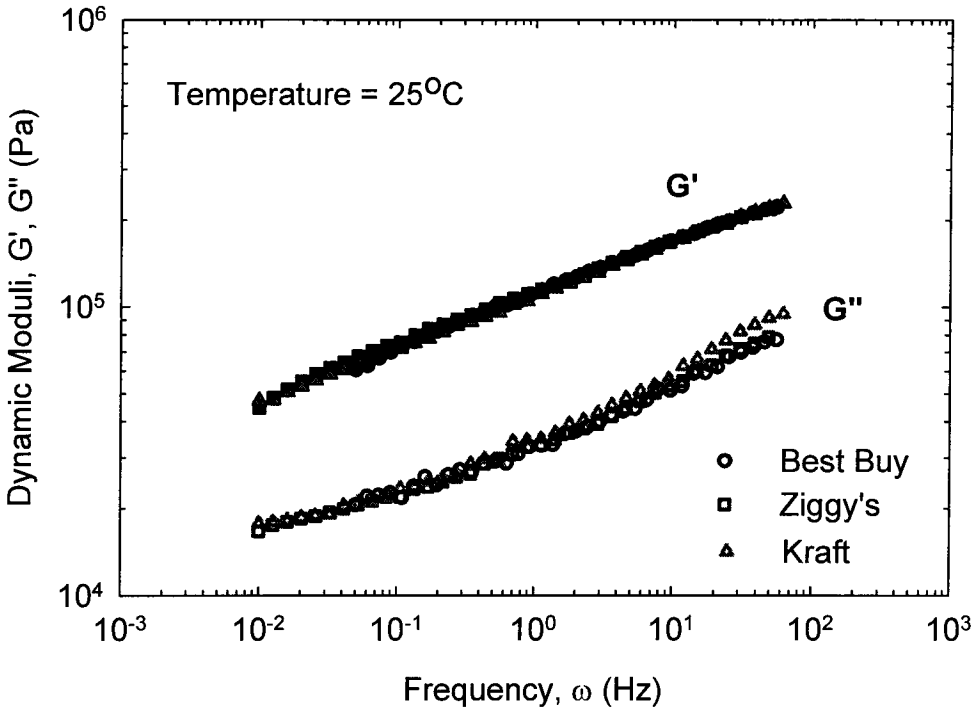


Fig. 10.5 Dynamic moduli of the three different brands of mozzarella cheese at 25°C.

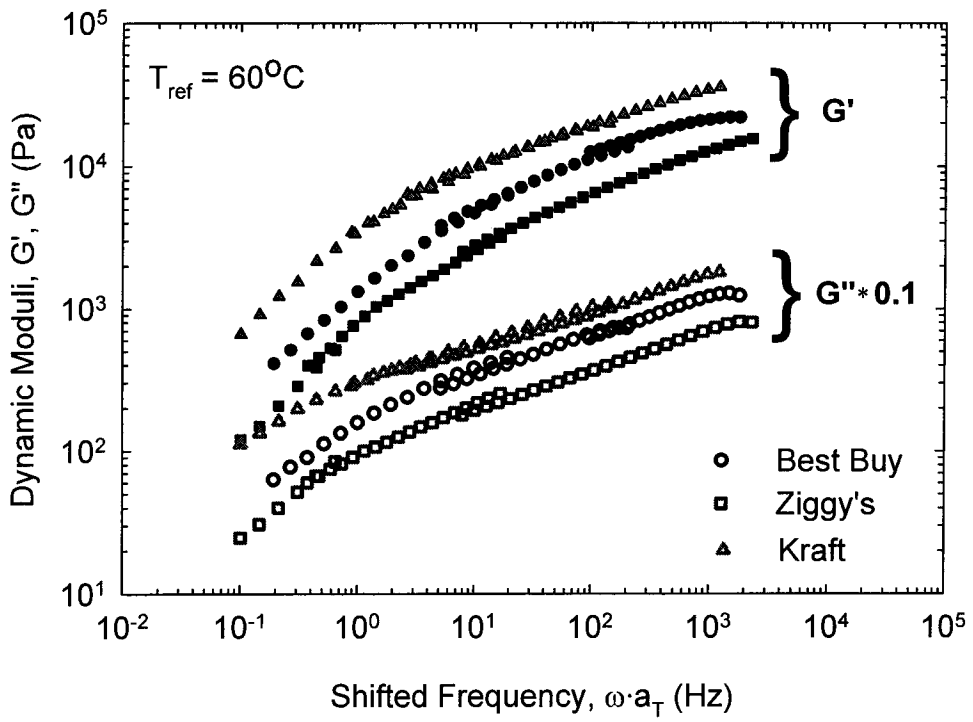


Fig. 10.6 Time-temperature superposed dynamic moduli of the three different brands of mozzarella cheese at a reference temperature of 60°C.

