FUNDAMENTAL RHEOLOGICAL PROPERTIES OF PROCESSED CHEESE SLICES

A THESIS PRESENTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF TECHNOLOGY IN FOOD TECHNOLOGY AT MASSEY UNIVERSITY

FRANCIS MELKIOR FARAAY

1995

To my wife, Rebeccah, and

my daughter, Dorothy

ABSTRACT

Fundamental rheological properties of two types of processed cheese slices, Individually Wrapped Slices (IWS) and Slice On Slice (SOS), produced under different process conditions, were determined. Shear creep, shear stress relaxation, dynamic impulse measurements and confocal laser scanning microscopy were used to determine the rheological properties and the texture of processed cheese slices. The shear creep, the shear stress relaxation and the dynamic impulse halfsquare measurements were carried out using an Instron Universal Testing Machine. A Texture Analyser TA.HD was used for the shear stress relaxation measurements. Comparison of shear stress relaxation results between the two instruments showed agreement.

The shear creep compliance of IWS cheese show higher values than that of SOS cheese at 21°C. On the other hand, the shear stress relaxation moduli indicated lower values for IWS cheese than SOS cheese at 21°C. This indicated that IWS cheese was more liquid-like than SOS cheese though there are no significant compositional differences. Higher shear creep compliance is related to less resistance of the cheese to deformation while lower shear stress relaxation modulus indicates less resistance to deformation. These results are also in agreement.

The melting properties of the two types of slices were studied with dynamic impulse measurements. IWS cheese melted at a lower temperature (50°C) than SOS cheese (60°C). Microscopic structure indicates more protein-protein interaction in SOS cheese than IWS cheese, which had smaller fat globules evenly distributed within the protein network, thereby reducing the protein-protein interaction and making the network integrity weak, thus confirming the shear creep and shear stress relaxation findings.

The rheological and textural differences between the two cheeses were attributed to different process conditions used during the cheese manufacture. These different process conditions are the heating temperature and time combination and the cooling rate. The comparison of static measurements, the dynamic measurements using small deformations

and the microstructure to determine the properties of processed cheese is a useful tool to determine the effects of different process conditions. It might enable the choice of those desired process parameters such as temperature-time combination and cooling rate for various processed cheese types.

ACKNOWLEDGEMENTS

I wish to express my appreciation and deep sense of gratitude to my supervisors Dr. Osvaldo H. Campanella, Dr. Owen J. McCarthy and Mr. Rod Bennett for their guidance and assistance in all aspect of this work. Their patience during long discussions in the preparation of this manuscript was invaluable.

I acknowledge and thank all the members of staff and postgraduate students in the department of Food Technology who provided valuable support during the experimental work of this project and the preparation of this manuscript.

I wish to express my gratitude to Professor Peter A. Munro for his support and advice especially in the choice of this project. The constant advice he gave me whenever I confronted him even with my personal problems was very valuable.

I am grateful to Tanzania Dairies Limited and the Tanzania Government for allowing me pursue my studies.

Thanks to the New Zealand Government for providing me with study fees through the Ministry of External Relation and Trade. The New Zealand Dairy Research Institute for funding this project. Particular thanks to Mr. Anthony Fayerman, Dr. Philip Watkinson, Mr. Anthony B. McKenna and Mrs. Katherine Bryce for their coordination and support of this project. And to Dr. Paul A. Deuritz and Dr. Siew Kim Lee for the discussion on certain aspects of this work.

Finally, I feel deeply grateful and indebted to my wife, Rebecca for so much patience, understanding, endless love and encouragement. Her moral support enabled me complete this task.

Francis Melkior Faraay.

March, 1995

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CHAPTER 1

INTRODUCTION

Dairy processing is one of the most important businesses for New Zealand. Exports of dairy foods include milk powders, butter, anhydrous milk fat and cheese. Cheese exports is a significant outlet to market milk solids in the world market. The rheological properties are of vital importance to the manufacturer and the consumer. These properties depend on the structure and the processing parameters used during cheese manufacture.

1.1 RHEOLOGY

"Rheology is the science of the deformation and flow of matter. It is the study of the manner in which materials respond to applied stress and strain" (Steffe 1992). The deformation and flow the matter experiences by the action of a force are related to the mechanical properties of the material. The mechanical properties of any material are a function of composition and the process conditions used to form their structure (British Standards Institution 1975).

"Stress is the response or the internal reaction of a material to an applied force and it is dependent on the area on which the force acts.

Deformation or strain is the relative change in dimensions and/or shape of a material subjected to stress. "The extent of deformation and stress depends on the magnitude of imposed stress and strain and on the material's characteristics" (Shoemaker et al 1992).

The material's response to applied stress and strain can be explained by the theory of viscoelasticity. Most foods are viscoelastic in nature; they exhibit both viscous (liquid) and elastic (solid) behaviour. These responses are categorised as mechanical

or rheological properties.

Fundamental rheological properties are those which give identical results regardless of the instruments used in their measurement. Rheological instruments range from simple inexpensive machines such as the Texture Analyser to complex expensive machines such as the Instron Universal Testing Machine. The instruments also vary in flexibility and versatility. However they have four important features in common (Voisey 1971):

i) a means of mechanically deforming the material,
ii) a means of recording the imposed force,
iii) a means of recording the applied deformation, and
iv) a test cell to hold the sample.

The mechanical behaviour of any material depends on its chemical and physical properties. The chemical composition, and the physical forces imposed during the manufacture and handling, result in specific structural integrity thus:

Chemical composition + Physical forces → Microstructure → Texture.

Understanding rheology is important in the food industry with respect to optimizing product development, process design and final product quality (Steffe 1992; Rao and Steffe 1992; Shoemaker et al 1992; and Whorlow 1992).

Data obtained from rheological measurements are used in:

i) process engineering calculations such as flow in pipelines, pumps, heat exchangers, homogenizers and extruders,
ii) determining ingredient functionality in product development,
iii) intermediate or final product quality control,
iv) shelf life testing,
v) evaluation of food texture,
and vi) analysis of rheological constitutive equations.

1.2 NATURAL CHEESE

Cheese is composed mainly of protein (casein), fat and water. The structure and arrangement of protein molecules largely determines its textural characteristics. During cheese maturation, chemical changes take place such as lipolysis, proteolysis and water content and distribution resulting in change in pH and the ionic strength. These changes affect the cheese texture which is an important factor in consumer perception of eating quality, and ease of usage, for example cutting, grating, spreadability, meltability and storage (Prentice 1972; Walstra and Peleg 1991).

Natural cheeses are classified into varieties with varying properties. However, natural cheese is composed of a three-dimensional particulate network with fat globules and moisture entrapped in a casein network. Moisture is mechanically held while fat is in globular form with its protein membrane mainly intact. The network consists of strands of fused paracaseinate micelles (Prentice 1987). Inter- and intra-strand integrity is attributed to calcium cross-linking through casein phosphoserine residues and ionized carboxyl residues (-COO$^-$ Ca^{+} $^-$OOC-), hydrophobic bonding, electrostatic attractions, van der Waal's forces and possibly colloidal calcium phosphate depending on pH (Knoop, 1977; Walstra and van Vliet 1982).

1.3 PRINCIPLES OF PROCESSED CHEESE MANUFACTURE

Processed cheese is produced by carefully blending shredded natural cheeses of the same or different varieties with differing degrees of maturity with salts, and by heating the blend under partial vacuum with constant agitation until a homogeneous mass is obtained.

The physico-chemical changes during the manufacture of processed cheese, in the presence of emulsifier salts, include ion exchange, pH displacement, buffering/stabilization, protein peptization and hydration, fat emulsification and structure formation.

i) **Ion exchange.** This involves exchange of the bivalent calcium of the Ca-paracaseinate network for the monovalent cations of the emulsifier salt. The removal/sequestering of calcium results in the disintegration of inter- and intra-strand links and of the matrix continuity and integrity. The Ca-paracaseinate network is converted to sodium paracaseinate, sodium phosphate caseinate and or sodium-calcium caseinate (Becker and Ney 1965).

ii) **pH displacement and stabilization.** Emulsifier salts possess a buffering capacity. Their use during processed cheese manufacture results in upward pH displacement (pH 5.0 - 5.4 in natural cheese to 5.4 - 5.9 in process cheese mix) and stabilizes the pH (Meyer 1973; Tatsumi et al 1975; Gupta et al 1984 and Caric and Kalab 1987).

The upward pH displacement increases the calcium sequestering ability of the emulsifier salts and promotes an increase in caseinate negative charge.

iii) **Protein peptization and hydration.** This is a result of ion exchange and the disintegration of calcium cross linkages, and the weakening of hydrophobic, van der Waal's and electrostatic attractions especially when the cooking temperature is raised to 80^{0}C during the manufacture of process cheese (Ben-Naim 1980; Kinsella 1982). The conversion of calcium paracaseinate to sodium paracaseinate and the increase in protein negative charge promote hydration and emulsification.

iv) **Emulsification.** Casein in the "soluble" form possesses good emulsifying properties due to the occurrence of highly hydrophobic and hydrophillic regions in its molecule (Geurts et al 1984; Southward 1985). In natural cheese, casein constituting the calcium paracaseinate network is insoluble and incapable of emulsifying free fat. The addition of the emulsifier salts promotes the sequestering of calcium and the disintegration of calcium cross linkages. It also increases casein charge by upward pH displacement and the sorption of anions. There is partial conversion of insoluble calcium paracaseinate to soluble sodium caseinate and thereby improved emulsification of free fat.

v) **Structure formation.** The structure of processed cheese consists of a protein matrix in which water and fat globules are distributed. The fat globules are evenly distribution unlike in natural cheese. The fat globule size in processed cheese ranges from 0.1 μm to 5 μm and the globules are mostly coated on the surface with caseinate particles thus confers them with the properties of the protein particles (van Vliet & Dentener-Kikkert 1982 and Walstra & van Vliet 1986). The protein phase exists in the form of a very fine particulate matrix with varying degree of continuity depending on the product type and on the degree of emulsification - which depends on processing conditions such as processing temperature and time (Rayan et al 1980). However, the matrix strands are much thinner in processed cheese than those of natural cheese.

Processed cheese may contain other dairy and non-dairy ingredients like skim milk, cream, nuts, shrimps and bacon.

Processed cheese has better keeping quality, reduced storage costs, and more convenience of use in cooking. Pronounced inhomogeneities which exist in natural cheese are greatly reduced and controlled in processed cheese, therefore increasing uniformity and stability (Caric and Kalab 1987).

1.3.1 Classification of Processed Cheese

Processed cheese is classified into varieties depending on composition, usage and sometimes processing conditions. These include the block-type, slices, spreadable, hi-melt and cuttable processed cheeses.

i) Block-type processed cheese:- Citrates alone or a blend of citrates and phosphates are the main emulsifier salts used in this variety. Moisture in fat-free matter ranges from 40% to 46%, fat in dry matter is 45% and dry matter 43%. Block type processed cheese is cuttable and elastic.

ii) Processed cheese slices:- Processed cheese slices are basically similar in

composition to block-type processed cheese. Slices can be used commercially in cheeseburger, sandwiches and slices for general consumption. Emulsifier salts for processed cheese slices are mainly citrate-based with a blend of sodium phosphate.

iii) Spreadable processed cheese:- This has high creaming properties with 10% more moisture than the block-type (47% to 55% moisture in fat-free matter, 45% fat in dry matter and 43% dry matter). It is used as a spread or as a topping of some foods. Emulsifiers salts used are mainly phosphates or a blend of phosphates.

iv) Hi-Melt (Non-Melt) processed cheese:- This type of processed cheese withstands the sterilization temperatures used for the main food and is incorporated as cubes in various Japanese foods such as fish paste. Normally a blend of citrate and phosphate is used as emulsifier with a higher proportion of phosphate than of citrate.

v) Cuttable processed cheese:- This type of processed cheese is soft and is not as elastic as block-type processed cheese. A blend of citrate and phosphate emulsifier salts is used in this type of cheese.

1.4 PROCESSED CHEESE EVALUATION

Texture is one of the most important quality factors of processed cheese. Others include flavour, nutrition, and appearance (Bourne 1982). The evaluation of cheese texture has been carried out using both sensory and instrumental (objective) measurements. The sensory measurements are more relevant to consumer perception with regard to the flavour, appearance and texture. However, these measurements are expensive because of the large number of panellists employed, they take a longer time, and the reproducibility of results is often relatively poor. The objective measurements on the other hand are more accurate, reproducible, and less labour is needed, so they

are more cost effective (Corey 1970).

According to Bourne (1982) the types and magnitudes of forces exerted on the material and the responses obtained must be well defined and must relate to the actual forces applied during consumption or sensory evaluations. The deformations or stress experienced by a slice in a sandwich or a cheeseburgers for example are relatively low. During objective evaluation it is important therefore to impose small deformations or low magnitudes of stress.

Meltability is an important property of processed cheese. It determines the use of the product in various foods. Studies done on processed cheese meltability (Harvey et al 1981) have been empirical in nature and have not yielded fundamental properties of the product (Campanella et al 1987).

Processed cheese meltability is a function of its composition, process conditions and the type of emulsifier salts used. The fundamental rheological properties can be accurately determined using small deformation especially in the linear viscoelastic region. Small amplitude oscillatory tests have been used by Nolan (1989) to study the melting properties of low moisture part-skim-milk Mozzarella.

1.5 OBJECTIVES

The objective of this investigation was to develop instrumental rheological methods for characterising the effects of processing conditions on the rheological and melting properties of processed cheese slices. In particular, the work aimed to:

a) determine the rheological characteristics at room temperature of processed cheese slices manufactured under different process conditions.

b) determine, using non-destructive low-deformation dynamic tests, the effects of processing conditions on the melting characteristics of processed cheese slices, and

c) determine the effects of processing conditions on the texture/microstructure of processed cheese slices using confocal laser scanning microscopy.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter reviews the factors that affect the rheological properties of natural and processed cheese and other related food materials. Emphasis has been placed on objective rheological measurements of cheese. The rheological characterization of foods was initially confined to empirical measurements due to food complexity and did not provide fundamental information regarding food structure. The introduction of advanced instruments in recent years has enabled the development of fundamental rheological measurements of materials providing knowledge of the dependence of food structure on composition and interactions among the constituents (Shoemaker et al 1992). The relation between the structure of processed cheese and its rheological characteristics as regards the use of different emulsifier salts and process conditions has been considered.

2.2 EFFECTS OF EMULSIFIER SALTS ON PROCESSED CHEESE TEXTURE

The most important ingredients in processed cheese are the emulsifying salts and natural cheeses. The emulsifying salts function as calcium complexers and buffers. Complexation of calcium initially associated with casein micelles allows fat emulsification within the processed cheese matrix formed mainly by casein subunits (Brunner 1977 and Rayan et al 1980). According to Thomas (1973), Anonymous (1976 and 1977) and Nakajima (1981) emulsifying salts are used to provide cheese with a variety of textural properties.

Acid emulsifier salts such as sodium pyrophosphate, monosodium citrate, monosodium phosphate, monopotassium citrate, monopotassium phosphate and sodium hexametaphosphate result in low pH (< 5.2), and when used alone they fail to emulsify fat effectively and result in a long protein strands. Thomas (1973) observed the effect

of long protein strands with sodium emulsifiers. This phenomenon might be explained by insufficiently ionized carboxyl or phosphate groups on casein molecules, thus allowing extensive protein cross-linkage in the cheese matrix. With the exception of sodium hexametaphosphate, these cheeses were not sliceable and showed poor meltability.

According to Waugh (1971) phosphate emulsifiers produce less meltable cheese than citrates. Therefore phosphate has better protein/protein cross-linking ability than citrate in the development of processed cheese structure. Kimura et al (1978), Taneya et al (1980), and Klostermeyer et al (1984) demonstrated that soft processed cheese with 1% sodium citrate and 1.5% polyphosphate consists predominantly of individual protein particles, whereas the protein matrix of hard cheese with 2.2% polyphosphates contains a higher proportion of protein in the form of long strands. It was assumed that these long protein strands contribute to the ability of processed cheese retaining its shape upon heating.

Heertje et al (1981) confirmed the existence of long protein strands in hard processed cheese made using sodium citrate. According to Prentice (1972) the structure and arrangement of protein molecules are largely responsible for cheese textural characteristics.

Proteolysis and lipolysis during natural cheese maturation result in shorter strands in cheese with less interaction between protein molecules unlike in younger cheeses. Ageing produces less elastic cheese because the long protein strands are broken down resulting in marked solubility in water, loss of structure and thus poor emulsification (Nakajima et al 1975 and Shimp 1985). Although emulsifying salts with cooking and agitation enhances the interaction of proteins and their linkage, highly mature cheeses might need a higher proportion of emulsifier salts to have similar effects. The action of emulsifier salts depends on the pH used in the blend, the degree of proteolysis, and whether the curd was made from acid or rennet casein. At the casein isoelectric pH of 4.6, there is little or no calcium bound to casein resulting in lack of calcium complexing especially with trisodium citrate or sodium aluminium phosphate, resulting in poor cheese meltability (Zittle et al 1958).

Levinton (1964), Nakajima et al (1975) and Rayan et al (1980) supported this in their report that insufficient binding of calcium in rennet casein processed cheese produced poor meltability and theorized that this was attributed to inadequate chelating properties of some emulsifiers (such as tetrasodium pyrophosphate and disodium phosphate) in removing calcium bound to rennet casein, while oxalates have strong binding properties by chelating all calcium in milk. For acid casein, calcium is more easily chelated because there is more ion exchange compared to rennet casein, that is, calcium is more strongly bound to protein in rennet casein than in acid casein.

During the process of emulsification fat globules are broken into smaller fat particles resulting into lesser effects on fat separation and melting as temperature increases between 20^0C and 23^0C unlike in most natural cheeses.

2.3 EFFECTS OF COMPOSITION ON MICROSTRUCTURE,RHEOLOGY AND TEXTURE OF NATURAL CHEESE

Cheese with reduced fat (from 35% to 17%) and 44% moisture, showed a firmer body and more elasticity than full fat cheese with 35% fat and 35% moisture, though the moisture levels are the same in fat free matter. Electron micrographs showed 30% more protein matrix in low-fat cheese compared to full-fat cheese (Kalab and Emmons 1978; Emmons et al 1980). In textural assessment this protein matrix has to be deformed exhibiting higher stresses (Emmons et al 1980). The use of low fat milk in cheese manufacture leads to more whey expulsion resulting in harder (less moisture) and more elastic products as demonstrated by Davis (1965).

Temperature influences the rheological properties of cheese especially due to temperature effects on fat. The lower the fat content the less the effects of temperature on cheese rheological properties (Prentice 1987; Luyten 1988). The Young's modulus of low fat cheese was higher than that of high fat cheese at the same deformation rates. Young's modulus of cheese decreased linearly as moisture in non-fat solids increased (Marshall 1989). Moisture in fat-free matter and protein were inversely related with respect to their

effects on rheological properties. As moisture in fat-free matter increases, the rheological parameters tend to decrease because moisture acts as a plasticiser in the protein matrix, thereby making the cheese less elastic and more easily deformed. Green et al (1985) suggested that fat does not actually contribute directly to rheological properties of cheese but appears to form weaknesses in protein matrix through which fracture occurs during deformation. According to Marshall (1989) at large and moderately high deformation rates, the rheological properties of cheese can be explained by the combined effects of the moisture in fat-free matter, the protein and the fat and not by any single component.

2.4 EFFECTS OF PROCESSING ON STRUCTURE AND TEXTURE OF PROCESSED CHEESE

The processing conditions, the age of cheese in the blend, the protein to fat ratio in the blend, and the degree of emulsification are the major determinants of processed cheese rheological characteristics, (Templeton and Sommer 1936; Heertje et al 1981; and Shimp 1985).

Three-dimensional calcium paracaseinate dominates the structure of natural cheeses with fat globules and moisture held mechanically. Fat and moisture do not contribute to structural integrity. During processing of natural cheese into processed cheese, the structure disintegrates with increased levels of calcium sequestering and protein peptization affected by emulsifier salts, and mechanical and thermal energy input. The remaining calcium-paracaseinate network will be open and non-continuous since interstrand crosslinks are severed.