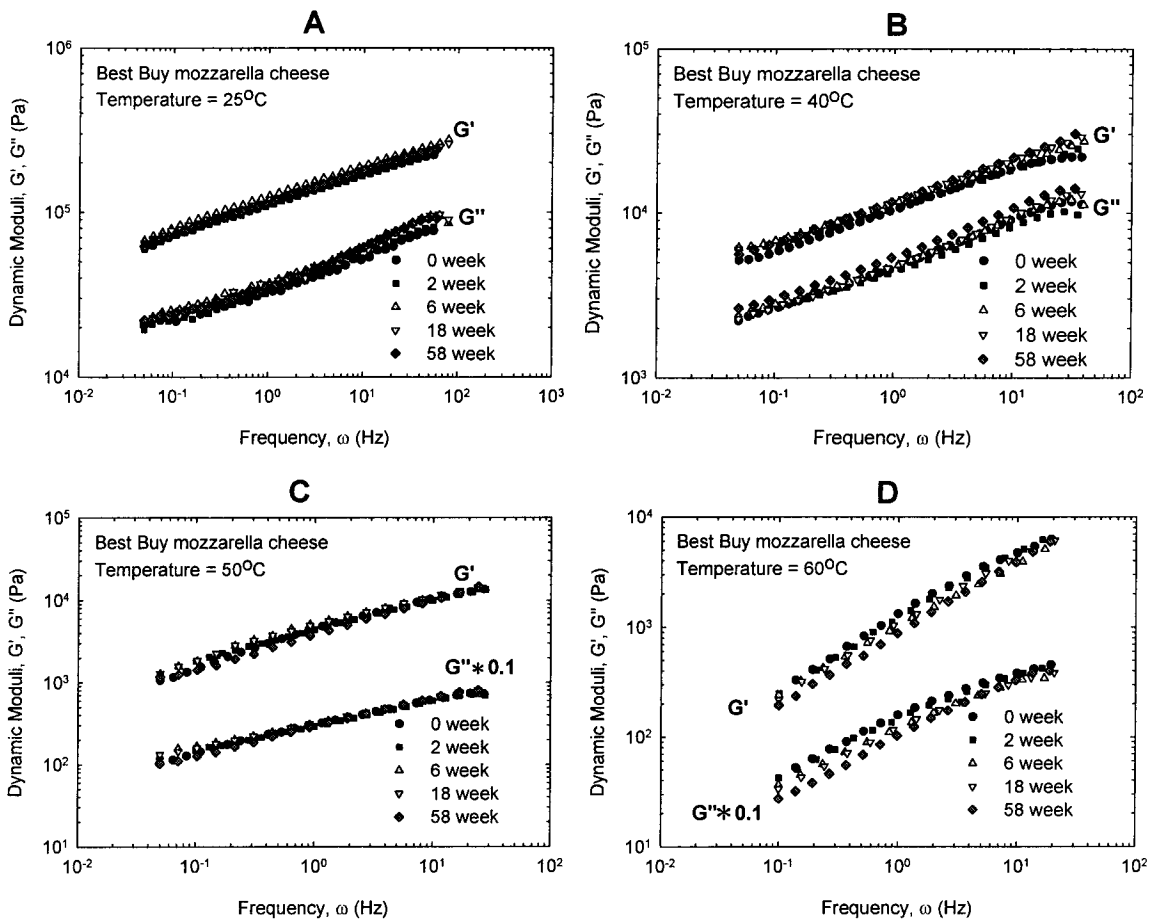


Fig. 10.7 The effect of frozen storage on the dynamic moduli of Best Buy mozzarella cheese at a temperature of A)25°C, B)40°C, C)50°C, and D) 60°C.