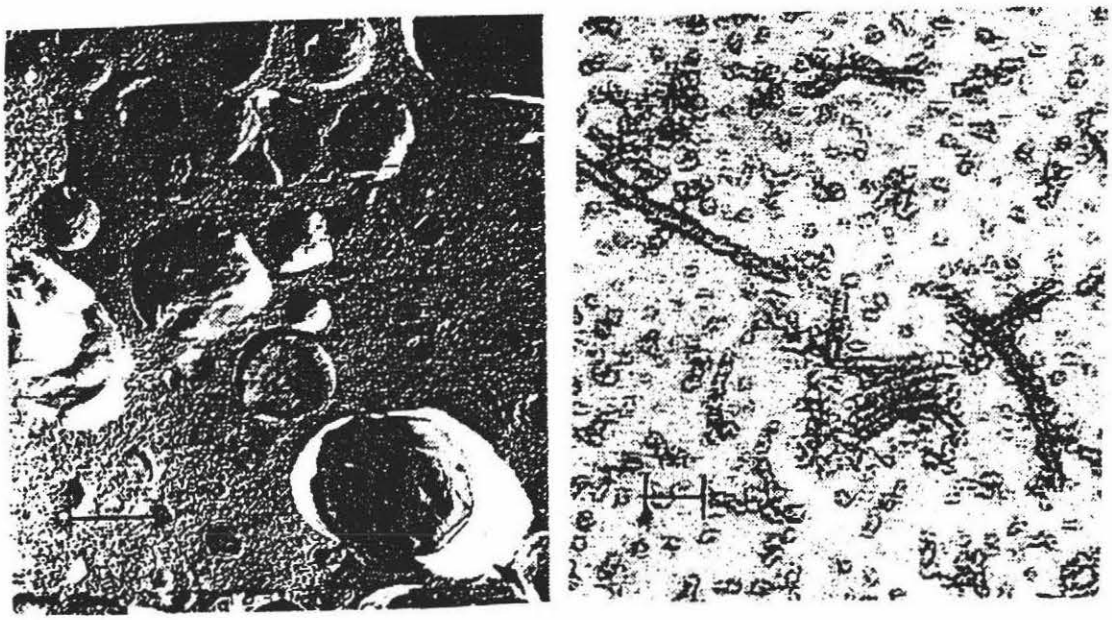
The insoluble calcium paracaseinate is converted into soluble sodium and calcium phosphate-caseinates. These bind water, and the higher the amount of bound water, the higher the product stability and structural integrity (Ferry 1948; Kinsella 1982). Free fat is melted during heating and is re-emulsified with soluble paracaseinates such that the caseinates are on the surfaces of fat globules. The fat globules act as loci for the connection of the relatively short protein strands and so contribute to matrix buildup (van

Vliet and Dentener-Kikkert 1982; Walstra and van Vliet 1986).

Rayan et al (1980) found that fat globule size decreased progressively as processing time increased from 0 to 40 minutes at 82°C regardless of the emulsifying salts used. However, the fat globule absolute size varied with salt type. The smallest size was obtained with tetrasodium pyrophosphate (polyphosphate), the largest with sodium aluminium phosphate, and an intermediate size with sodium citrate, and disodium phosphate. According to Lee et al (1981) the fat globule size and mean diameter can be further reduced by increasing the concentration of emulsifier salts, especially the polyphosphate (1-4%), and increasing the processing temperature between 80 - 140°C, thus increasing cheese firmness. However, the use of emulsifiers at levels above 3% may lead to flavour defects.

The protein phase in processed cheese exists in the form of a very fine particulate matrix with varying degrees of continuity. According to Kimura et al (1979) and Taneya et al (1980 and 1981) differences exist between soft and hard processed cheeses. Hard processed cheese consists of inter-connecting strands made up of casein particles which are strung together to form chains 100 nm long and 20 nm in diameter (Figs. 2.1 a and b illustrate the fat globules and the protein structures). Soft processed cheese has casein particles 20 nm in diameter which are more uniformly dispersed with a lesser degree of inter-particle connection into strands.

Hard processed cheese is rigid and more force is needed to deform it. Increase in processing temperature and in time increases the length of protein strands to up to 300 nm, resulting in an increase in product firmness (Rayan et al 1980; Lee et al 1981; Heertje et al 1981).



a) Shows round fat globules b) Shows string-like protein structures

Figure 2.1 a and b. Microstructure of Hard Processed Cheese Examined by Scanning Electron Microscope - Scale 0.1 μm (From Heertje et al, 1981)

Cooling makes the processed cheese firmer and the extent of firmness depends on the cooling rate. This may be attributed to fat crystallisation, matrix build-up and increase in viscosity. The cooling rate, which also affects the rate of matrix build-up determines the sliceability, spreadability, and meltability of processed cheese.

According to Meyer (1973), Ben Naim (1980), Kinsella (1982) and Ca'ric & Kalab (1987) slow cooling leads to sliceable cheese while rapid cooling leads to spreadable cheese because protein-protein interaction is inhibited by rapid cooling. and there is reduced hydrophobic bonding. Slow cooling promotes hydrophobic interactions, especially around 60-80^{0}C.

2.5 RELATIONSHIP BETWEEN INSTRUMENTAL AND SENSORY (SUBJECTIVE) TEXTURE EVALUATION OF CHEESE

The texture of cheese must be expressed ultimately in sensory terms. By examining a wide variety of cheeses, correlation between sensory and instrumental measurements of texture can be readily observed.

Definitions: (IDF Bulletin 268, 1991).

i) Elasticity is the tendency of a material/body to recover the shape and dimensions it had before it was stressed after the removal of the stress.

ii) Viscoelasticity is the tendency of a material to exhibit partly viscous and partly elastic behaviour when subjected to stress or strain.

iii) Texture is the attribute of a substance resulting from a combination of physical properties and perceived by the sense of touch, sight and hearing.

iv) Modulus in the case of an imposed strain is defined as the ratio of the increase in stress to the strain from which it arises (under specified experimental conditions).

v) Young's Modulus is the physical quantity that relates a uniaxial stress to the extension in the direction of stress.

vi) Adhesiveness is the quantity to simulate the work necessary to overcome the attractive forces between the surface of the food and the surface of the material it comes in contact with (such as teeth, palate and tongue).

vii) Chewiness is the quantity to simulate the energy required to masticate a solid food product to a state ready for swallowing.

viii) Firmness is the stress (force) necessary to attain a given deformation, or the stress required to compress between two molar teeth to a given deformation or penetration.

ix) Hardness of cheese is its resistance to penetration.

x) Crumbly is the tendency of material to break down easily into small, irregular particles.

Davis (1937), and Brennan et al (1970) observed good correlations between instrumental and sensory hardness of cheese. Lee et al (1978) and Chen et al (1979) observed good correlations between sensory and instrumental chewiness and adhesiveness of cheese.

While in sensory evaluation of cheese firmness can be scaled as soft or hard, springiness as inelastic or elastic, crumbliness as viscous or brittle, with instrumental evaluation these characteristics can be assessed as the force to cut and deform, the height recovery on removal of a compressing load, and the change of height or degree of permanent deformation after application of a force.

Shama and Sherman (1973), Boyd and Sherman (1975) and Lee et al (1978) reported that instrumental measurements of the mechanical properties of cheese are greatly influenced by the magnitude of the stress or strain, crosshead speed and the duration of the imposed stress or strain.

The rates of application of force during instrumental cheese evaluation might be different to those in sensory biting or mastication. Instrumental test conditions should be of the same order as those used in sensory tests (Shama and Sherman 1973).

Green et al (1985) reported that during the cutting of a cheese with a wire, there is deformation and fracture on those areas where there is most stress and along the grain boundaries. It was clear that the wire had cut straight through the curd grains. The sample compressed using the Instron showed shear fractures at about 45^0 to the direction of compression. There was no sign of tearing of the matrix, fracture occurring mostly along the grain boundaries. Evidence shows that most fractures are adjacent to the areas of fat and are more on those areas with high fat concentrations (weaker boundaries). This led to the conclusion that the mechanism of fracture depended on both the way the force

was applied and the composition of the material. Such components as fat and water in cheese might contribute to weak boundaries along which fracture occurs, leading to a smaller compression modulus.

However, in processed cheese, the effects of localized fat and water concentrations are greatly reduced, if not totally absent, because processed cheese is homogeneous.

2.5.1 Firmness

Different studies of firmness were carried out using deformations of 20 to 90% (Lee et al 1978; Imoto 1979 and Casiraghi 1989). It was observed that between deformations of 20% to 80%, the correlation coefficients between sensory and instrumental firmness varied between 0.90 and 0.95. However, the findings by Qvist 1987 differred in that the correlation coefficient between sensory and instrumental evaluation were better at higher deformation (50% to 80%) in the case of Danbo cheese.

Boyd and Sherman (1975) mentioned in their report that the rate of mastication is between 40 and 80 per minute with the average masticating cycle being one second. The speed of compression in an instrumental test should be 0.8 mm per second to correspond to a mastication rate of 42 cycles per minute, as in the texturometer (Friedman et al 1963).

Shama and Sherman (1973) found that sensory evaluation always rated Gouda cheese as firmer than white Stilton, while at the instrumental crosshead speed of 50 mm per minute the force for a given deformation for Gouda cheese was lower than that of Stilton cheese at all deformations. At crosshead speeds of 200 mm per minute and above, and a deformation range of 38-62%, the force for a given deformation was higher for Gouda than for Stilton cheese, emphasising the importance of deformation rate on the results of compression experiments.

Cheese is less firm at high temperatures. Culioli et al (1976) and Dickinson et al (1980)

demonstrated that the stress needed for deformation, or deformation to fracture decreases with increase in temperature. Taneya et al (1980) reported that the elastic moduli of Gouda and Cheddar were sharply decreased at temperatures above 35°C, confirming the changes of cheese firmness with temperature.

2.5.2 Springiness (Elasticity)

Springiness is thought to be related to the height recovered after a large deformation as demonstrated by Lee et al (1978), Imoto et al (1979) and Qvist (1987). It has been reported (Zoon 1991) that recovery depends on compression rates. Less recovery occurring at slow rates of compression and more recovery at higher rates of compression. Imoto et al (1979) deformed samples of different cheeses from 20% to 80% compression and found that the correlation between instrumental and sensory springiness increased with compression; at above 50% the correlation coefficient was 0.85 - 0.95. These results support those of Lee et al (1978), who used 80% compression. There was no significant correlation between the sensory springiness and the residual force after one minute deformation of a sample at 20% compression as demonstrated by Green et al (1985). This led to the conclusion that springiness is related to the recovery of the cheese sample after a large deformation (Szczesniak 1963 and Zoon 1991).

2.5.3 Cheese Hardness

Shama and Sherman (1973a) evaluated hardness of cheese as the force required to penetrate and compress the cheese with the teeth. With instrumental evaluation the force deformation curve at a given deformation was used. It was concluded that hardness highly depends on the rate at which the force (stress) is applied and the level of compression used.

Hardness can be evaluated by using the Instron to measure the force needed to attain a given deformation, or by using a wire to measure the resistance to passage of a wire

through the cheese as it cuts and deforms the cheese matrix.

Emmons et al (1980) reported the relevance of instrumental hardness of cheese by measuring forces during cutting of cheese with knives and the bite test through the effect of initial bite. It was suggested that mastication involves shearing between molars in presence of saliva which causes different fracture and mouth feel. The matrix actually cracks rather than deforming leading to the observation that teeth actually cause little cutting (Green et al 1985).

Inhomogeneity within cheeses of the same variety for example due to age, the presence of holes, slits or changes during maturity such as proteolysis, lipolysis, rind which is dryer than the sample obtained from the centre of a cheese block contributes to differences in the relation between sensory and objective rheological evaluation of cheese. To have a precise rheological classification of any cheese further information may be needed for instance the microstructure of cheese as examined under a microscope and as pointed out by Walstra and van Vliet (1982).

The objective measurements of rheological properties of cheese are thought to be more advantageous, they are easier to perform, they can be reproduced and standardized and require fewer trained people than sensory evaluation where a group of trained judges from 5 to 20 people are needed (Bourne 1982). This is both expensive and time consuming.

2.6 TEST METHODS IN RHEOLOGICAL EVALUATION OF CHEESE

Several methods have been developed for the evaluation of rheological properties of cheese. The measurements show essentially the mechanical properties of cheese under various experimental conditions (Konstance and Holsinger 1992).

Cheese is a viscoelastic material, that is a material with both liquid (viscous) and solid (elastic) properties, or the behaviour of simultaneously dissipating and storing mechanical

energy. The method to be used in rheological characterisation depends therefore on the following aspects (van Vliet 1991):

(a) The kind of rheological property to be measured such as apparent Young's modulus, apparent shear modulus, the apparent viscosity in shear or elongation, and the dynamic moduli or the fracture stress.

(b) The time-scale of the measurement (the deformation rate) since this affects the magnitude of the rheological responses.

(c) The measuring method such as strain at constant stress or measuring stress at constant strain or strain rate.

(d) The instrument, which also determines the size, shape and orientation of the test piece.

An appropriate combination of these aspects may be used to measure various rheological properties. The use of different test methods may give different results. The same time-scale (loading or deformation rate) should be employed to get similar mechanical properties of cheese from different methods.

Even with the use of the same-time scale, different properties, such as apparent Young's modulus measured in tension or bending will differ from apparent shear modulus measured in shear or torsion. The relationship between the two is given by:

$$E=2G(1+\mu) \qquad (2.6.1)$$

where E = Young's modulus, G = Shear modulus and μ = Poisson ratio (which is about 0.45 for cheese with holes Luyten 1988). This equation is not valid for a viscoelastic material.

The following methods have been commonly used to evaluate the rheological properties

of natural and processed cheese:

2.6.1 Tensile Test

This test is mainly done to measure the strain/stress to breaking of a material. The specimen is gripped at both ends. While one end is fixed force is applied to the other end, and the material is stretched uniaxially. Most viscoelastic materials such as cheese exhibit necking and slippage resulting in localized stress and strain (Zapas and Crissman 1985). As force is applied, there is elongation and a decrease in the cross section. Slippage often occurs at the ends thus introducing artifacts resulting in poor reproducibility.

2.6.2 Compression Test

Uniaxial compression is normally applied to a cylindrical specimen. Long thin cylinders may not retain their shapes even under the imposition of a small stress or strain. Sample barrelling and friction may make the data-interpretation unreliable. Slippage between plate and the sample can be minimized by bonding or by use of serrated plates, lubrication or bonding reduces or eliminates the effects of friction (Whorlow 1992).

2.6.3 Simple Shear Test

A sample is inserted between two parallel plates and a small stress or strain is applied parallel to one plate. The corresponding displacement is measured and the stress, strain or the strain rate can be derived. The advantages of this test configuration are that anisotropic materials can be sheared in various directions relative to their structure by suitably orientating the test piece between the shearing surfaces. Large deformations can also be applied rapidly, which provides a useful way of studying transient and non-linear effects (Whorlow 1992).

It is assumed that the shear stress is uniform throughout the test area, especially if the sample is properly bonded. A rectangular and thin sample with a uniform thickness is a prerequisite for this test (Gent et al 1974). In simple shear strain, successive layers of material move in their own plane relative to the reference layer such that, the displacement of a layer is proportional to the distance from the reference layer. According to Whorlow (1992) there is no change in dimension perpendicular to the plane of shear. Fig. 2.2 show a thin test piece before and after shearing.

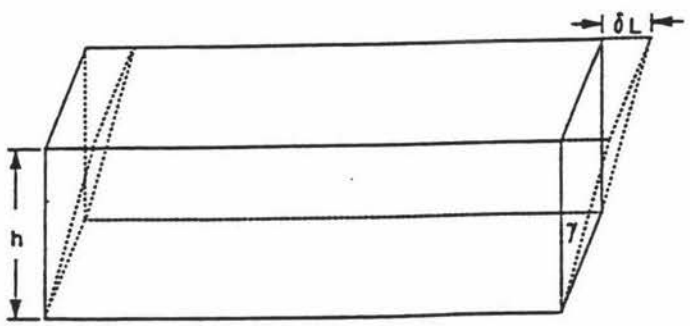


Figure 2.2 The application of simple shear to a rectangular block (From Steffe 1992)

The material measurements can be classified depending on:

(1) How the sample is stressed either by imposing a constant stress σ, strain (γ) or strain rate ($\dot{\gamma}$), (static measurements).

(2) According to the sample being subjected to harmonically varying strain or stress with time (dynamic measurements).

2.6.4 Static Measurements

Static measurements consists of either the application of a constant deformation and measurement of the resulting stress as a function of time (stress relaxation) or the application of constant stress and measurement of the resulting deformation as a function of time (creep test). The prerequisite of these test is that the maximum deformation or force must be reached instantaneously. For cheese, properly obtained data can provide an insight into the type of protein-protein bonds that form the material structure (IDF Bulletin 268, 1991).

Mechanical analogues composed of springs and dashpots are used to conceptualize the rheological behaviour of viscoelastic materials. The spring is an ideal solid element obeying Hooke's Law:-

$$\sigma = G\gamma \tag{2.6.2}$$

and the dashpot is an ideal fluid element obeying Newton's Law:-

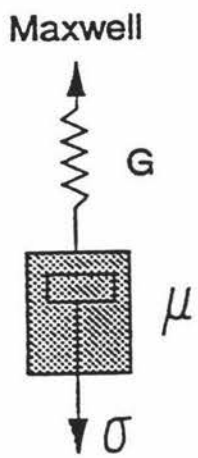
$$\sigma = \eta\dot{\gamma} \tag{2.6.3}$$

Where σ = Stress; G = Elastic modulus; γ = Strain; η = Viscosity, and the $\dot{\gamma}$ = strain rate defined as

$$\dot{\gamma} = \frac{d\gamma}{dt} \tag{2.6.4}$$

A spring can be connected in series with a dashpot resulting in the Maxwell body (Figure 2.3) or in parallel resulting in the Kelvin/Voigt body (Fig. 2.4). These mechanical analogues/models portray the mechanical behaviour of viscoelastic materials (Ferry 1980; Steffe 1992; and Whorlow 1992). Different combinations of dashpots and springs can be used to model the same set of experimental data (Steffe 1992).

In a Kelvin/Voigt body, the spring and the dashpot are arranged in parallel. Although the Maxwell body contains the same elements (spring and a dashpot), its configuration causes it to behave differently. The Kelvin/Voigt body is arranged so that the spring and the dashpot must move the same amount at any time. As the dashpot cannot undergo an instantaneous deformation, the stress relaxation test cannot be used on the Kelvin body.



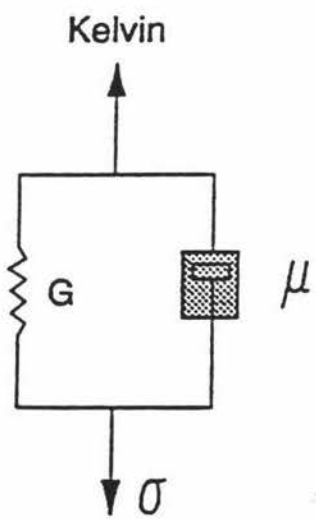


Figure 2.3 Maxwell Body **Figure 2.4 Kelvin/Voigt Body (From Steffe 1992)**

2.6.4.1 Creep Measurements

In creep tests a force is applied instantaneously at time zero and the strain is measured

over time while the force is kept constant (Mitchell 1980).

The Kelvin/Voigt body is frequently used to conceptualize the creep behaviour. It is desired that the time of imposition of force be as short as possible. The results of creep test are expressed as strain function of time $\gamma(t)$ for a particular stress σ or as creep compliance J(t) calculated with the following equation:

$$J(t)=\frac{\gamma(t)}{\sigma_{constant}} \tag{2.6.5}$$

For a Kelvin/Voigt body

$$\gamma=(\gamma)_{spring}=(\gamma)_{dashpot} \tag{2.6.6}$$

and

$$(\sigma)_{constant}=G_1\gamma+\eta\dot{\gamma} \tag{2.6.7}$$

by rearranging eq. (2.6.7) the following is obtained

$$\frac{d\gamma}{dt}=\frac{G_1}{\eta}\left(\frac{\sigma_0}{G}-\gamma\right) \tag{2.6.8}$$

where $\sigma_0 = \sigma_{constant}$

In creep, the stress does not change with respect to time, therefore by integration of equation (2.6.8) and considering the undeformed state for t = 0 the following is obtained

$$\gamma(t)=\frac{\sigma_0}{G_1}\left[1-\exp\left(\frac{-t}{\lambda_{ret}}\right)\right] \tag{2.6.9}$$

where $\sigma_0/G_1 = J_0$ = instantaneous compliance and $\lambda_{ret} = (\eta/G_1)$ is the retardation time, this is time for strain to reach the value (e - 1)/e.