From Fig 10.7, it can be seen that the dynamic moduli of Best Buy mozzarella cheese at the different temperatures do not seem to be significantly altered from frozen storage up to 58 weeks, except perhaps at 60°C. This is not the case, however, for Kraft and Ziggy's mozzarella cheese, as seen in Figs 10.8 and 10.9. For these brands, the dynamic moduli at 25°C do not seem to be affected by frozen storage up to 60 weeks. However, at relatively higher temperatures, there seems to be a more obvious effect of frozen storage and the effect is more pronounced with an increase in temperature. Observing the data at 60°C, it can be seen that the dynamic moduli of the Kraft and Ziggy's mozzarella

cheese decrease after 1 week of frozen storage. The dynamic moduli remain relatively constant after this initial 1 week of storage, until up to 20 weeks of storage. The dynamic moduli decrease further after frozen storage of 60 weeks.

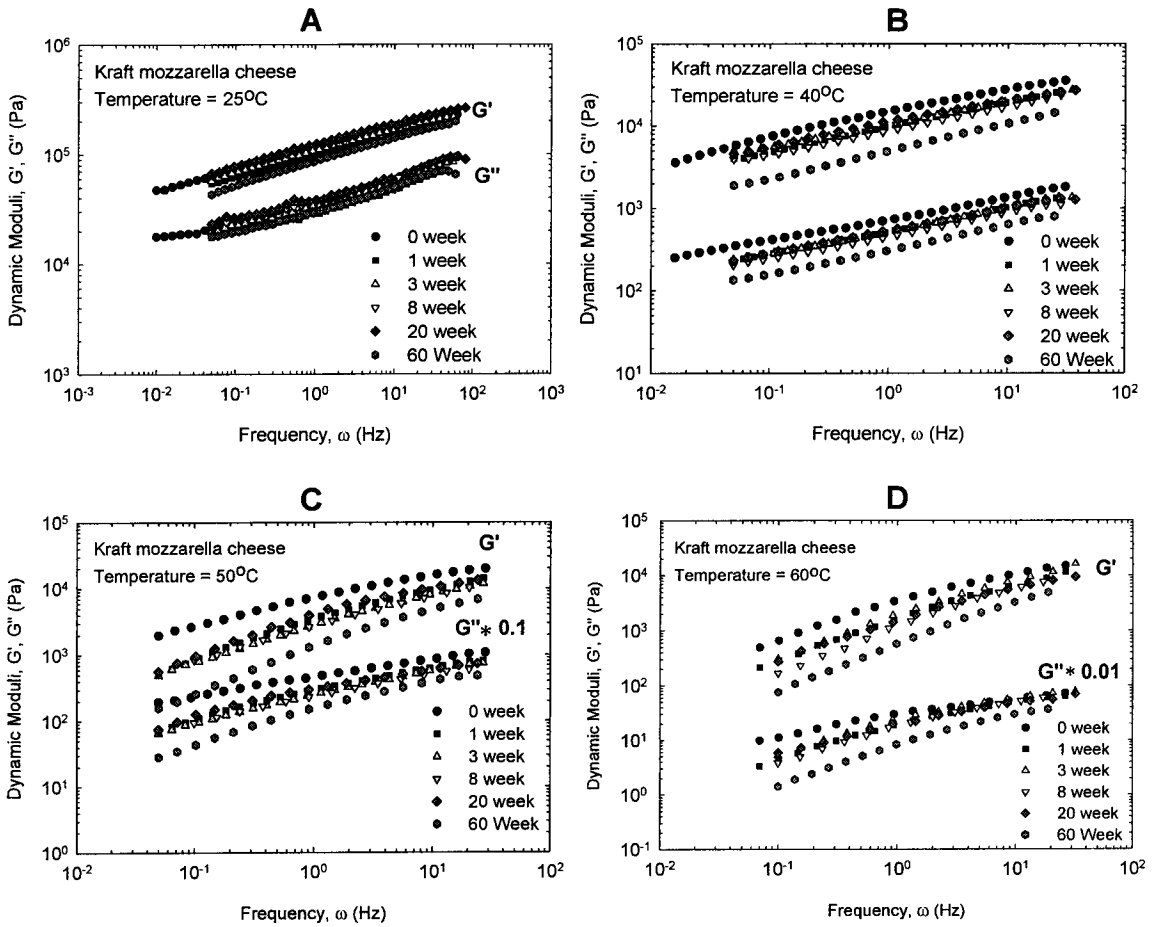


Fig. 10.8 The effect of frozen storage on the dynamic moduli of Kraft mozzarella cheese at a temperature of A)25°C, B)40°C, C)50°C, and D) 60°C.