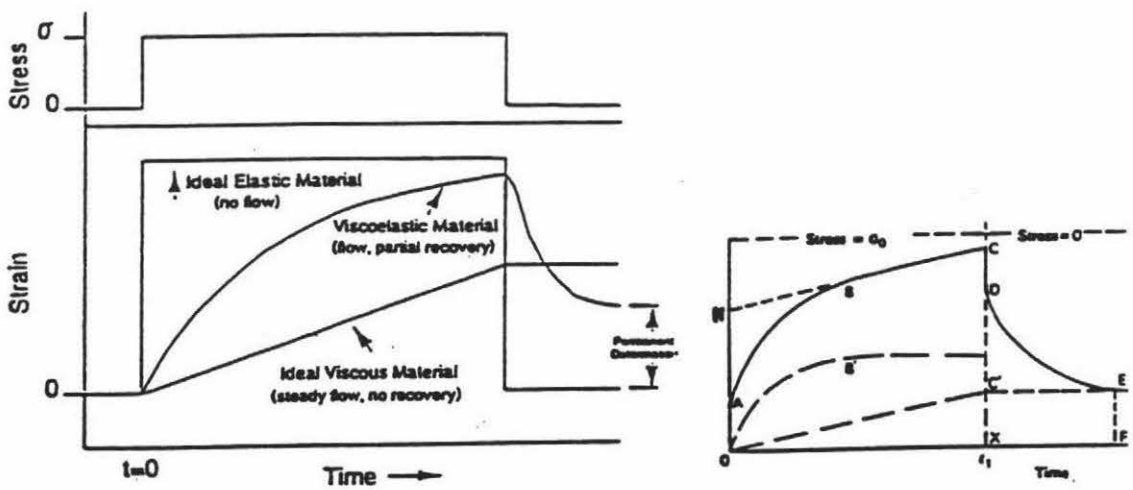
The creep compliance curve (Fig. 2.5b) can be divided as follows:

OA is the region of instantaneous strain. It may mean the strain when the first reading was taken or the strain obtained by rather dubious extrapolation of measured strain at t = 0.

CD is the region of instantaneous recovery.

AB is the region of non-linear strain as the strain increases with time (primary creep).

BC is the region of linear strain as the strain increases with time (secondary creep). It is worth noting here that boundaries between regions are ill-defined; significant curvature can be detected in what is thought to be the linear region if the experiment is continued long enough.



(a) (b)

Figure 2.5 a and b: Typical Creep Curves for a Viscoelastic Material (from Steffe 1992 and Whorlow 1992)

2.6.4.2 Stress Relaxation

In stress relaxation, an instantaneous strain/deformation is imposed on a sample and the stress/ force required to maintain the deformation constant is measured as a function of time. A viscoelastic material will reduce the resulting stress over time at a constant strain. The time required for the resulting stress/force to decay to 36.8% of its initial value is called the relaxation time (Konstance and Holsinger 1992).

According to mechanical models the ideal elastic material will exhibit no relaxation while the purely viscous material will exhibit an instantaneous relaxation. Viscoelastic materials such as cheese will relax gradually over time depending on the ratio of viscous to elastic components. Fig. 2.6 shows typical stress relaxation responses of different materials.

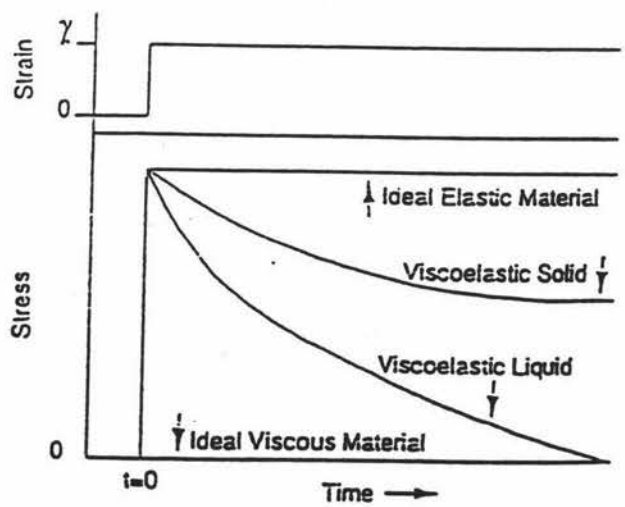


Figure 2.6 Typical Stress Relaxation Curves for Different Materials (from Steffe 1992)

Stress relaxation data is commonly presented in the form of a stress relaxation modulus derived from a single Maxwell body. When the strain is kept constant during the experiment, the time-dependence of the stress can be derived from Maxwell's equation:-

$$\frac{d\gamma}{dt}=\frac{1}{G_1}\frac{d\sigma}{dt}+\frac{\sigma}{\eta} \qquad (2.6.10)$$

since strain does not change with time,

$$\frac{d\gamma}{dt}=0 \qquad (2.6.11)$$

Therefore

$$\frac{d\sigma}{dt}=-G_1\frac{\sigma}{\eta} \qquad (2.6.12)$$

and by integration of eq. (2.6.12)

$$\sigma(t)=\sigma_0\exp(\frac{-t}{\lambda_{rel}}) \qquad (2.6.13)$$

where $\lambda_{rel} = \eta/G_1$ is the relaxation time, and σ_0 is the instantaneous stress.

According to Rao and Steffe (1992) most food experimental data cannot be explained using a Maxwell model which decays to zero stress with time; most foods exhibit a residual stress even after a long relaxation time. A Maxwell model connected in parallel with a spring was used to address this problem, thus including an equilibrium or a residual stress σ_e. The stress relaxation equation described by this mechanical model (Fig. 2.7) is:

$$\sigma(t)=\sigma_e+(\sigma_0-\sigma_e)\exp(\frac{-t}{\lambda_{rel}}) \qquad (2.6.14)$$

where $\sigma_e = \gamma_0 G_e$, with the free spring representing the equilibrium stress.
Dividing through by the constant strain γ_0 gives

$$G(t)=G_e+G_M\exp(\frac{-t}{\lambda_{rel}}) \qquad (2.6.15)$$

where G(t) = stress relaxation modulus, G_e = equilibrium modulus, G_M = modulus on the Maxwell element, and $G_e + G_M = G_0$ (the instantaneous modulus at time t = 0).

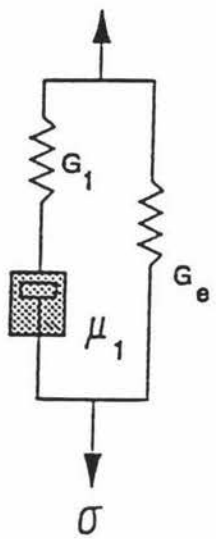


Figure 2.7 Maxwell Body Connected in Parallel with a Spring (From Steffe, 1992)

The instantaneous strain causes the spring component of the Maxwell element to extend due to generated stress. The dashpot begins to flow and relieves the stress imposed on the spring, and the stress relaxation curve decreases with time. If left long enough, the stress will decrease to zero. In other words, the molecules within the deformed sample realign themselves to their original loci during relaxation (Ferry 1980).

The degree of complete relaxation of a material depends on its rheological characteristics, the imposed strain rate and the strain magnitude. The stress relaxation modulus for viscoelastic materials is only reliable for time (t) longer than 10 times the time needed to impose the constant strain, due to uncertainty in time at t = 0, because stress relaxation starts as soon as deformation is started (Kelchner and Aklonis 1971).

Peleg (1980) noted two major problems in collecting and analyzing stress relaxation data for foods:

1) When foods are subjected to large deformations, they usually exhibit non-linear viscoelastic behaviour.

2) Natural instability or biological activity make it difficult to determine the equilibrium mechanical parameters.

The above factors led to stress relaxation data being fitted with the following linear equation:

$$\frac{\sigma_0 t}{\sigma_0 - \sigma(t)} = k_1 + k_2 t \qquad (2.6.16)$$

Where σ_0 = initial stress; $\sigma(t)$ = decaying stress at time t; and k_1 and k_2 = constants where the first constant depicts initial decay rate while the second depicts the hypothetical value of asymptotic normalized stress.

Eq. (2.6.15) is commonly used to curve fit the stress relaxation modulus whereas equation (2.6.16) is commonly used to curve fit stress relaxation data. Since the applied strain is constant during the experiment, the use of any of the equations will basically fit the strain-stress data as illustrated in Fig. 2.8.

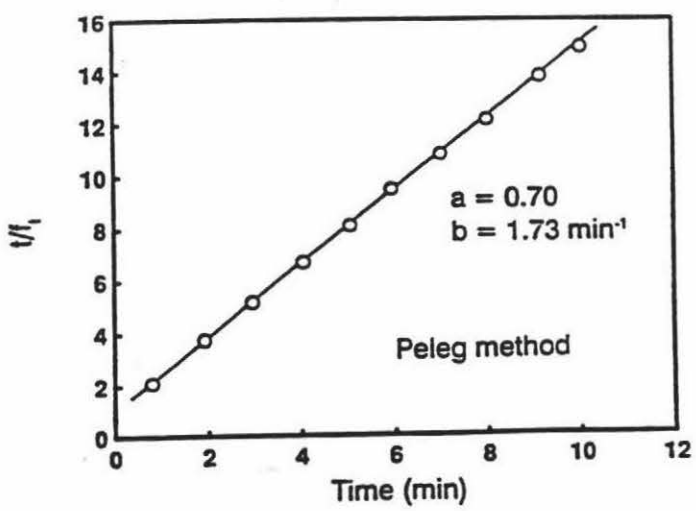


Figure 2.8 Reciprocal Baseline Data Normalised Stress Relaxation (Peleg method)

Masi (1989) demonstrated for Galbanino cheese (Figs. 2.9 and 2.10) that the apparent modulus after compression is a function of deformation level. The relationship between stress and strain is nonlinear even at low deformations. With increasing deformation there is progressive weakening of cheese. Stress relaxation tests with varying deformation levels show non-linearity. The relaxation data derived from tests made under different deformations do not fall on a single curve instead each deformation level has its own curve.

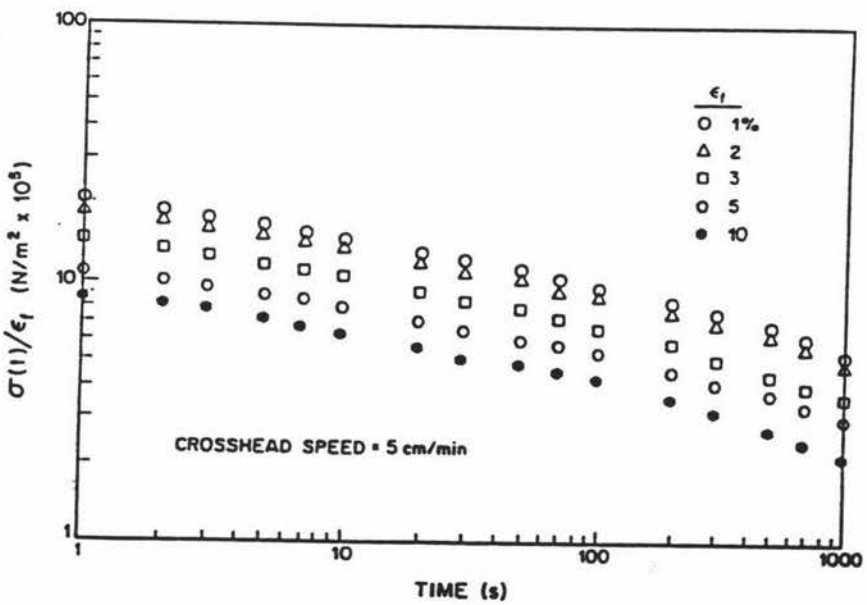


Figure 2.9 Influence of Deformation Level on Stress Relaxation Behaviour of Galbanino Cheese (From Masi 1989)

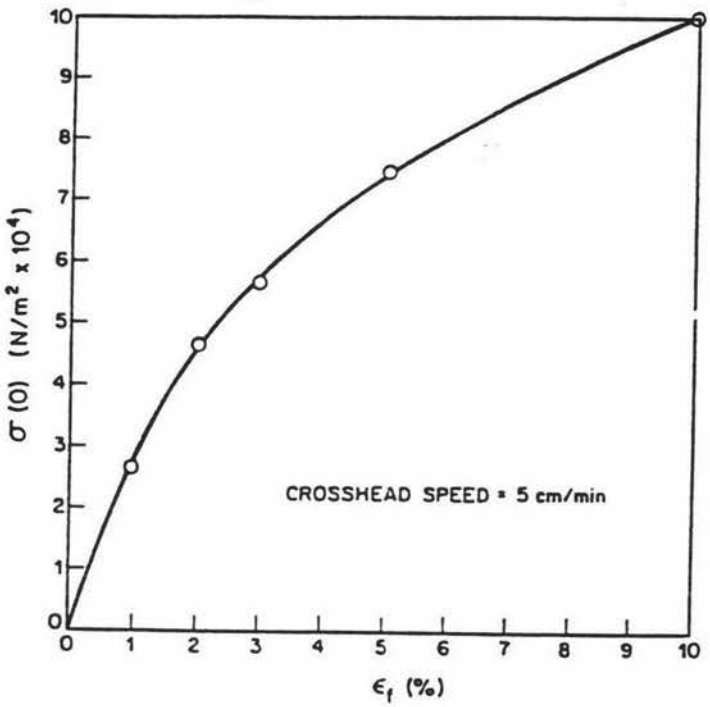


Figure 2.10 Effect of Strain on Instantaneous Stress for Relaxation Experiments of Galbanino Cheese (From Masi 1989)

Masi (1989) also found that at the same deformation level, different crosshead speeds (for setting test strains) produced corresponding variations in the relaxation modulus. These variations could be explained by considering that relaxation occurs during deformation. Similar results were obtained by Shama and Sherman (1973) with Cheddar and Edam cheeses.

According to Masi and Addeo (1986), as cheese is deformed, part of the internal stress relaxes. The relaxation for example, of four Italian cheeses (Mozzarella, Silano, Provoline, and Caciocavallo) showed that young cheeses with higher water content and smaller calcium (mineral) content relax further and more rapidly than aged cheeses. Shama and Sherman (1973b) and Taneya et al (1979) suggested that the relaxation mechanism is related to intermolecular links. According to Ferry (1980) the relaxation process in polymers is due for example to the existence of physical entanglements in the polymer network. Accordingly, stress relaxation which depends on entanglement concentration is due to the progressive disappearance of entanglements in the strained

network.

The conclusion of Ferry (1980) disagree with findings by Masi & Addeo (1984b) that by deforming a Mozzarella sample for the second time after the first relaxation, the second relaxation curve could be superimposed exactly on the first. This suggests that after the first deformation and relaxation, the casein network was not significantly different from its original configuration, thus concluding that relaxation in cheese occurs through simultaneous breakage and reformation of weak intermolecular bonds such as hydrophillic and hydrophobic bonds, or links due to Van der Waal's forces rather than the disappearance of physical entanglements.

2.6.5 Dynamic Measurements

This refers to the application of a harmonically changing stress, strain or strain rate with time. One of the form of change is sinusoidal and the time-scale of the measurement can be varied by changing the frequency of the oscillation. The controlled variables here could be the maximum amplitude of shear strain and the frequency. The measured responses are the maximum amplitude of the shear stress and the phase difference between the applied strain and the stress. Alternatively, a sinusoidal shear stress can be applied and the strain measured.

Dynamic experiments can be used to determine the elastic and viscous components of a viscoelastic material such as cheese (Whorlow 1980 and 1992; Luyten 1988; and Zoon et al 1988). When a dynamic shear strain is applied to a purely elastic material, the stress and strain are exactly in phase, in other words the phase lag, δ is equal to 0^0.

Viscoelastic materials being both elastic and viscous in nature, exhibit an intermediate phase shift of between 0^0 and 90^0 (Shoemaker et al 1992; Konstance and Holsinger 1992). In molecular terms these responses can be explained by the frequency at which molecular motion is occurring relative to the imposed stress within the material (Carter 1989). Fig. 2.11 show the stress-strain relationship of a viscoelastic material under

dynamic testing, while Fig. 2.12 gives a comparison between an elastic solid and a viscous fluid when subjected to a sinusoidal strain.

For a viscoelastic material the stress response to a sinusoidally varying strain is given by:

$$\sigma=\sigma_0\sin(\omega t+\delta) \tag{2.6.17}$$

The storage modulus G'(ω) and the loss modulus G"(ω) are then calculated as:

$$G'(\omega)=\frac{\sigma_0}{\gamma_0}\cos\delta \tag{2.6.18}$$

$$G''(\omega)=\frac{\sigma_0}{\gamma_0}\sin\delta \tag{2.6.19}$$

Other rheological parameters such as the complex/absolute modulus G*(ω) and the complex viscosity η* can also be calculated as:

$$G^*(\omega)=\frac{\sqrt{G'^2(\omega)+G''^2(\omega)}}{\omega} \tag{2.6.20}$$

$$\eta^*=\frac{G^*(\omega)}{\omega}=\frac{\sqrt{G'^2(\omega)+G''^2(\omega)}}{\omega} \tag{2.6.21}$$

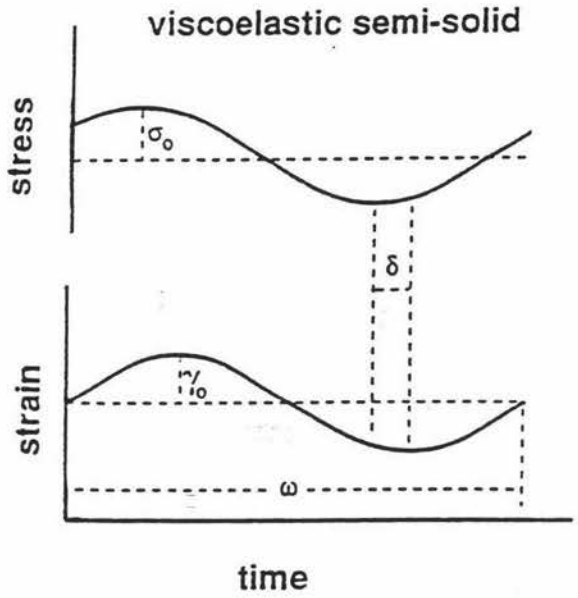


Figure 2.11 Shear Stress Response of a Viscoelastic Material Under Oscillatory Shear Strain (From Shoemaker et al 1992)

2.6.5.1 Application of Dynamic Measurements in Evaluation of Rheological Properties of Cheese and Related Foods

Dynamic measurements offer a rapid result with minimal physical and chemical changes to the material. Mechanical properties of food can be determined such as dynamic storage (elastic) modulus and dynamic loss (viscous) modulus at various frequencies and temperatures within a short time. Extremely small strains, usually up to 1% are used for viscoelastic food materials. These are within the linear range (Rao and Steffe 1992). The ratio of loss modulus G" to storage modulus G' is the measure of viscous to elastic components of a viscoelastic material as depicted by the loss tangent (tan δ). Fig. 2.12 illustrate the differences between an elastic solid and a viscous fluid.

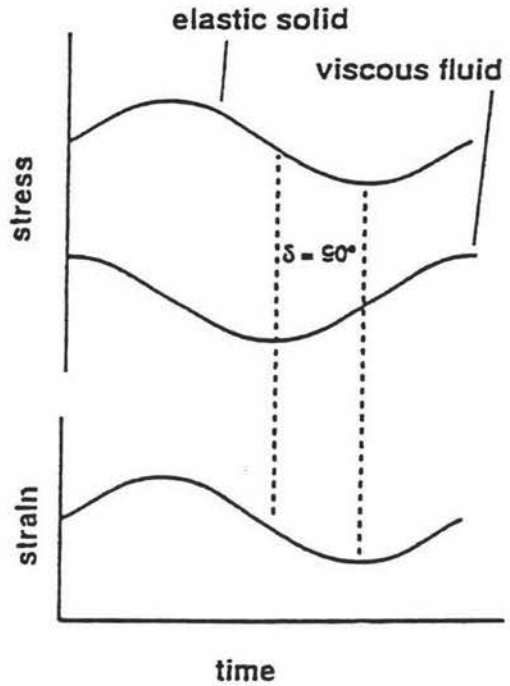


Fig.2.12 Comparison of the Shear Stress Responses of an Elastic Solid and a Viscous Fluid Under an Oscillatory Shear Strain (From Shoemaker et al, 1992)

$$\tan\delta = \frac{G''}{G'} \qquad (2.6.22)$$

Barnes et al (1989) found that the measurement of the dynamic moduli of milk gels was a sensitive way of detecting inherent natural differences between gels. According to Alexandri et al (1990) these differences were due to the genetic (whole group of casein protein) variation of casein protein which has two kappa variants, κ-CNA and κ-CNB, with different gel strengths. Thus the difference in their dynamic moduli was due to greater numbers of casein micelles in κ-CNB than in κ-CNA.

Tunick et al (1989) reported the non-uniformity of fat distribution within cheese as the factor contributing to the decrease in shear storage modulus G' and this is shown by the reduction of thermal stability of cheese (fat has lower storage modulus than casein at

temperatures above 21°C). They suggested that similar factors may cause similar effects on viscous/loss modulus.

Dynamic measurements which resolves the viscoelastic responses into storage and loss moduli of a material essentially detects the changes in the state of molecular motion as temperature is scanned (Carter 1989). The changes depicted by the loss tangent as temperature is raised indicates the molecular movement within the cheese sample as the sample becomes more liquid like/melts.

According to Nolan et al (1989) dynamic rheological measurements (mainly complex viscosity) determined up to a temperature of 70°C and frequencies from 0.10 to 100 radians per second follow an Arrhenius type relationship.

Nolan et al (1989) and Tunick et al (1990) also observed that the complex viscosity of Cheshire and Cheddar cheese decrease with temperature increase as indicated in Table 2.1. A plot of complex viscosity versus reciprocal of absolute temperature, (1/T) gives a straight line indicating agreement with Arrhenius equation;

$$\eta^* = A_{visc} \exp\left(\frac{E_{visc}}{RT}\right) \qquad (2.6.23)$$

A_{visc} = Arrhenius constant, E_{visc} = activation energy, R = gas constant (4.18 J/K mol) and η^* = complex viscosity.

The complex viscosity of the cheshire cheese at 20 and 60 weeks shows the effects of proteolysis during ripening.

Table 2.1 Values of Complex Viscosity of Cheese at Various Ages (log of Viscosity in dyne/cm^2;Tunick et al, 1989)

Temp.(^{0}C)	chesire (20 wk)	chesire (60 wk)	cheddar (60 wk)
20	6.05	5.94	6.19
25	5.90	5.71	5.74
30	5.64	5.50	5.40
35	5.24	5.23	5.00
40	4.91	4.96	4.60

Dynamic measurements are also indicative of the addition of ingredients to cheese. For example when 1% calcium caseinate is added to natural Mozzarella, a change in the storage and loss moduli was observed (Table 2.2).

Table 2.2 Shear Moduli of Natural and Imitation Mozzarella at 20^{0}C (Nolan et al,1990)

SAMPLE	G'(DYNES/CM^2)	G"(DYNES/CM^2)
Natural Mozzarella	$2.27 \times 10\ \omega^{0.17}$	$1.03 \times 10\ \omega^{0.19}$
With 1% calcium caseinate	$5.92 \times 10\ \omega^{0.20}$	$1.98 \times 10\ \omega^{0.14}$

According to Darby (1976) dynamic complex viscosity η^* can be separated into "in-phase" and "out-of-phase" components as:

$$\eta^* = \eta' - i\eta'' \qquad (2.6.24)$$

where η' = in-phase viscosity, η'' = out-of-phase viscosity, i = imaginary number ($\sqrt{-1}$).

$\eta'$the in-phase component is a measure of dissipated energy or loss energy, while η'' the out-of-phase component is a measure of stored energy. These relate the material's oscillatory strain rate to the corresponding oscillatory shear stress and are related to storage modulus G' and loss modulus G" as reported by Bistany and Kokini (1983) such that:

$$\eta' = \frac{G''}{\omega} \qquad (2.6.25)$$

and

$$\eta'' = \frac{G'}{\omega} \qquad (2.6.26)$$

2.7 FACTORS AFFECTING THE INSTRUMENTAL EVALUATION OF CHEESE

Objective rheological measurements depends on the factors such as sample slippage within the holding cell, structural integrity and defects of the sample, how the sample was taken from the bulk material, sample size and shape, environmental factors such as temperature and test method. Others are associated with instrumental responses such as time and friction between the sample and holding cell. Because these factors might determine the validity of rheological test results they must be understood.

2.7.1 Effects of Wall Slip

According to Cohen and Metzner (1985), Mannheimer (1982), Yoshimura and Prud'homme (1988) concentrated emulsions, suspensions, foams and polymer solutions often appear to slip along the confining walls. This apparent slip is usually caused by large velocity gradients in the thin region adjacent to the wall, where the viscosity is low because of a reduced concentration of the suspended phase. Wall slip can have large effects on steady shear rheological measurements. If slip occurs, the apparent viscosity can be significantly lower than the actual viscosity because only the viscosity of the low concentration zone is measured. The effects of wall slip on dynamic oscillatory shear measurements are less well understood. Slip effects should be eliminated in dynamic oscillatory measurements if one is to obtain proper and accurate data for interpretation of rheological properties of food materials.

To establish the occurrence of slip, waveforms have to be measured with two different gap separations at the same strain and frequency. Two identical waveforms resulting from two measurements will indicate absence of slip while difference in waveforms indicate slip has occurred (Nolan et al 1989).

Casiraghi et al (1985a) studied the effects in compression testing of a lubricated sample-platen interface, bonding of the sample to the platen and a non-lubricated non-bonded sample to determine the reproducibility and repeatability of results as affected by frictional and slip effects. It was found that these effects can be resolved better by bonding the sample to the platen.

Navickis and Bagley (1983) resolved the problem of slip in compression tests of Mozzarella and Cheddar cheese by bonding the samples to parallel plates of the Instron using a cyanoacrylate ester adhesive. The slip was attributed to the diffusion of milk fat on the specimen surface at room temperature. Different methods were used to counter the problem; these were, sandpaper attached to the aluminium plates, and bonding the sample directly to the aluminium plates using cyanoacrylate ester adhesive. There was a temperature difference between the set and the actual sample temperature in samples with sandpaper than samples bonded with cyanoacrylate adhesive. It indicates that the temperature difference was due to resistance imparted by sandpaper. This led to the conclusion that repeatable results with no evidence of slippage may be obtained with Mozzarella or Cheddar cheese samples bonded to the instrument parallel plates with cyanoacrylate resin adhesive.

2.7.2 Effects of Structural Defects

Inhomogeneities occur between cheese varieties and even within the same cheese variety. Walstra and van Vliet (1982) reported that within a sample size of 0.1 to 0.04 m (diameter or length) only those inhomogeneities larger than 0.001 m can disturb or cause poor reproducibility of the results. Even for a uniform product like processed cheese, minor differences cannot be totally discounted.

These inhomogeneities should be avoided as much as possible otherwise their effect should be determined first. During cheese maturation different sizes of holes may be formed. Some cheeses might lose moisture and form a hard surface or rind which might have higher compression forces than a sample from the centre of a cheese block. It is recommended that samples be taken from the middle of the block and in the same direction (van Vliet and Peleg 1991). If inhomogeneities such as structural defects are well distributed, the probability of finding them in a sample increases with sample size/volume.

2.7.3 Effects of Sampling Methods

There should be reproducibility in the way the sample is prepared. This includes the way the sample is taken from the whole cheese block either by using a wire cutter or cork borer. This has to be done such that no deformation occurs before the actual test. The use of oil as a lubricant is recommended to avoid distortions, and the dimensions of the test piece can be determined later. During sample preparation, stresses that could affect or cause deformation should be avoided, as for example, during placing in the measuring device (van Vliet and Peleg 1991).

Casiraghi et al (1985b) showed that samples taken near the surface of the cheese not protected from moisture loss required higher forces to achieve a given deformation while those from the centre of the same cheese need lower forces to obtain a given deformation. Casiraghi et al (1985b) suggested that to obtain a uniform sample shape, cheese blocks have to be cooled to 4^{0}C prior to cutting the sample.

2.7.4 Effects Related to Sample Shape and Dimensions

The sample shape depends on the type of test to be done. For uniaxial compression cylindrical samples are more suitable with diameter to height ratio of 1:1 to 3:1. This is due to the effect of changing height during compression. With shear experiments a

rectangular sample with uniform thickness is normally used (nothing in literature on cheese has been found, but this has been discussed earlier in section 2.6.3).

Sample bulging at the centre was experienced with an increase in contact area between the sample and the compressing plates. There was a maximum extension at the central part of the sample while minimum extension was observed at the compressing plates. With changes in temperature during deformation tests, complex sample behaviour may occur such as convex deformation near the contact surfaces and concave deformation at the sample centre (Carter and Sherman 1978).

Compression:

In compression tests, the stress-strain relationship is independent of sample size in ideal frictionless situations. This is not the case however in real compression where friction is encountered between instrument and sample surface in contact.

Friction causes part of the applied force to be used to overcome the friction between the lower and upper sample surfaces and the instrumental plates with which they are in contact. At 20% compression, lateral expansion occurs causing barrelling. This can be avoided by using lubrication oils such as mineral oils with low viscosity (Culioli and Sherman 1976).

According to Chu and Peleg (1985) cylindrical specimens of height to diameter ratio of 0.12 to 1.0 of potato, bologna sausage and processed American cheese, when uniaxially compressed, showed increased stiffness as the sample become flatter. It was demonstrated that correction procedures applied to calculations of modulus from dimensions yielded inconsistent results. This is an evidence that the relationship between stiffness, strength and shape also depends on factors other than the material composition.

Tension:

The length of the cheese sample should be twice the width in tensile experiments. This

is because the energy needed for fracture is obtained from the elastic energy stored in the volumes next to the growing crack. The size of the test piece should be such that this volume is outside the part between the grips holding the test sample. Large structural defects must be avoided. If fracture starts only on a few places in the sample, it will take some time before the fracture plane goes through the whole sample. During this time deformation continues resulting in an (apparently) higher fracture strain for a larger test-piece.

Peleg (1977) recommended that the mechanical properties of foods should not be compared when tests were performed at distinctly different sample dimensions.

2.7.5 Effects of Temperature

Temperature has a major influence on the mechanical properties of cheese. Experiments should be done under known and constant temperature conditions (Luyten 1988). Temperature history must be well recorded, this is to say the treatment that the sample was subjected to prior to testing, such as heating up, where the fat part may change from solid at low temperatures to liquid at temperatures above 23°C for non-homogenized natural cheese.

Carter and Sherman (1978) showed that between 20°C and 36°C at the same crosshead speed, the force required to achieve a given deformation of natural cheese decreases as the temperature increases. At temperatures above 23°C natural cheese became softer and fat droplets appeared on the cheese surface. Luyten (1988) demonstrated using Gouda cheese the effect of fat on shear modulus when fat is in solid or liquid form. The shear modulus of solid fat is about the same as that of protein matrix. As the portion of fat liquifies above 23°C, its shear modulus decreases.

Due to cheese inhomogeneity and sample size, samples should be prepared such that enough time is given for the centre of the sample to temperature-equilibrate. Significant water evaporation can be avoided during equilibration or sample preparation by sealing

the samples in vapour barrier films. The results obtained by Culioli and Sherman (1976), and Carter & Sherman (1978), on temperature-dependence using Leiceister and Gouda cheeses showed that at lower temperature and a given deformation, one needs more stress to deform a sample while less stress is needed for the same deformation at a higher temperature. This was supported by Casiraghi et al (1985) using Mozzarella, Cheddar and processed cheese.

2.7.6 Effects of Test Method

Cheese is a viscoelastic material that can store and dissipate mechanical energy. The viscous or flow properties are time-dependent, while the elastic behaviour, fracture stress and fracture strain depend on the rate of strain/deformation. The viscoelastic characteristics of cheese influence its rheological and fracture behaviour as demonstrated by Mulder (1946), Shama and Sherman (1973), Dickinson and Goulding (1980), Creamer and Olson (1982) and Luyten (1988). They concluded that several influences are more specific such as :

(a) At lower strain rates more bonds between the structural elements are able to relax during deformation. The stress needed to reach a certain strain is lower resulting in smaller values of Young's modulus (E) and shear modulus (G). With decreasing strain rate the stored strain energy per unit area/volume at a given strain decreases.

(b) Cheese may flow even before fracture occurs leaving a lasting deformation after the removal of the stress. The magnitude of flow depends on the time of application of the stress. Deformation at slower strain rates results in higher strain to fracture as observed by Luyten (1988) with Gouda cheese.

c) At high strain rate, less energy is available for crack propagation and this may lead to the increase of strain to fracture with increasing strain rate. Masi (1989) concluded that cheese compression relaxation test responses depend to a large

extent on the experimental conditions under which the tests are run.

(d) Bagley and Christianson (1986) supported the findings in (c) as a result of differences in a stress-growth function. The differences observed appear to related to the differences in the time required to deform a sample under various experimental conditions.

Alfrey (1948) showed that if stress was applied previously, then the resultant total deformation at any time (t) equals to the sum of the total deformations observed at time (t) for each of the loads applied separately.

Shama and Sherman (1973) concluded that linearity and nonlinearity of viscoelastic behaviour using the Instron was due to the finite time required to apply the force in creep or deformation in stress relaxation experiments. With changes in crosshead speed the time needed to obtain a given deformation varies such that linear viscoelastic materials might show nonlinear behaviour. In this case they suggested that a correction should be applied for short time creep or stress relaxation experiments to establish whether the food sample is linearly or nonlinearly viscoelastic.

2.8 EVALUATION OF MELTING PROPERTIES OF CHEESE

Melting characteristics are the most important physical property of processed cheese, Cheddar, Mozzarella and cheese analogues. Melting properties determine the use of cheese in cooked foods, toasted sandwiches, cheeseburgers, pizza and popular Japanese and Italian Foods (Weik et al 1957; Olson & Price 1958; Rayan et al 1980; Park et al 1984; Campanella et al 1987; Kindstedt et al 1989; and Savello et al 1989).

Evaluation of cheese meltability (degree of melting) using instrumental measurements is complicated by factors such as cheese inhomogeneity, changes in shape during heating, temperature gradients within the sample, and phase separation during heating or oiling off causing slippage of samples between the holding plates.

According to Park et al (1984) the difficulty in objective evaluation of cheese melting characteristics are related to both heat transfer, thermal phase change of the solid to liquid cheese, and the flow properties of the melt. These factors are determined by cheese composition and microstructure, but these factors are interdependent and sometimes transient. Factors such as external temperature distribution and humidity have to be considered during the measurements, and the assumption that a single factor can be used as a means of describing cheese meltability might be inappropriate (Park and Rosenau 1984).

Ruegg et al (1991) reported the requirements of good cheese meltability as:

(1) that the cheese should melt in a certain temperature range.

(2) that cheese should remain homogenous in appearance, that there is no fat separation and no granular texture in the mouth and,

(3) that the apparent viscosity should be low enough for the material to flow clearly but high enough for the flow to be not too fast, ie there should be optimum viscosity.

Most of the research work on cheese meltability has been empirical, and the data obtained from these experiments could not be used to predict melting characteristics other than those specific to the process or product concerned (Bagley and Christianson 1987). However, these empirical test are important as they serve as an index of product quality and processing characteristics and can be used in process control (Szczesniak 1977; Prentice 1983).

2.8.1 The Oven Method

A sample of known dimensions is placed in the oven at a specified temperature for a given time. The change in sample dimensions is measured after the specified heating time has elapsed and the percent change is calculated as the percent melt.

Different indices of meltability have been used, for example change in height of the

sample, change in sample diameter, time required for melting, distance of flow from a reference line (Campanella et al 1987). Temperatures used for evaluation of melting also varied from one study to another. The time for heating cheese also varied, and the type of cheeses evaluated were different.

This might have led to poor correlation between melting indices of cheeses as for example in a report by Kosikowski (1977) where correlations between Schreiber and Arnott tests were poor because of the different test methods used. While Arnott measured the change in height of a cheese sample using an oven at 100°C for 15 minutes, Schreiber measured the change in diameter of a cheese sample using an oven at 232°C for 5 minutes (Kosikowski 1977). Park et al (1984) demonstrated that the lack of correlation between these two tests was due to measurements of different meltability indices and that heat has different effects on cheese according to differences in heat transfer coefficients, period of heating, and the temperature.

Ruegg et al (1991) suggested standardization of the test conditions such as sample pre-treatment, sample geometry and size, time-temperature combinations, and heating and measuring devices. They observed that during tests evaporation of water takes place from cheese samples, and the rate of heat transfer to and within the sample in relation to the sample size and shape has to be considered. The final diameter or percent increase in the area may also depend on the surface tension of the melted cheese.

2.8.2 Dropping and Softening Points

Another method of measuring meltability was suggested by Schluep and Puhan (1987). Using Raclette cheese melting quality was related to organoleptic evaluation and physical properties such as "dropping point"(the temperature at which the melted sample falls of a nipple) and "softening point"(the temperature at which the first drop of a melted cheese sample starts to flow out of a nipple). For Raclette cheese the dropping point was between 65°C and 67°C with softening points 9°C lower. Their findings indicated that there was no relation between fat content, moisture content, fat free dry matter and the

melting quality. Instead melting quality was related to pH and calcium bound casein and especially to breakdown of α_s, and pre-α_{s1} casein during maturation. Eberhard et al (1988) used Raclette cheese to evaluate meltability and found out that meltability has a linear relationship with pH and water content. It was confirmed that Raclette cheese from pasteurised milk has a dropping point of about 65^{0}C and when the dropping point is lower than 65^{0}C, the meltability is mostly good. Cheese with poor melting property has low water content, fat, and intact protein but higher contents of sodium chloride, calcium and water soluble nitrogen.

Blumenthal et al (1976) used the standard dropping point to measure the melting properties of Raclette cheese. This method has several draw-backs such as the control of heat transfer, oiling-off before reaching the dropping temperature or the drop not falling because of the viscosity of the cheese (Eberhard et al 1986 and Ruegg & Moor 1988). Eberhard et al (1986) recommended that the dropping and softening points be used to study zonal variations within a cheese block rather than cheese texture and/or viscosity owing to the small sample size required for the test.

2.8.3 Squeezing Flow Rheometry

Conventional instrumental determinations of cheese meltability are limited by slippage and viscoelastic effects. Casiraghi et al (1985) demonstrated a way to overcome these effects by use of squeezing flow rheometry based on the compression of a sample between two parallel plates. The presence of slip due to self-lubrication causes a distorted shear flow or plug flow. The lubrication of the parallel plates and therefore the incorporation of the slip and lubrication effects in the calculations of the results was used as a way of solving this problem (Campanella and Peleg 1987; Campanella et al 1987). Fig. 2.13 illustrate the sqeezing flow rheometry.

According to Chatraei et al (1981) with squeezing flow rheometry, a biaxial elongation viscosity can be determined such that:

$$\eta_b = 2F(t)\left(\frac{H_o - V_z t}{\pi R^2 V_z}\right) \qquad (2.8.27)$$

where η_b = biaxial elongation viscosity, F(t) = momentary compressive force, H_o = initial height of the specimen, R = plates radius, V_z = vertical squeezing velocity.

Since melted cheese is a non-Newtonian fluid, the biaxial elongation viscosity is a function of biaxial extensional strain rate ε_b so that η_b is an apparent biaxial elongation viscosity. The biaxial extensional strain rate is given by the following equation:

$$\dot{\varepsilon}_b = \frac{\dot{\varepsilon}_z}{2} = \frac{V_z}{2(H_o - V_z t)} \qquad (2.8.28)$$

where $\dot{\varepsilon}_z$ = uniaxial strain rate.