The significant decrease in dynamic moduli for the different brands of mozzarella cheese, at least in the first few weeks, is most likely due to the freezing of the proteins, since it is unlikely for the mozzarella cheese to undergo some degree of proteolysis activities while kept in a frozen storage within this time frame (Chaves et al. 1999). The change in the linear viscoelasticity with frozen storage time can also be due to the rate of cooling and the cooling cycle of the freezer. It has been found that rapid cooling of cheese is required to maintain

its textural attributes (Luck, 1977; Gunasekaran and Ak, 2003). If a cheese is slowly frozen, it may need some tempering time to regain the desired functional attributes of unfrozen cheese (Gunasekaran and Ak, 2003). In this project, the cheese was kept in a residential freezer and thus the rate of freezing was slow. Furthermore, with a residential freezer, there was also the possibility of a cooling cycle in the freezer, which may present additional variable to consider in assessing the effect of frozen storage. It seems, then, that the effect of frozen storage on the mozzarella cheese really dependent on the cheese type, temperature of storage, rate of cooling, cooling cycle, as well as thawing period; as noted also by Gunasekaran and Ak (2003).

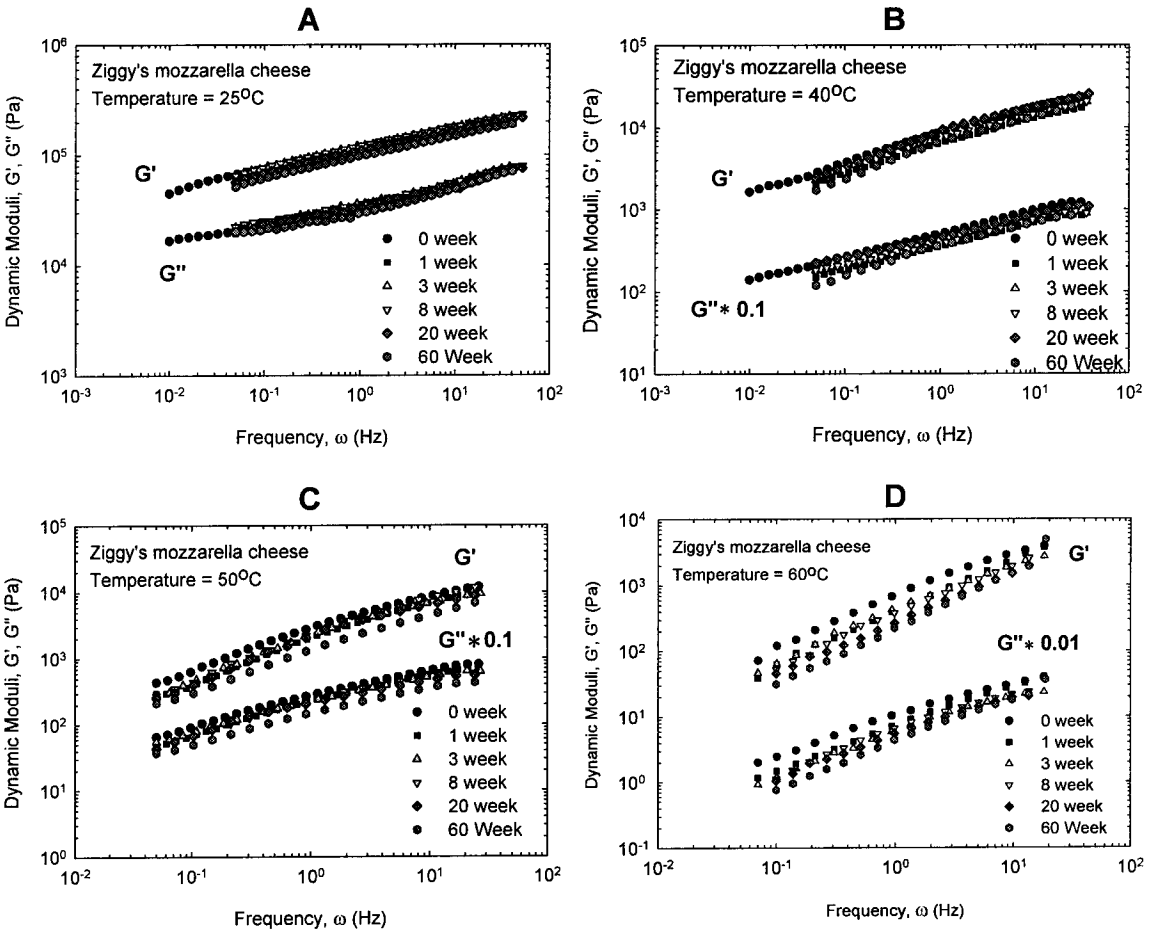


Fig. 10.9 The effect of frozen storage on the dynamic moduli of Ziggy's mozzarella cheese at a temperatue of A)25°C, B)40°C, C)50°C, and D) 60°C.

10.5 Summary

In this chapter, the rheological properties of three different brands of mozzarella cheese were compared. The different mozzarella cheeses do not exhibit linear viscoelastic differences at room temperature. They do, however, show significant difference at 60°C. This illustrates the different heating properties of the different brands of mozzarella cheese. In terms of the extensional property, the processed mozzarella cheese exhibit anisotropy which is due to the orientation of its protein fiber, while the other two brands of mozzarella cheese were isotropic. As more food products are available as frozen foods, understanding the rheological changes of mozzarella cheese during frozen storage is very practical. It was illustrated that the effect of frozen storage is dependent on the cheese type, temperature of storage, rate of cooling, cooling cycle, as well as thawing period. However, it can be generally inferred that freezing of the cheese results in the weakening of the protein, causing the cheese to exhibit decreased dynamic moduli. Over a longer period of frozen storage, proteolysis activities may additionally weaken the protein matrix and causes further decrease of dynamic moduli.

CHAPTER 11:

CONCLUSIONS

11.1 General Conclusions

In this thesis, a study on the rheology of mozzarella cheese has been performed. Rheology provides insights on the practical characteristics, such as melting and flow properties of mozzarella cheese as a consumer end product. Its linear rheology was probed using a parallel plate rheometer, while its extensional behavior was assessed using an extensional rheometer. Capillary rheometer was used to determine the non-linear flow properties as well as to assess the suitability of extrusion process as a post-production technique for mozzarella cheese. The general deformation behavior of mozzarella cheese under roll forming was also assessed. Finally, the effect of frozen storage of different mozzarella cheese on the rheological properties was investigated. Experimental work were performed at varying temperatures (25°C to 60°C) and due to the highly complex and dynamic structure of mozzarella cheese, its rheology is fundamentally different than that of most synthetic polymers.

According to its linear rheology, at room temperature, mozzarella cheese is a visco-elasto-plastic material and upon heating, exhibits a continuous and gradual change towards a viscoelastic fluid. In general, the linear viscoelasticity of mozzarella cheese can be described by a multi-mode generalized Maxwell model. This behavior was also reflected on its extensional properties, where at room temperature, mozzarella cheese exhibits brittle fracture, and at higher temperatures, it exhibits significant strain softening. It has also been illustrated that the capillary flow of mozzarella cheese at room temperature can be described by a Herschel Bulkley model. Furthermore, it was proved that extrusion and rolling are techniques which could and should be further investigated to be adopted as a post-production method for mozzarella cheese.

The structure of mozzarella cheese was found to be highly temperature-dependent. With continuous increase in temperature, mozzarella cheese loses its moisture and at the same time, the fat melts and the protein becomes mobile. Consequently, phase separation between the fat and protein occurs, which led to the agglomeration of fat particles and re-arrangement of the protein matrix. These changes cause irreversible thermal effect on the structure of the cheese. This was the principal cause of the inconsistencies between the rheological properties obtained from the experimental methods, where temperature effects are significant (parallel plate and extensional). In capillary extrusion, structural changes on the mozzarella cheese due to temperature are relatively less significant, due to the highly destructive nature of the extrusion process. In this case, yield stress is a more relevant variable that affects the consistency of its measurements with linear rheology.

Mozzarella cheese is also commonly found as an ingredient in frozen foods. Thus, its stability under long term frozen storage is of interest commercially. Three different brands of mozzarella cheese were tested under the same frozen storage conditions. Although, at room temperature, there were no obvious differences, these different mozzarella cheeses exhibit markedly different linear viscoelastic properties at higher temperatures, which point to the possible presence of different preservatives/additives which affect their properties differently at higher temperatures. Furthermore, the effect of frozen storage on these different mozzarella cheeses seems to be more pronounced at elevated temperatures. This illustrates the sensitivity of the structure of mozzarella cheese with an increase in temperature.