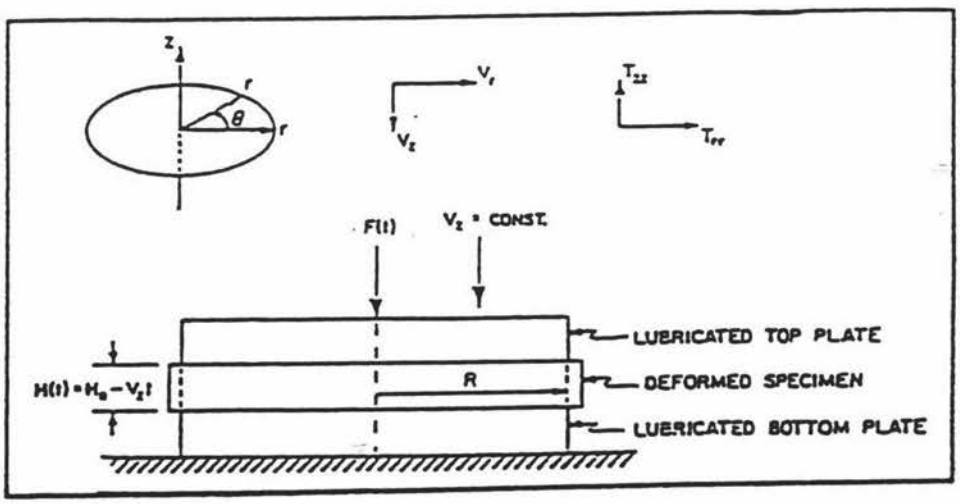


Figure 2.13 Schematic View of the Geometry of Lubricated Squeeze Flow, Only with the Absence of Friction will the Flow Front be Flat (plug flow) Otherwise the Front will be Parabolic and the Forces Much Higher (From Campanella et al 1987)

Plots of elongational viscosity against the biaxial strain rate (Fig. 2.14) of squeezed processed American cheese at various temperatures show that at low rates the elongation viscosity has weak dependency on the rate thought to be a result of elastic effects dominating. However, the plot shows that after a short period of transient flow regime, the viscosity reached a maximum and remained stable or slightly declined as the strain rate increased (Campanella et al 1987). The plots indicate a steep transient region caused by melts viscoelasticity. Cheese viscosities taken from the plateau regions of the plot at different temperatures do not obey the Arrhenius relationship. The plots of elongation viscosity η_b against the reciprocal of temperature (1/T) are not straight lines. They were either concave upwards or downward depending on cheese type (Ruegg et al 1991).

Elongation viscometry is said to be a useful method to study cheese meltability because it eliminates slip as a source of artifacts, the method is relatively simple, requires fairly cheap equipment, and does not require instrumental and procedural refinement (Campanella et al 1987 and Ruegg et al 1991).

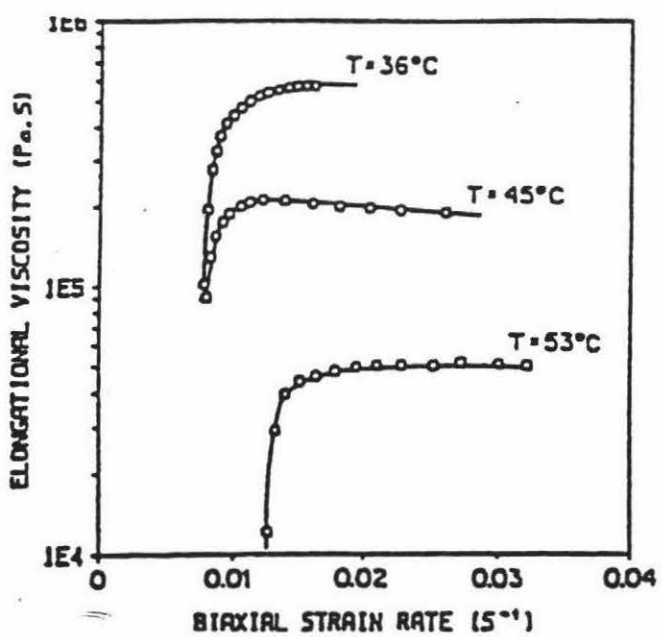


Figure 2.14 Elongation Viscosity v's Strain Rate of Processed American Cheese at Various Temperatures (From Campanella et al 1987)

2.8.4 Rotational Viscometry

Lee et al (1978) used the Brookfield viscometer to measure the meltability of various cheeses. The initial melting temperature was defined as that at which the instrument reading became less than full scale. This method was discounted due to dependence of results on the geometry of the instrument and the experimental parameters used; it can provide only the arbitrary scale for comparison. Owing to slip and viscoelastic effects, rotational viscometry is not an appropriate method for obtaining rheological data cheese melts (Smith et al 1980; Park et al 1984; Ruegg et al 1991).

2.8.5 Capillary Viscometry

Smith et al (1980) used this method to determine the flow properties of a melted Mozzarella cheese. The method is based on well-defined parameters such as shear stress and shear rate. Other than the method being time consuming, with elaborate procedures and expensive equipment, the method is reliable for this type of cheese.
The shear stress at the capillary wall σ_w is given by:

$$\sigma_w = \frac{\Delta P R}{2L} \qquad (2.8.29)$$

where R and L are capillary radius and length respectively and ΔP is the pressure drop along the capillary length. The shear rate at the capillary wall is given by:

$$\dot{\gamma} = \frac{4Q}{\pi R^3} \qquad (2.8.30)$$

and Q is the volumetric flow rate in the capillary. (Equation 2.8.30 is strictly valid only for Newtonian liquids).

Using mathematical procedures, the slip and viscoelastic effects can be evaluated using

experiments with different capillaries and flow rates (van Wazer et al 1967). With the exception of Mozzarella cheese, this method is not suitable for other cheese melts because artifacts caused by slip, end, and viscoelastic effects dominate the flow pattern (Smith et al 1980).

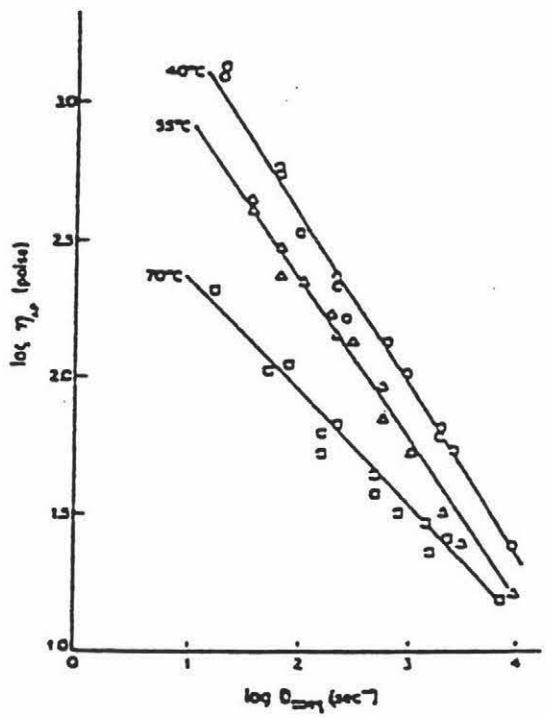


Figure 2.15 Apparent Viscosity v's Shear Rate for Mozzarella Cheese at Various Temperatures (From Smith et al 1980)

2.8.6 Differential Scanning Calorimetry

Tunick et al (1989) used this method to distinguish natural Mozzarella from imitation Mozzarella made from calcium caseinate. The enthalpy of the melting fat transition at 18°C decreased with increase in the concentration of calcium caseinate. Scanning electron microscopy revealed an agglomeration of lipids in imitation cheese whereas the

natural cheese has uniformly distributed fat globules. The addition of caseinate apparently reduced the enthalpy due to its effects on fat crystallization.

The discernible endothermic effects reflect the melting of fat. Other physical changes that result in textural modification and flow apparently involve gradual low-energy transitions undetected by the standard differential scanning calorimetry procedure (Tunick et al 1989; Ruegg et al 1991).

2.8.7 Dynamic Viscoelasticity

Taneya et al (1979) determined the melting properties of Gouda, Cheddar, soft and hard processed cheese using dynamic viscoelasticity with temperatures varying from -5°C to 90°C by applying vertical oscillation with amplitude of 0.1 mm and frequencies of 3 to 100 Hz.

Natural cheese has a relaxation time distribution of 1 to 10^{-4} second which shifts towards longer relaxation times as maturation proceeds (caused by moisture loss and break-down of protein-protein bonds due to proteolysis). The cheese becomes harder and less meltable. It was pointed out that for natural cheese, interaction between casein particles become weaker because water molecules interact with the casein particles, acting as a plasticizer. During very long maturation periods, water may be lost resulting in less plasticizing and therefore harder cheese.

Processed cheese has a relaxation time distribution of 1 to 10^{-6} second which extends into a shorter relaxation time range than natural cheese. This can be explained by more hydration of casein micelle in processed cheese than in natural cheese. The comparison of network structure of natural cheese and processed cheese indicate that processed cheese has a weaker structure (Taneya et al 1979).

Experiments done using Gouda, Cheddar and processed cheeses (Taneya et al 1979) confirmed the effect of maturation and thus protein-protein interaction in cheeses as

follows:

2.8.7.1 Gouda Cheese

At a fixed frequency of 10 Hz, the storage modulus G' decreases suddenly at 15°C, 29°C and 32°C for one month, three months and five months maturation periods respectively. At the same frequency and cheese of the same maturation times, the loss modulus G" show peaks in the higher temperature range with longer maturation periods. The dynamic loss tangent for one month old cheese show peak at about 45°C. These peaks shift towards higher temperature range with three and five months old cheese. Fig. 2.16a-c illustrate the effects of maturation on dynamic properties of Gouda cheese.

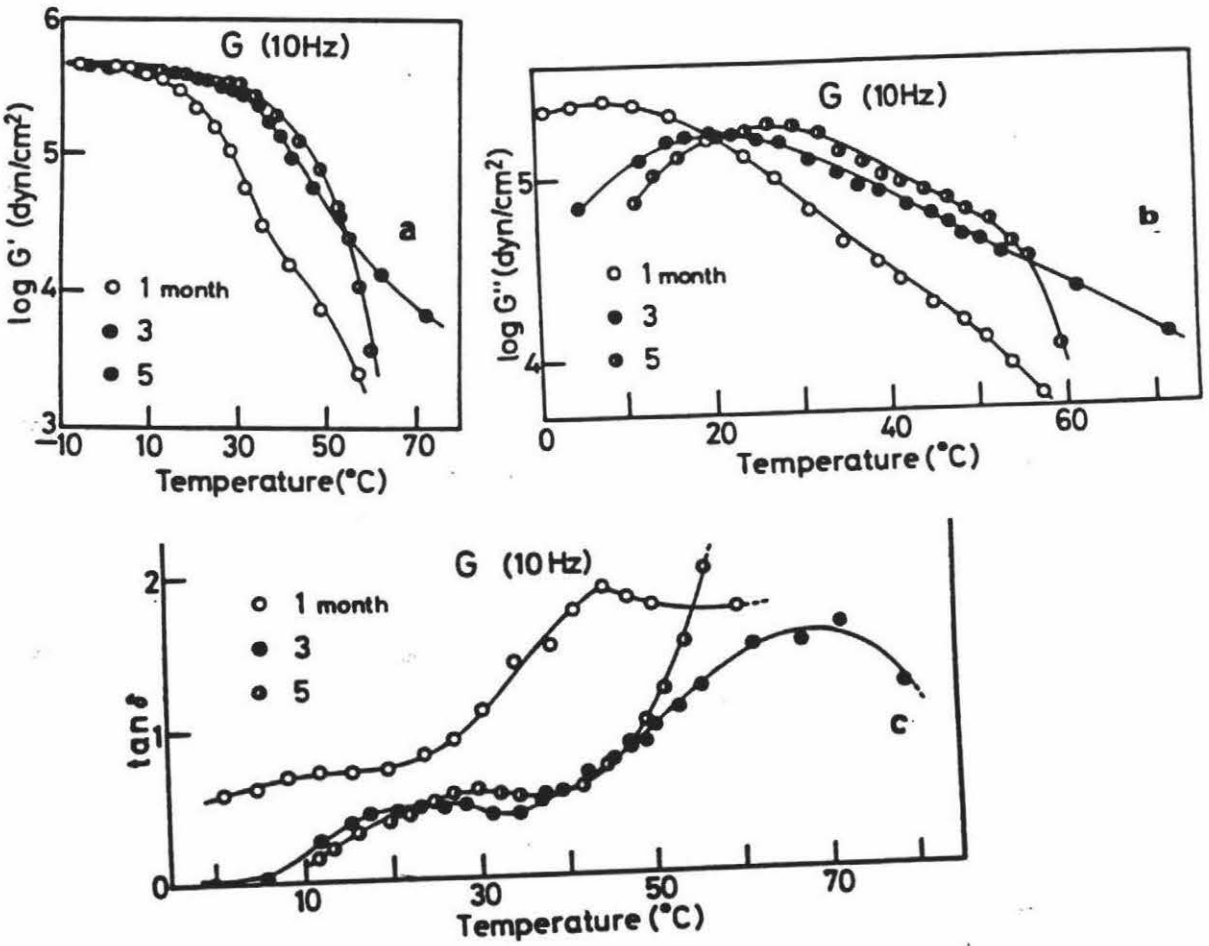


Figure 2.16 The Effect of Maturation Time on the Dynamic a) Storage Modulus, b) Loss Modulus and c) Loss Tangent of Gouda Cheese (From Taneya et al 1979)

2.8.7.2 Cheddar Cheese

Temperature dispersion for Cheddar cheese show similar trend as that of Gouda cheese. There was a sudden decrease in storage modulus at 20°C for one month old cheese, this increased with maturation time to 28°C and 41°C for three and five months old cheeses respectively. However, it was noted that the peak temperatures were higher for Cheddar than those corresponding to Gouda cheese in each respect. The same trend follows for loss modulus G" and loss tangent (tan δ). Fig. 2.17a - c illustrate the dynamic properties of Cheddar cheese of varying maturation time.

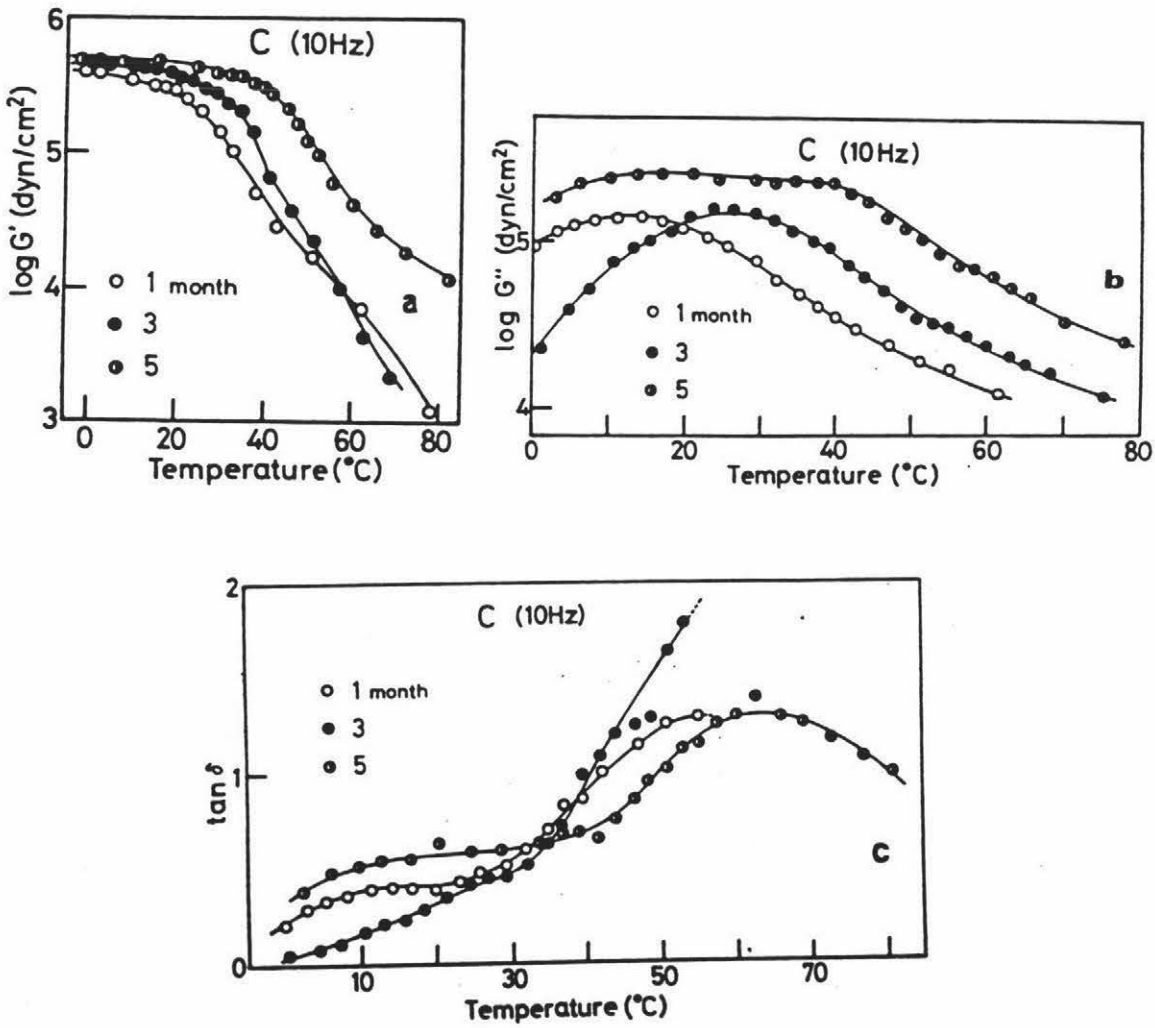


Figure 2.17 The Effect of Maturation Period on a) Storage Modulus, b) Loss Modulus and c) Loss Tangent of Cheddar Cheese (From Taneya et al 1979)

2.8.7.3 Processed Cheese

Taneya at al (1979) measured the dynamic properties of two types of processed cheese. These were hard processed cheese and soft processed cheese. The temperature dispersion of hard processed cheese at a frequency of 10 Hz was similar to those of natural cheese, with a sudden decrease in storage modulus G' at 15°C. Within the measured temperature range , the storage modulus G' for soft processed cheese was lower than that of hard processed cheese. The loss modulus G" of hard processed cheese increases to a temperature of about 20°C and then decreases whereas that of soft processed cheese decreases gradually without any peak. The loss tangent (tan δ) for hard processed cheese show a sudden decrease at 60°C whereas that of soft processed cheese does not have any distinct peak. Fig. 18a to c illustrate the dynamic properties of soft and hard processed cheese.

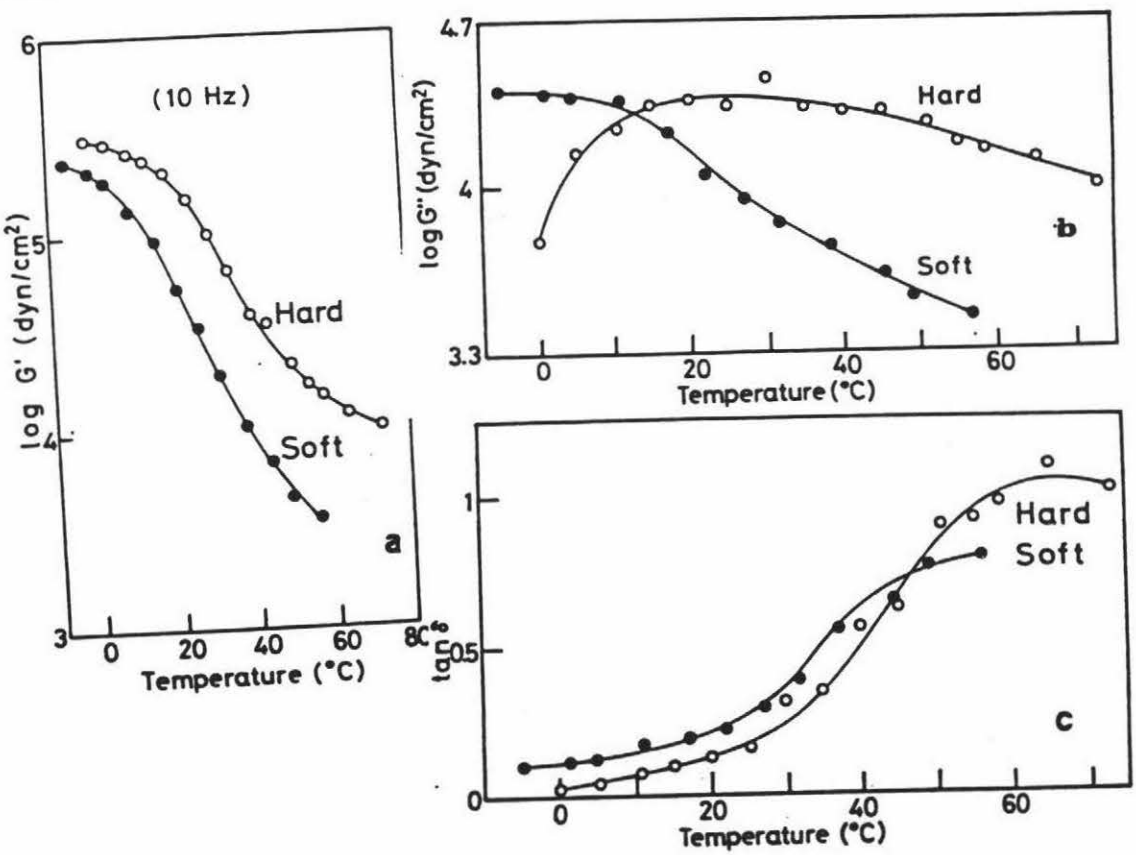


Figure 2.18 Effects of Temperature on Dynamic a) Storage Modulus, b) Loss Modulus and c) Loss Tangent of Soft and Hard Processed Cheese (From Taneya et al 1979)

2.7.4 General discussion

The temperature corresponding to the point of sudden decrease in G' is referred to here as the softening point while the temperature corresponding to the decrease in G" is referred to as the transition point. As moisture content increases, these temperatures become lower. The effect of maturation is an increase of softening and transition points upon heating. In soft processed cheese, the lower values of G' and G" are associated with protein hydration and therefore weaker protein-protein bonds (loose casein structure).

The existence of artifacts cannot be ruled out especially as fat separation takes place in most natural cheeses. Since melting is a gradual process, it is not easy to detect the exact melting point with current methods of dynamic testing. Preliminary experiments indicate that the tan δ against temperature plot may be promising in the evaluation of melting characteristics of various cheeses (Ruegg et al 1991).

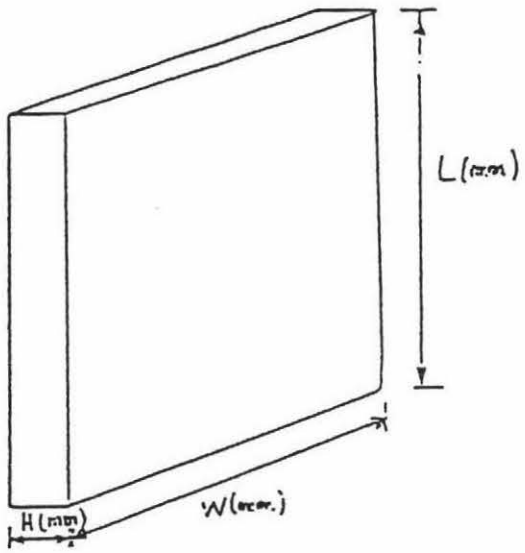
2.8.8 Impulse Halfsquare Small Amplitude Deformation

Farris R.J. (1984) developed a new technique of measuring mechanical properties of ageing viscoelastic material using impulse small amplitude deformation. An important aspect of the impulse method is that it is independent of a particular piece of equipment or mode of deformation (Vratsanos M. S; 1987). Under the assumption of linear viscoelastic behaviour, assuming an equilibrium starting condition and the stress returning to its initial value after the deformation, it is considered that the path of the deformation is arbitrary.

This method seems to simplify data treatment and may be adaptable for simple machines like the Texture Analyser.

One deformation that could be used in impulse viscoelasticity is the half-square shear waveform configuration which is available with the Instron Universal Testing Machine Model 4502. Figure 2.19a and b gives the sample configuration and a typical stress-

strain responses.



H = Sample thickness [mm]

W = Sample width [mm]

L = Sample height [mm]

D = Amplitude of deformation [mm]

Figure 2.19a Sample Dimensions

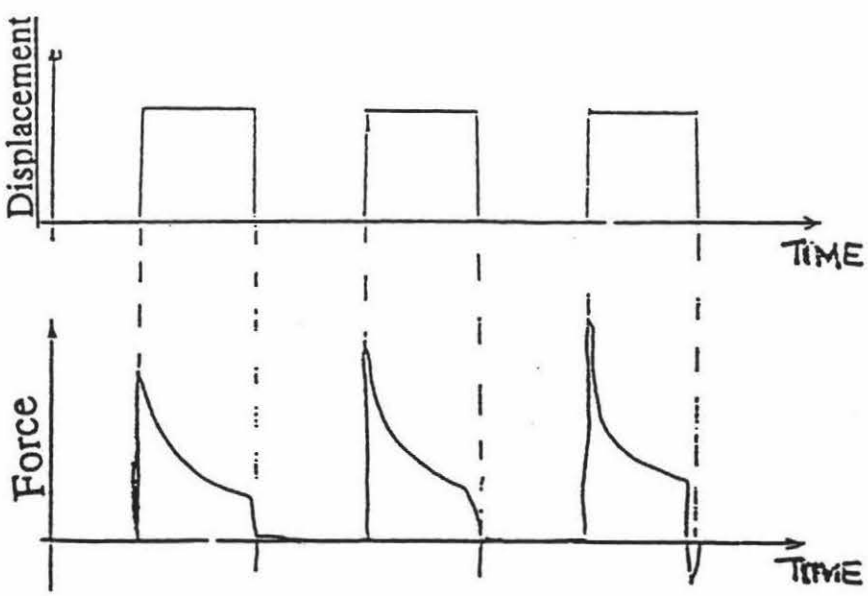


Figure 2.19b Typical Displacement/Force v's Time Responses (From Vratsanos M.S. 1987)

Strain can be calculated as: strain = Displacement (amplitude)/ Sample thickness

$$\%\gamma = \frac{D}{H} x100 \tag{2.8.31}$$

and the storage and loss moduli for shear test was derived from Farris R. (1984)

$$G'(\omega) = 10^6 x \frac{\pi f H}{2DWL} \int_0^{\frac{1}{2f}} F(t)\sin(2\pi f t)dt \tag{2.8.32}$$

$$G''(\omega) = 10^6 x \frac{\pi f H}{2DWL} \int_0^{\frac{1}{2f}} F(t)\cos(2\pi f t)dt \tag{2.8.33}$$

phase difference is calculated as:

$$\tan\delta = \frac{G''(\omega)}{G'(\omega)} \tag{2.8.34}$$

and dynamic viscosity is calculated as:

$$\eta' = \frac{G''(\omega)}{\omega} \tag{2.8.35}$$

where, $\omega = 2\pi ft$, G' = storage modulus [Pa], G" = loss modulus [Pa], F = Force [N], f = frequency [cycle per second], t = time [seconds], η' = dynamic viscosity and δ = phase angle.

Note. Frequency is referred to as the number of times per second a full cycle is repeated. The frequency of a waveform is therefore a reciprocal of its period (T) = 1/f. For half cycle waveforms T = 1/2f.

CHAPTER 3

MATERIALS AND METHODS

3.1 INTRODUCTION

In this study, the rheological and melting properties of processed cheese slices were measured using shear stress relaxation, shear creep and dynamic impulse halfsquare to measure storage modulus, loss modulus and loss tangent. The measurements were carried out using an Instron Universal Testing Machine (Instron) and a TA.HD Texture Analyser (TA.HD). The cheese microstructure was examined using a confocal laser scanning microscope.

This chapter describes the materials, the principles of each piece of equipment and the methods used to carry out the work.

3.2 PROCESSED CHEESE SLICES

These were provided by the New Zealand Dairy Research Institute (NZDRI). The cheese slices were consumer products manufactured by Pastoral Foods Limited of Eltham, New Zealand. The processed cheese slices were of two types manufactured under different process conditions as follows.

3.2.1 Slice On Slice (SOS)

The blend was cooked under partial vacuum at 75^{0}C for 2.5 minutes by direct injection of steam. The cheese melt was then slowly cooled to below 10^{0}C by pumping the melt through a narrow gap of chilled rollers rotating at low speed. A thin layer measuring 2.0 mm thick was formed and this was cut in slices measuring 80 mm length and 80 mm width. These were piled on top of each other to a weight of 500 g and packed in moisture-impervious polyethylene film.

3.2.2 Individually Wrapped Slices (IWS)

The blend was cooked at 83°C for 3.5 minutes by direct injection of steam. Cooking was under partial vacuum. The cheese mix was then pumped through a shearing pump to an extrusion film (2.5 mm) where a package was formed, filled and sealed. These were then cooled rapidly to below 10°C by passing through a chilled water bath at high speed. These slices measured 2.5 mm thick, 80 mm long and 80 mm wide. These slices were individually wrapped in moisture impervious polyethylene film and then packed in a secondary package to a weight of 250 g.

Chemical compositions were measured by the NZDRI. The compositions of the two types of slices are given in Table 3.1

TABLE 3.1 The Chemical Composition of Processed Cheese Slices

Sample	Calcium mMol/kg	Fat %w/w	Lactose (mono)%w/w	Moisture %w/w	pH	Salt %w/w	Protein %w/w
SOS	122.0	27.0	0.90	41.30	5.27	2.23	20.29
IWS	138.0	25.0	0.90	46.40	5.31	2.20	19.65

The table show minor differences in main components such as protein, fat and the moisture.

3.2.3 Other Materials

These were materials used during the experimental work. They included (i) cleaning chemicals such as acetone and Loctite 703 quick clean, (ii) Loctite 702 IS activator, (iii) Loctite 406 cyanoacrylate adhesive, (iv) liquid carbon dioxide and (v) staining reagents such as Nile red, Nile blue, Fluorescein and Rhodamine.

3.3 EQUIPMENT

The stress relaxation measurements were carried out using an Instron Universal Testing Machine and a TA.HD Texture Analyser, and the results obtained from the two instruments were compared. The shear creep test and the dynamic tests were done using the Instron only. The confocal laser scanning microscope was used to examine the microstructure of processed cheese slices. The operating principles of each piece of equipment are given below.

3.3.1 Instron Universal Testing Machine

Instron Universal Testing Machine (model IX series 4502 manufactured by Instron Company of Coronation Road, High Wycombe, Bucks. England.) comprised a table-mounted frame and a front panel connected to a tower/microprocessor based control console. Figs. 3.1a and 3.1b. show the table mounted frame and the microprocessor.

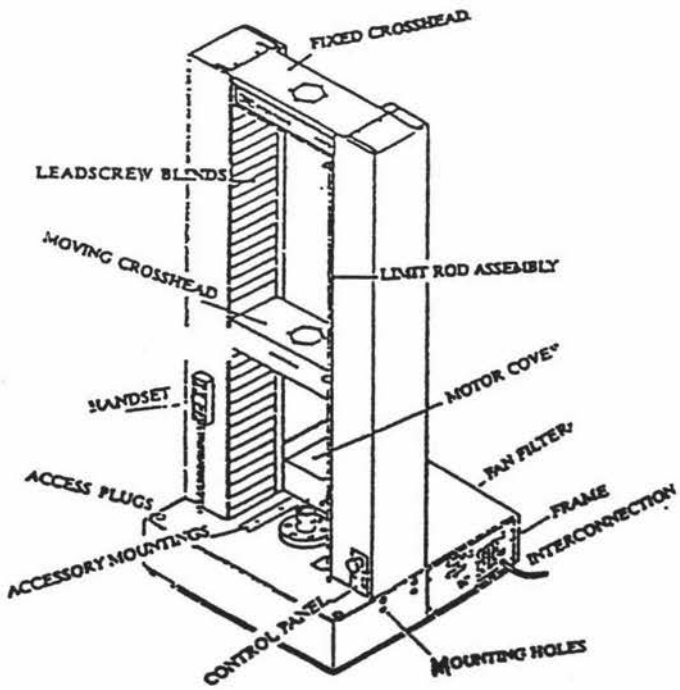


Figure 3.1a Table Mounted Frame Showing Components (From Instron User Manual 1989)

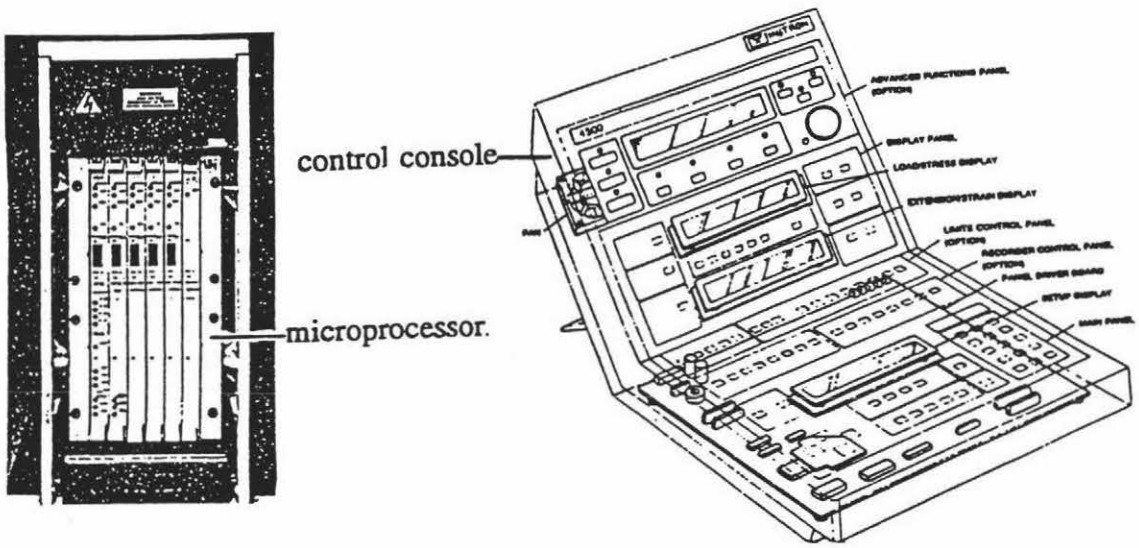


Figure 3.1b Microprocessor and the Control Console (From Instron User Manual 1989)

The Instron model IX series 5402 has a maximum load capacity of 10 kN and a minimum of 10 N. The minimum force measurable is 0.25% of the full-scale load cell capacity. Thus the load cell used determines the forces which could be imposed during the experimental work. A load cell of 100 N was used in this work and force measurement could be recorded from 0.25 N to a maximum force of 100 N. This load cell was selected with the assumption that the forces applied during the testing of cheese slices would be within the load cell capacity. The crosshead speed ranges from a minimum of 0.05 mm per minute to a maximum of 1000 mm per minute. This permitted the choice of a wide range of forces and crosshead speeds as desired according to the properties of the material on test.

The Instron has fixtures and accessories such as a temperature-control cabinet with in-built heating element, a carbon dioxide inlet and an internal fan for heat distribution. Several Instron-made extensions can be attached to the crosshead. Several test modes such as tension, compression, flexure and shear are available. Measurements could be

either stress, strain, average strain or position, with generation of waveforms to control the crosshead movement such as sine, square, triangle, ramp, halfsine, halfsquare, and halftriangle. The shear strain and the shear stress were chosen for static tests while the shear halfsquare waveform was chosen for dynamic tests.

The commands to the crosshead drive motor are derived from the microprocessor and the crosshead positional information, and information regarding specimen responses during the test are passed back to the front panel for display and control purposes. The Instron is interfaced with PC-type IBM compatible 386 SX-33 MHz with 2 MByte memory for data acquisition.

3.3.2 The Texture Analyser TA.HD

The TA.HD Texture Analyser version 5.09 is a microprocessor controlled texture analysis system manufactured by Stable Micro System, Blackdown Rural Industries, England. It has similar operational principles to the TA.XT2 Texture Analyser with the latter being more limited to the 0.1 mm minimum displacement while the former has special operational functions which allows measurements of displacements below 0.05 mm.

It consists of two separate modules, the test-bed and the control console (keyboard). The probe carrier could be moved up or down according to command. Figs. 3.2a and 3.2b show the main components of the TA.HD.

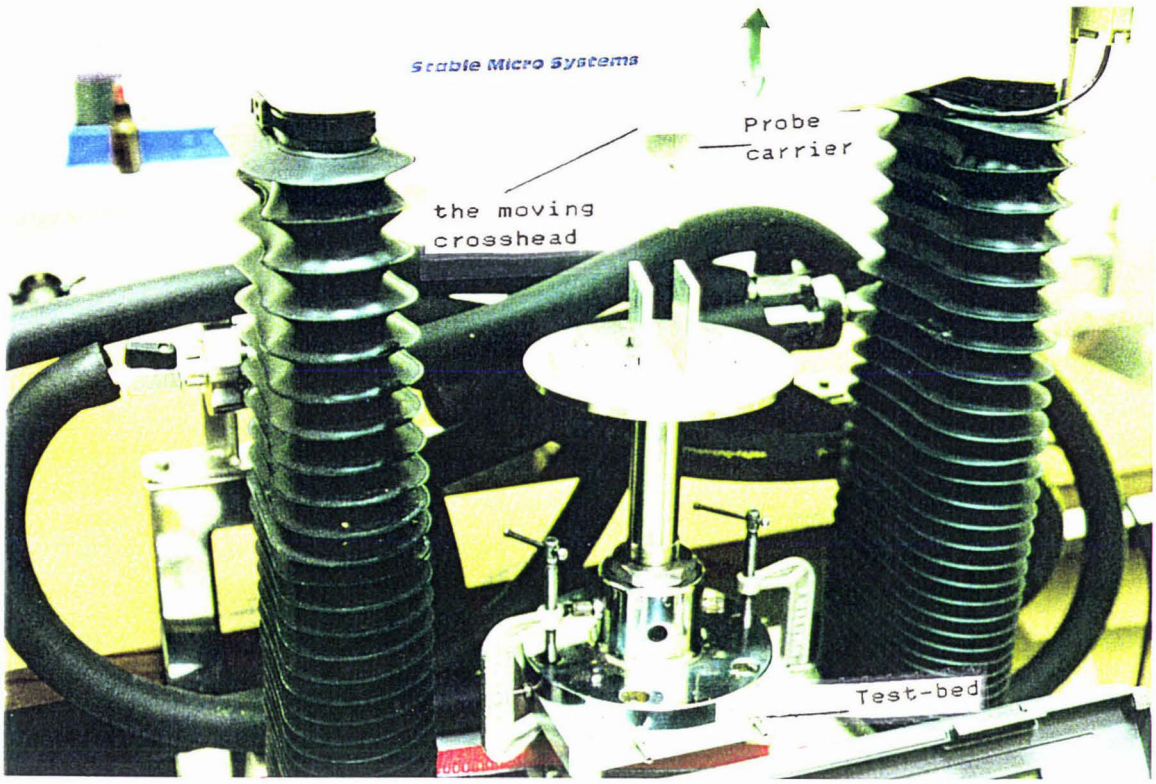


Figure 3.2a Texture Analyser TA.HD Showing Components

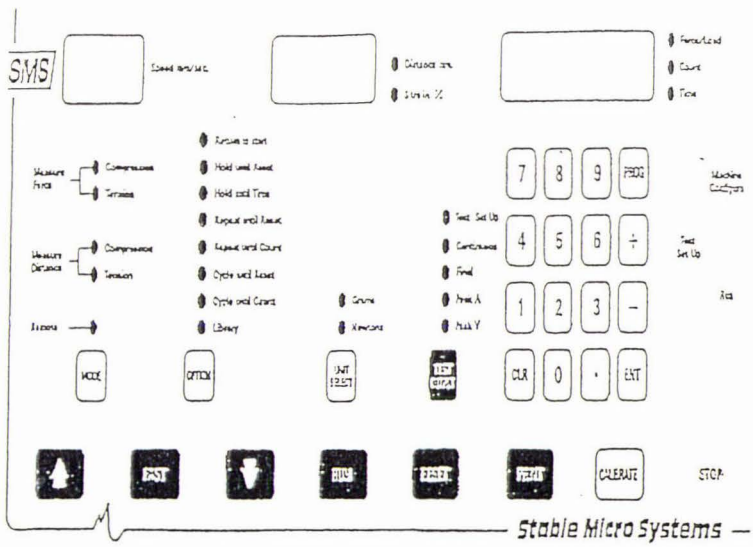


Figure 3.2b The Control Console Showing Available Commands (From user manual 1993)

The TA.HD has a maximum load capacity of 50 N and a distance resolution of 0.0025 mm, with a minimum probe speed of 0.1 mm per second and a maximum speed of 10 mm per second. Any speed between these limits could be chosen as desired. Available test modes are tension and compression. The options for carrying out these tests are either to impose a force and measure the resulting displacement or impose a strain/displacement and measure the resulting force. The texture analyser is interfaced with a PC-type IBM compatible with Stable Micro System XTRA.Dimension Software for data acquisition and analysis.

3.3.3 The Confocal Laser Scanning Microscope

The confocal laser scanning microscope is manufactured by Leica Lasertechnik GmbH, Wetzlar, Germany and uses the laser source Ar/Kr 488 nm, 568 nm and 647 nm for the illumination of the object. A point in the object under examination reflects or fluoresces and is then imaged via a detector pinhole to a photomultiplier as illustrated in Fig. 3.3a.