11.2 Practical Implications

Although more in-depth study should be done to understand the implications of the applied processing techniques on the composition and texture of mozzarella cheese, a few design guidelines, derived purely from this thesis can be extracted. These are as follows:

1. Extrusions should be done at 60°C while the cheese is in the melt state. This not only reduces the extrusion pressure, but also ensures that the extruded products are more cohesive and exhibit a smooth profile. Of course, in food industry, one may find distortions on the extrudate surface to be a marketable property, in which case, extrusion should be done at lower temperature (eg. 25°C).
2. It was found that mozzarella cheese exhibits non-reversible thermal effects. Thus, extrusion of mozzarella cheese at high temperature can be performed during its manufacture (kneading step, which is usually carried out in the melt state). In this way, the processing can be done efficiently and at the same time, the thermal effects on the finished products are avoided.
3. Roll forming at 25°C can be used to shape mozzarella cheese as long as the reduction ratio is kept below 2.3. This ensures that the rolled samples do not disintegrate. Although, hot rolling (60°C > T > 35°C) was not performed in the current work, it is of interest as it is expected that higher reduction ratios can be achieved when the cheese is near its melt state.
4. Subtle changes which occur in mozzarella cheese during storage can be assessed using rheological measurements, especially if the measurements are performed at higher temperatures. Thus, it may be more practical for quality measurements to be performed at high temperature (60°C).

11.3 Contributions to Knowledge

The research work has yielded a few novel contributions to knowledge. The most significant are identified as follows.

1. The consistencies of the behaviors of mozzarella cheese under different deformations have been studied. In essence, this illustrates the effects of relevant variables such as moisture, yield stress, duration of experiments, sample size, and testing geometry on the rheological properties under different deformation modes.

2. The capillary flow of mozzarella cheese has been studied. The results provide an understanding on how capillary extrusion can be used as a feasible mean of post-production processing technique of mozzarella cheese. This is novel experimental work that can lead to improved manufacturing and processing technique to produce improved cheese products (for example, see Cortes-Martines et al., 2005).
3. Roll forming behavior of mozzarella cheese has been studied. Although, this work is in its preliminary stage, it can lead to novel post-production processing technique for mozzarella cheese.

In summary, the research work has provided a clearer insight on the rheology and structure-property of mozzarella cheese, as determined from well-developed rheological techniques. More in-depth studies need to be performed to understand completely this highly complex material and implement the results into practical applications as discussed earlier. This research work, however, provided the initial steps towards these practical applications, and therefore, hopefully stimulate food engineers and scientists to take on new approaches in the post-production processing of mozzarella cheese (or food materials in general for that matter).

11.4 Recommendations for Future Work

As stated earlier, the research work is an initial step towards a full understanding of the rheology of mozzarella cheese (or cheese in general) and the implementation of synthetic polymer processing methods in food processing. As such, there are several important aspects of the rheological study of mozzarella cheese that need further examination. These are recommended below.

1. The rheological characterization performed in this study was limited to a temperature range of 25°C to 60°C. It would be ideal to study the rheology at relatively low temperatures to simulate the property of a mozzarella cheese being consumed immediately from refrigerated storage.

Regretfully, this was not performed in the current research due to the unavailability of the proper experimental instruments.

2. Utilizing visualization tools such as cameras, microscopes, and transparent measuring systems, the flow and deformational behavior of mozzarella cheese can be better understood. This will help, for example, in the analysis of slip phenomenon, especially at elevated temperatures and also in providing a better understanding of the thermal effects on the properties of the cheese.
3. In order to make the capillary flow study of mozzarella cheese more complete, the effects of such deformation on the composition of the cheese can be studied. Further study can also include the textural analysis of the extruded cheese. In addition, extrusions using other types of dies such as hyperbolic and annular dies can be carried out, as these dies can have more practical applications. For example, annular dies can be used to co-extrude different cheeses (or a cheese with other food material together) to produce complex and commercially attractive products.
4. More detailed roll forming experiments can be carried out, with particular emphasis on the roll forming at elevated temperatures. Also, it would be ideal to obtain a more complete set of rheological parameters, such as roll separating force and points of attachment and detachment to and from the rollers from this experiment for modeling purposes.
5. A mathematical model to describe the processing of mozzarella cheese, especially for capillary extrusion and roll forming operations, can be developed. This can be used to improve manufacturing and develop innovative processing equipments.

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