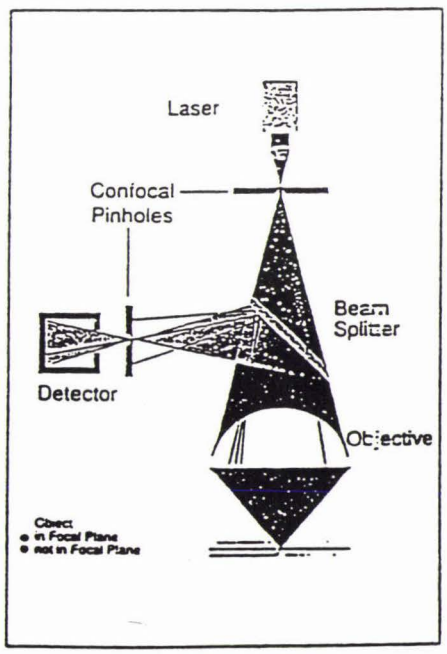


Figure 3.3a The Principles of Confocal Laser Microscope (From User Manual 1992)

The arrangement of a single detection pinhole and illumination pinhole ensures that only the information from the focal plane reaches the detector. Optical clarity and a high resolution of 0.1 to 0.15 μm under reflectance, and 0.15 to 0.20 μm under fluorescence, are achieved.

Depending on the material density, sections at 1 μm intervals to a depth of 180 - 200 μm can be examined. The confocal laser scanning microscope is interfaced with a fast CPU system based on a VME bus running at 20 MHz with 4 MByte RAM and 2 MByte frame store. Fig. 3.3b shows the system setup at Auckland Medical School, Image Processing Unit.

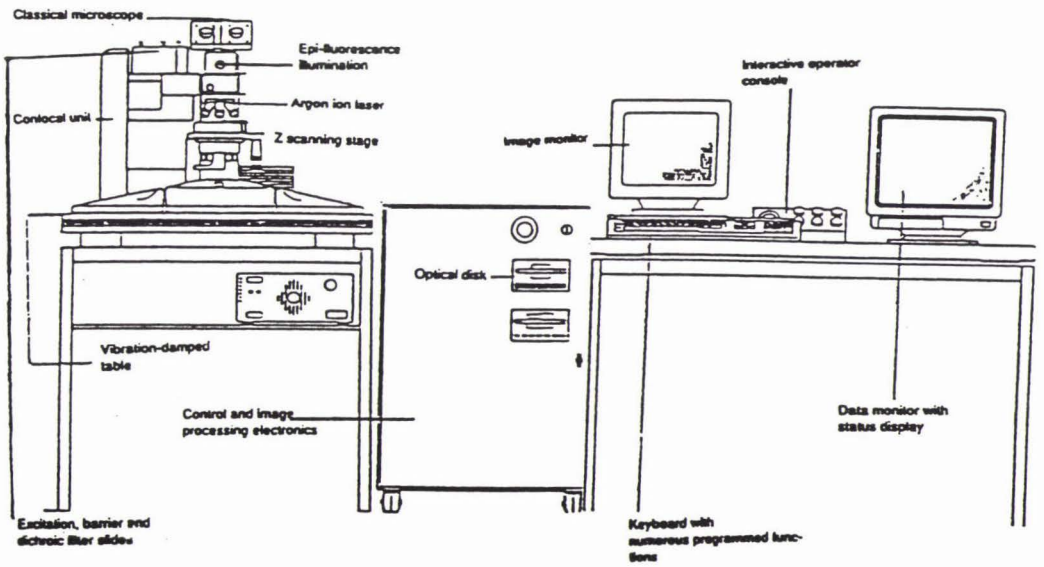


Figure 3.3b The CLSM System Setup

3.4 METHODS

In rheological measurements, sample handling history prior to testing have to be specified. This would indicate the forces or deformations to which the specimen has been subjected prior to the tests. Any deformations during sample preparation were kept to a minimum such that they hopefully had insignificant effects on the results. This section describes sample handling and the experimental methods used, which were shear creep, shear stress relaxation and the dynamic testing using the impulse halfsquare waveform.

3.4.1 Sample Preparation

The processed cheese slices were supplied packed in polyethylene plastic film with 80% nitrogen and 20% carbon dioxide. They were stored in a temperature controlled cold room at $4^0C \pm 0.5^0C$ to minimize deterioration during the period of test.

Processed cheese slices were removed from the cold store, unwrapped and placed on the plastic slab mounted on the wire cutter as illustrated in Fig. 3.4.

The lever on the wire cutter was lowered such that the thin piano wires placed at the dimension of 48 mm by 45 mm cut through the slice. The wire cutter was then rotated at 90^0 to complete cutting a rectangular specimen. This was repeated for the second slice for IWS, while for SOS two samples were cut at the same time and the slices peeled to separate into individual pieces. These samples were used for the Instron. The sample dimensions for the TA.HD were 30 mm by 30 mm owing to space limitations. All sample cutting was done at 4^0C as recommended by Casiraghi et al (1985).

After cutting the samples to the required size, they were wrapped in polyethylene plastic film and placed on the bench for about 8 minutes to allow their temperature to rise to about 15^0C, while a similar slice was used to monitor the temperature by inserting a thermocouple, and the temperature change observed. The samples were then placed in a temperature-controlled box (15^0C) for a further 15 minutes. This was to make sure the

temperature was constant throughout the sample prior to bonding them on the holding cell.

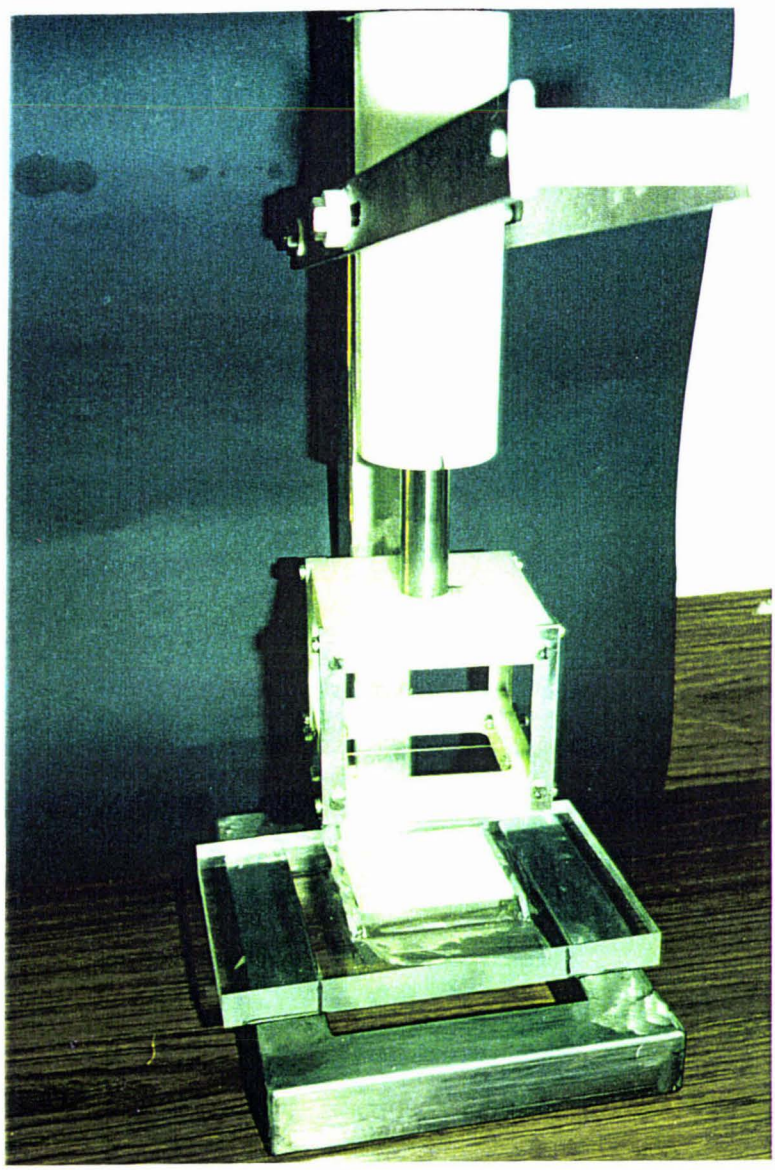


Figure 3.4 A Thin Piano Wire Cheese Cutter

The holding cell consisted of two adjacent parallel plates screwed to a base plate mounted to the table frame of the Instron. A similar holding cell was mounted on the test-bed of the TA.HD and held in position using clamps. The centre plate was connected to the

moving crosshead as illustrated Figs. 3.5a and 3.5b.

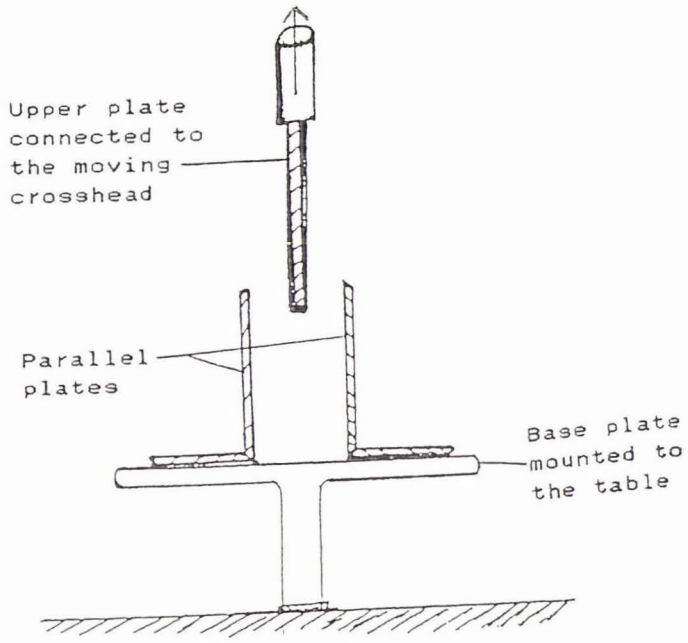


Figure 3.5a A Sketch Diagram of the Instron Sample Holding Cell

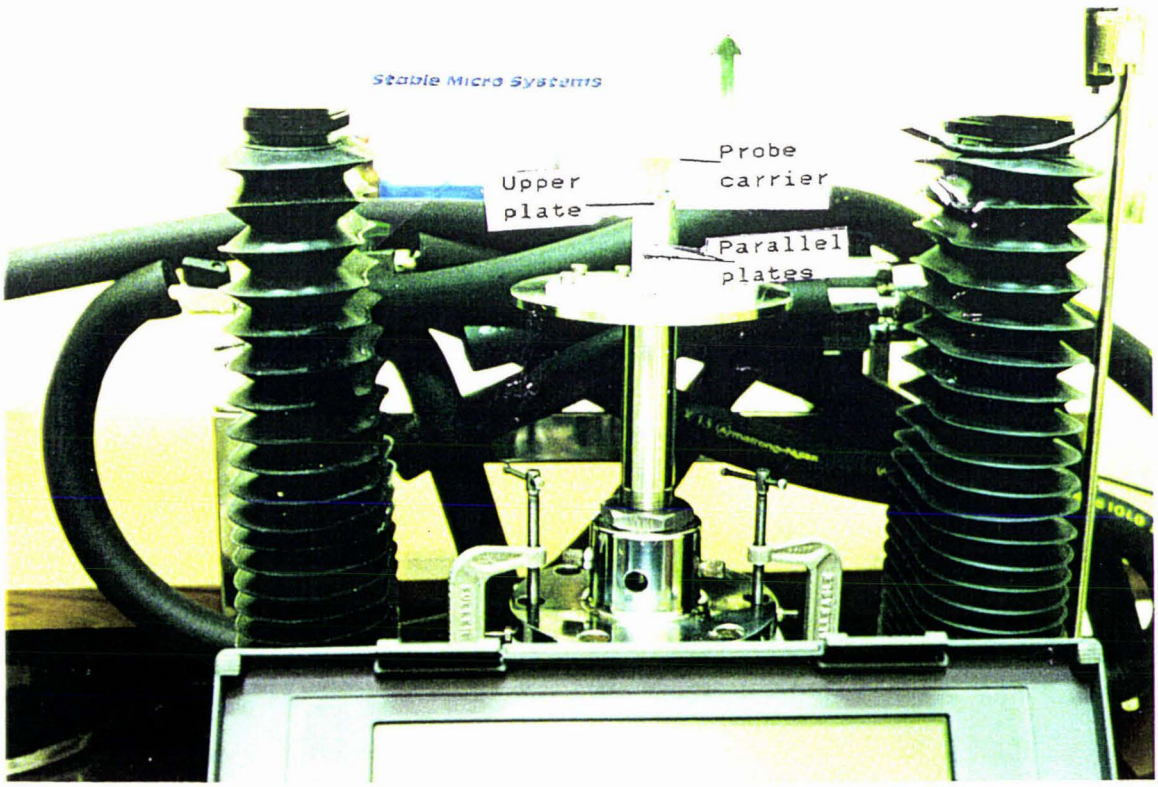


Figure 3.5b A Photograph of TA.HD Sample Holding Cell

The sample holding cell/parallel plates were cleaned using acetone to remove any fat or greasy material and finally cleaned with Loctite 703 quick clean. They were then held on the base plate with screws such that they could be moved towards or away from each other. The plate connected to the crosshead was exactly at the centre of the two base parallel plates.

Two identical test-pieces were unwrapped, placed on a slab and then sprayed with loctite 702-IS activator. The activator could reduce the binding time from several minutes to 2.5 seconds and full cure to 5 minutes. At the same time it could prevent the penetration of the adhesive into the cheese slice. The activator was left to evaporate from the surface of the sample for 2 minutes, and the Loctite 406 cyanoacrylate adhesive was then applied in the form of small drops at 6 mm spacings over the surface of the slice. The specimen was then fixed to the plate attached to the crosshead by pressing it lightly, and the procedure was repeated for the second slice. (One slice was fixed at a time). The outsides of the two slices were sprayed with Loctite 702 IS activator, left for 2 minutes to allow evaporation of the activator, and the Loctite 406 cyanoacrylate adhesive drops were then applied to the upper end of each slice such that the adhesive spread downwards all over the slice surface. The centre plate was then lowered such that the top of the slices aligned with the upper end of the parallel plates which were then moved towards the centre until they touched the slices. A slight pressure was then applied with the fingers for 1 minute, and the sample was left for 5 minutes to cure. Fig. 3.5c shows the test geometry with a double sandwich specimen.

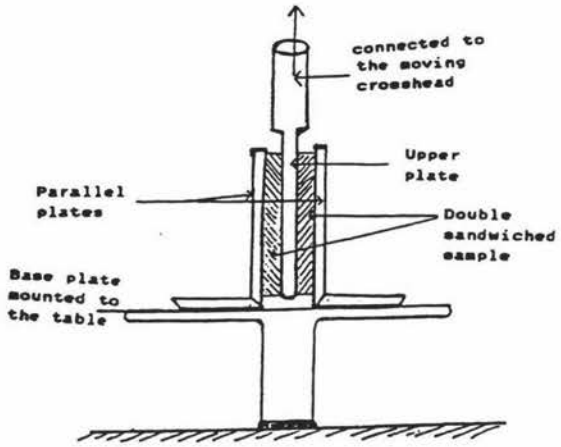


Figure 3.5c A Double Sandwich Sample/Platen Interface

This procedure was repeated whenever a new sample was used, and in each case two slices identical in geometry were taken from the same batch.

3.5 EXPERIMENTAL PROCEDURE

3.5.1 Shear Creep Experiments

In shear creep experiments, a given load/force was applied rapidly on the sample and the resulting displacement measured over time while the applied force was kept constant. Shear creep experiments were carried out using the Instron using the following procedure:

The temperature control cabinet was switched on and the temperature set to 21°C. A thermocouple was inserted to about 5 mm into one half of the sample sandwich from the top to monitor the sample temperature during the experiment.

The Instron control console was programmed for creep tests as follow.

The minimum load position was set at 0.0 N. This was the load at which the machine would stop or the position to where the crosshead would return at the end of the test.

The maximum load was then set to the specified maximum value. When that force was reached the machine would hold the force constant for 300 seconds. The change in displacement was measured. The speed to "instantaneously" reach the maximum force was set at 30 mm per minute. At this crosshead speed, the maximum force could be reached rapidly. At slow crosshead, too much creep occurred before the measurements are started whereas high crosshead speeds caused the force to overshoot. The computer was then programmed for data acquisition by entering the sample dimensions and setting the control console to 'enabled' mode. This mode enables the Instron microprocessor to collect the data which was then acquisitioned by the computer through the control console.

The test was started after zeroing the load and the displacement displays on the control console. The 'up' button was pressed and the crosshead moved at a speed of 30 mm per minute. It stopped at the specified force and this force was held constant for 300 seconds, while the displacement was measured and recorded versus time.

The experiment was carried out using imposed forces of 2.137 N, 4.237 N, 6.926 N and 7.817 N for IWS and 3.37 N, 6.73 N, 10.20 N and 12.10 N for SOS cheese. Twelve replicate experiments were done at each force setting for both IWS and SOS. A fresh sample was used in every experiment. Raw data was analyzed using the Scientific Figure Processor and Parameter Fitter software version 6.0c (FP 60). Shear creep compliance was calculated using Quattro Pro 3.0 version 5.0. The curves displacement versus time and shear creep compliance versus time were drawn for various stress settings.

Stress was calculated as:

$$\sigma=\frac{F}{2A} \qquad (3.5.1)$$

where σ = shear stress (Pa), F = imposed force (N) and A = area of slice in contact with the moving plate (m^2). The imposed force and the sample area were constant, so the stress was also constant. The strain was calculated as:

$$\gamma=\frac{D}{L} \tag{3.5.2}$$

where γ = shear strain, D = displacement (mm), and L = sample thickness (mm).
The creep compliance J(t) per Pa was calculated using equation (2.6.5).

$$J(t)=\frac{\gamma}{\sigma_{constant}} \tag{2.6.5}$$

3.5.2 Stress Relaxation Experiments

In stress relaxation experiments, a given displacement was applied rapidly to the sample and the resulting forces measured over time while the displacement was held constant. These experiments were carried out using the Instron and the TA.HD using the procedures given in sections 3.5.2.1 and 3.5.2.2

The temperature used throughout these experiments was 21°C which was set on the temperature control cabinet of the Instron, and a room with 21°C was used for the TA.HD. A thermocouple was inserted about 5 mm into one half of the sample sandwich from the top to monitor the sample temperature. The input displacement values were found from pre-calculated % strain as follows:

$$D=\frac{\%\gamma L}{100} \tag{3.5.4}$$

where, γ = shear strain, D = displacement (mm) and L = sample thickness (mm).

3.5.2.1 Instron Shear Stress Relaxation

These tests were carried out with the Instron's control console on 'disabled' mode. All inputs (displacement, crosshead speed and holding time) were directly entered into the computer and the responses (force and time) recorded by the computer.

The computer was programmed for stress relaxation experiments as follows.

The minimum displacement was set at 0.00 mm. This was the displacement at stop position or the position to which the crosshead should return when the test was stopped. The maximum displacement was then set to the specified value. The action when the maximum displacement was reached was to hold that displacement constant for 300 seconds. The rapid speed to attain the maximum displacement was set to 30 mm per minute. At this crosshead speed, the time to impose the displacement was less the 0.2s The load and the displacement displays were zeroed and the test started.

The test was started by pressing the return/enter button on the computer. The crosshead moved up to the specified position, and the resulting force was then measured and recorded over 300 seconds while the displacement was kept constant. This procedure was carried out for strain values of 1.6 to 5.0% for SOS and 1.6% to 4.8% for IWS cheese (differences are due to difference in sample thickness). Twelve replicate measurements were done for each cheese type and at each setting. A fresh sample was used in every experiment.

3.5.2.2 TA.HD Shear Stress Relaxation

The minimum measurable displacement with the TA.HD under normal operating conditions was 0.1 mm. This corresponded to 5% strain for SOS and 4% for IWS. It was considered that these values might be in the non-linear viscoelastic region. To achieve lower displacements a special programme was used where probe height (the gap between the test-bed and the lower end of the moving crosshead) could be calibrated.

The distance/displacement was then pre-calculated using specified strain values as follows.

The base plate was clamped to the TA.HD test-bed without the lower parallel plates. The probe carrier with the upper parallel plate tightly fixed was lowered to about 10 mm from the base plate. The calibrate button on the control console was pressed, and the probe carrier moved down until the plate touched the base plate and then moved up and stopped. The lower parallel plates were then screwed on the base plate and the centre plate adjusted manually such that the top ends of the plates were in line. This gap/distance was used to calculate the desired input as follows:

$$I_{dis}=\frac{\%\gamma xLx100}{PrHx100} \qquad (3.5.4)$$

where PrH = the calibrated probe height (mm), I_{dis} = % input displacement, % γ = % desired strain and L = sample thickness (mm).

The programme recognized the probe height setting as the start or zero position and it returned to this position when the test was stopped. Experimental settings were carried out on the machine control console. The maximum displacement was set to the specified value. This was the displacement at which the probe carrier stopped to enable the displacement to be held constant for 300 seconds. The "instantaneous" speed to reach the maximum displacement was set to 30 mm per minute.

A computer with Micro Stable System XTRA.Dimension software was set to the stress relaxation programme and was used to start the test and collect the raw data. Strain values of 1.6%, 2.4%, 3.2%, 4.0% and 4.8% for IWS and 2.0%, 3.0%, 4.0% and 5.0% for SOS were set, with twelve replicates at each setting. A fresh sample was used for every experiment.

The software FP 60 was used to analyze and fit the stress relaxation data using equation (2.6.15).

3.5.3 Dynamic Impulse Halfsquare Shear Experiments

The impulse halfsquare test was used to evaluate the dynamic and melting properties of processed cheese slices. Test temperatures were varied from 10°C to 70°C while the strain was varied between 0.8% and 4% using the Instron.

The impulse halfsquare method was developed by Farris (1984) to measure the viscoelastic properties of polymers during curing. The method was adapted for cheese slices using small amplitude impulse shear deformations with the parallel plate and double sandwich sample geometry.

In standard dynamic experiments, a sinusoidally oscillating strain is applied to a sample and the resulting stress is measured. From the resulting stress, the applied strain and the phase angle difference between the stress and the strain, it is possible to calculate the dynamic storage and loss moduli. In impulse shear experiments eqs. (2.8.32), (2.8.33) and (2.8.34) were used to calculate the dynamic storage modulus, loss modulus and loss tangent.

The following procedure was used. The control console was set to cyclic test mode and the halfsquare waveform configuration was selected from the control console. The amplitude of deformation was set to the specified value. This was the maximum displacement peak the waveform would reach before it returned to complete the halfsquare. The frequency of impulse was set to 0.05 Hz and it takes 20 seconds to complete a halfsquare. The temperature of the sample was lowered to 10°C at 2°C per minute by injecting liquid carbon dioxide into the temperature control cabinet with the fan on to distribute the coolant within the cabinet. The temperature was then held constant for 5 minutes for equilibration before the test was started. The computer was programmed to record the data, the displacement and the load displays were zeroed and the start button on the control console pressed to start the test while the computer control was on enabled mode.

This procedure was repeated for other amplitudes and higher temperatures using the

internal heater to raise the temperature and the fan for distribution of heat within the cabinet. Twenty replicates for both SOS and IWS were tested at each temperature and amplitude setting. The effects of frequency on the rheological properties were evaluated at 21°C by varying the frequency of impulse between 0.025 Hz and 0.25 Hz. Data were analyzed statistically using the software FP 60.

3.5.4 The Confocal Laser Scanning Microscopy

The microstructure of processed cheese slices was examined using a confocal laser scanning microscope. Small pieces were cut from the processed cheese samples (IWS and SOS) and two samples from each cheese type were stained with protein staining dyes. These were Rhodamine and Fluorescein respectively. The stained samples were placed in moisture barrier packaging and left overnight for the dye to diffuse deeply into the aqueous phase. Samples were also stained with lipid staining dyes (Nile Red and Nile Blue) and placed in moisture barrier packaging and left overnight for the dye to partition into the lipid phase.

The samples were examined using the confocal laser scanning microscope after 24 hours as follow.

The sample was fixed on the microscope slide using a slide cover. The slide was then placed on the microscope stage and the laser source Ar/Ak 647 nm illuminated the object. A point on the cheese under examination reflected the light and was then imaged via a detector pinhole to the photomultiplier. A computer displayed the point as a pixel on a high resolution screen. The complete image was produced by the light point being moved (scanned) over the sample. The procedure was repeated using laser source Ar/Ak 568 nm for fluorescence and 488 nm for the lipid stained specimen for both reflectance and fluorecsence.

The information was stored on optical discs and a photo unit with high resolution was used to document and print colour photographs.

CHAPTER 4

EXPERIMENTAL RESULTS

4.1 INTRODUCTION

The fundamental rheological properties and the melting characteristics of two types of processed cheese slices, Individually Wrapped Slices (IWS) and the Slice On Slice (SOS) were measured. The experimental work comprised of (i) the shear creep test where a constant force was applied while the resulting displacement was measured as a function of time at 21°C (ii) the shear stress relaxation test where a constant deformation was applied while the resulting force was measured as a function of time at 21°C and (iii) the melting characteristics were measured at varying strain with a constant frequency of oscillation and temperature was varied from 10°C to 70°C. (iv) The confocal laser scanning microscope was used to evaluate the effects of different process conditions on the cheese microstructure.

Replicates experimental data for shear creep, shear stress relaxation and the dynamic impulse halfsquare results were each analyzed statistically to determine their reproducibility. The reproducibility of shear creep test tended to decrease as the applied force was increased whereas that of shear stress relaxation was good within the measured range. The dynamic test results indicated very good reproducibility from a strain of 0.8% to a strain of 4.0%. The reproducibility was poor at a strain of 0.4% especially when the temperature was raised above 50°C. The standard error bars are not shown on the dynamic curves due to closeness of the curves. However, the standard errors of the mean (SEM) of twenty replicates ranged from 0.01% to 0.10% for both types of cheeses between the strain of 0.8% and 4.0% and measurement temperature of 10°C to 70°C.

The experimental results are given under the following sections:

4.2 Shear creep,

4.3 Shear stress relaxation,

4.4 Dynamic impulse halfsquare,

4.5 Confocal Laser Scanning Microscopy.

4.2 SHEAR CREEP

The results in Figs. 4.1a and 4.1b depict the deformations of processed cheese IWS and SOS respectively. The curves exhibit an increase in displacement with time as imposed force was kept constant over a period of 300 seconds. There was a better data reproducibility at lower forces and this decreases as the applied force was increased as shown by the standard error bars. Figs. 4.2a and 4.2b show the creep compliance of the two types of cheese slices at various forces. They indicate an increase in creep compliance as the imposed force was increased. Fig. 4.3a is the comparison of creep compliance of IWS and SOS measured at the same temperature and force. The curves show a marked difference in that the creep compliance for SOS was lower than that of IWS. Figs. 4.3b and c show the curve fitted data for IWS and SOS respectively. Table 4.1 show the instantaneous compliance J_0, the retardation time and the correlation coefficient (r^2) of the fitted data indicating the relation between the experimental (symbols) and the fitted points (line). The fitting model might not be very appropriate because the fitted curve does not intercept the Y-axis.

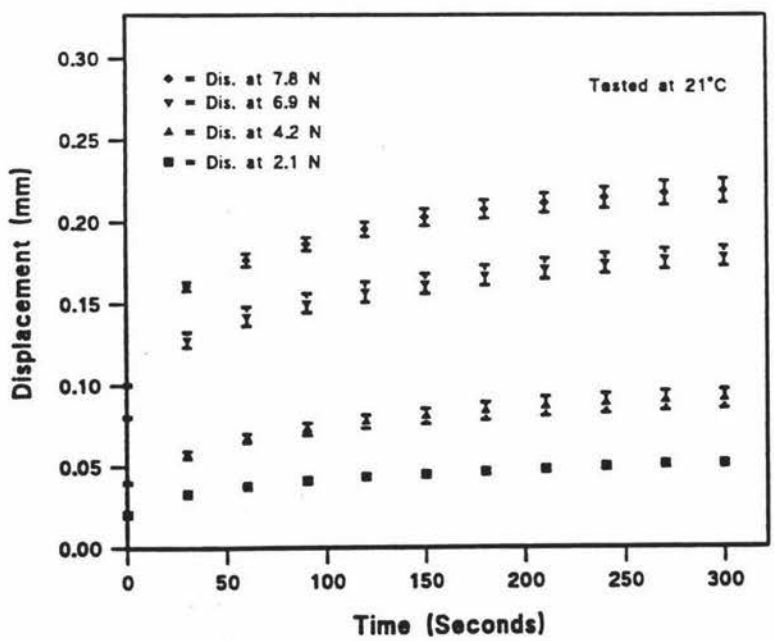


Fig.4.1a Shear Creep Responses Showing Displacement versus Time for IWS Measured at Different Initial Applied Force

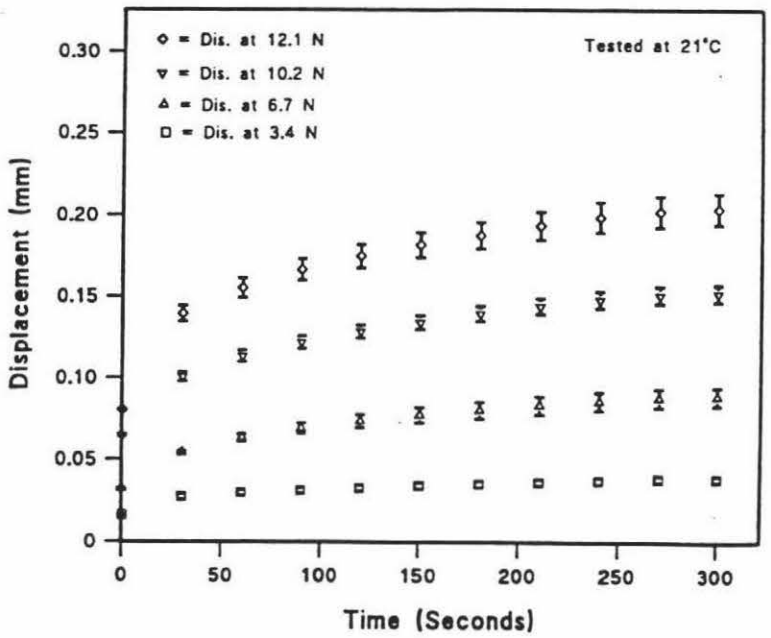


Fig. 4.1b Shear Creep Responses Showing Displacement versus Time for SOS Measured at Different Initial Applied Force

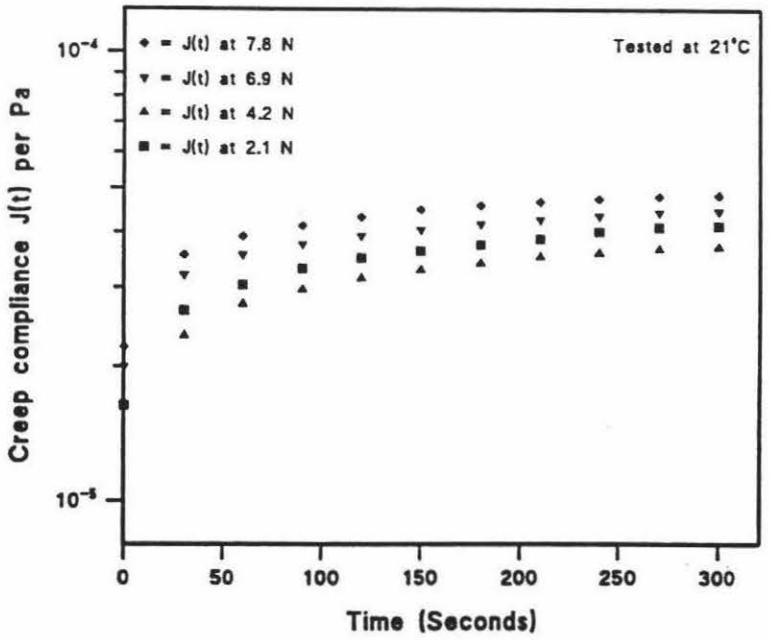


Fig. 4.2a Shear Creep Compliance of IWS versus Time Measured at Different Initial Applied Force. J(t) was Calculated Using eq. (2.6.4)

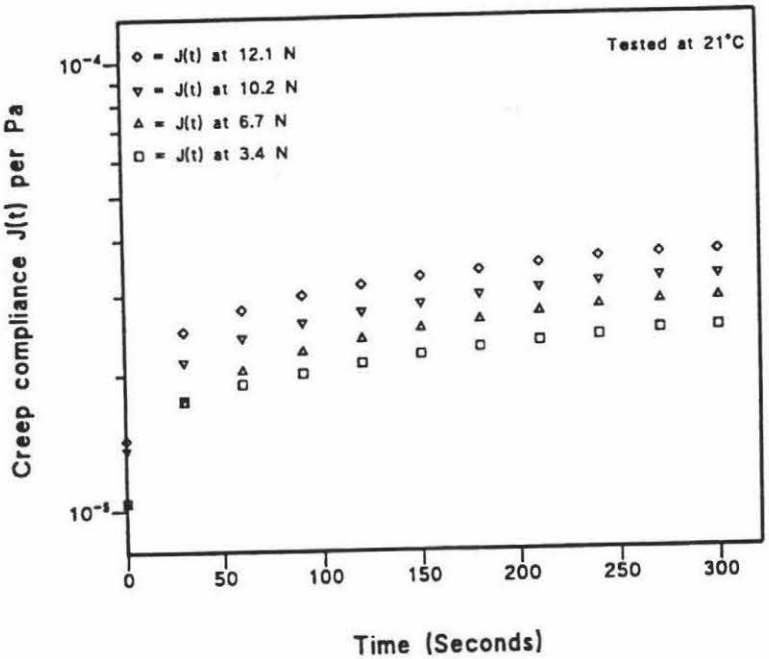


Figure 4.2b Shear Creep Compliance of SOS versus Time Measured at Different Initial Applied Force. J(t) was Calculated Using Eq. (2.6.4)

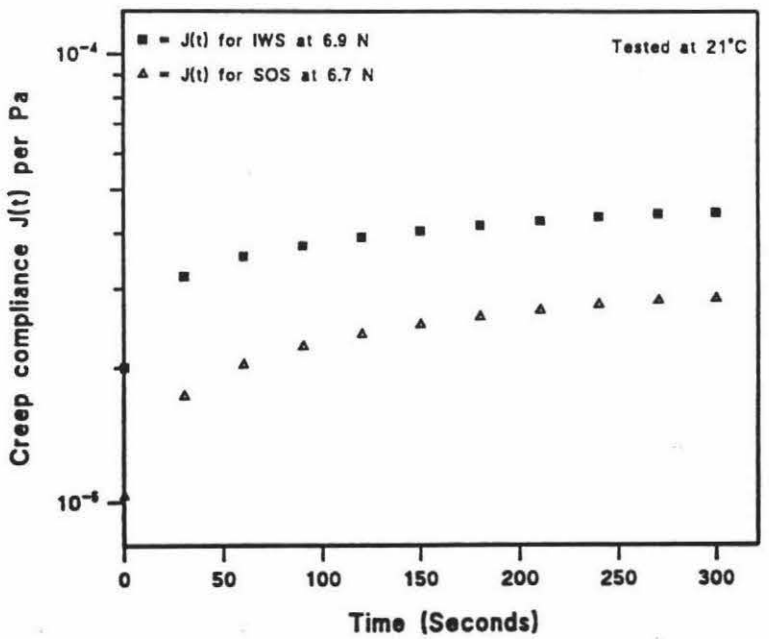


Figure 4.3a Comparison of Shear Creep Compliance for IWS and SOS Measured at the Same Applied Force

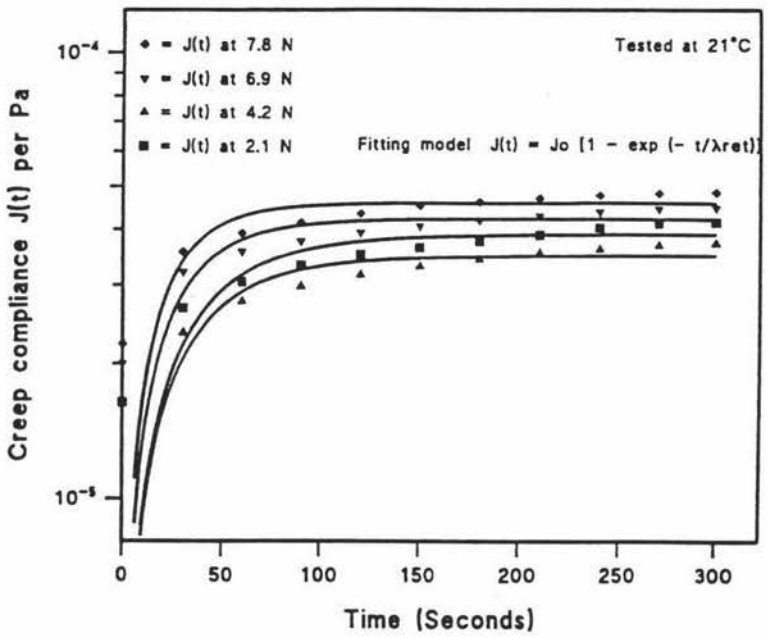


Figure 4.3b Curve Fitted Shear Creep Compliance versus Time for IWS at Various Applied Force

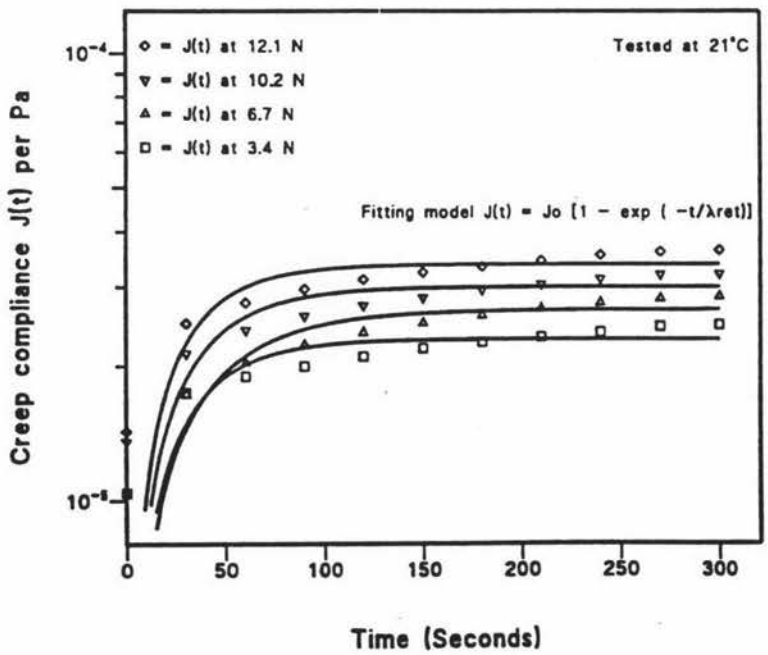


Figure 4.3c Curve Fitted Shear Creep Compliance versus Time for SOS at Various Applied Force

Table 4.1 Calculated instantaneous compliance J_0, retardation time (λ_{ret}) and the correlation coefficient (r^2)

Type of cheese	Force (N)	comp (J_0) per Pa	Ret.time(λ_{ret}) sec	Cor. coefficient r^2
IWS	2.1	2.68E-5	33.36	0.88
	4.2	3.48E-5	33.99	0.87
	6.9	4.21E-5	26.28	0.89
	7.8	4.56E-5	22.31	0.87
SOS	3.4	2.30E-5	28.66	0.88
	6.7	2.67E-5	38.61	0.91
	10.2	3.01E-5	30.91	0.86
	12.1	3.39E-5	27.64	0.88

4.2 SHEAR STRESS RELAXATION

The shear stress relaxation experimental results are given in the Figs. 4.4 to 4.8. Fig. 4.4a to 4.4d show the mean force/time relationship of twelve replicates as for strains between 1.6% and 5.0% and for both the Instron and the TA.HD texture analyser. Statistical analysis showed better reproducibility of results from both pieces of equipment at lower strain. There was a decrease in reproducibility as the strain was increased as illustrated by the standard error bars. Fig. 4.5a to 4.5d show the calculated shear stress relaxation modulus for IWS and SOS at the same temperature and similar variation of the strain. The curves show no particular trend between the stress relaxation modulus and the strain as strain was increased. However, there was a good agreement between instruments at all strains for each type of cheese. For a given instrument - cheese combination, the effect of strain in the range studied was small.

Relaxation modulus at 1.6 and 2.0% strain and tested at 21°C for both IWS and SOS are shown in Fig. 4.6. This figure clearly depicts the relaxation modulus of IWS cheese results lower than that of SOS cheese.

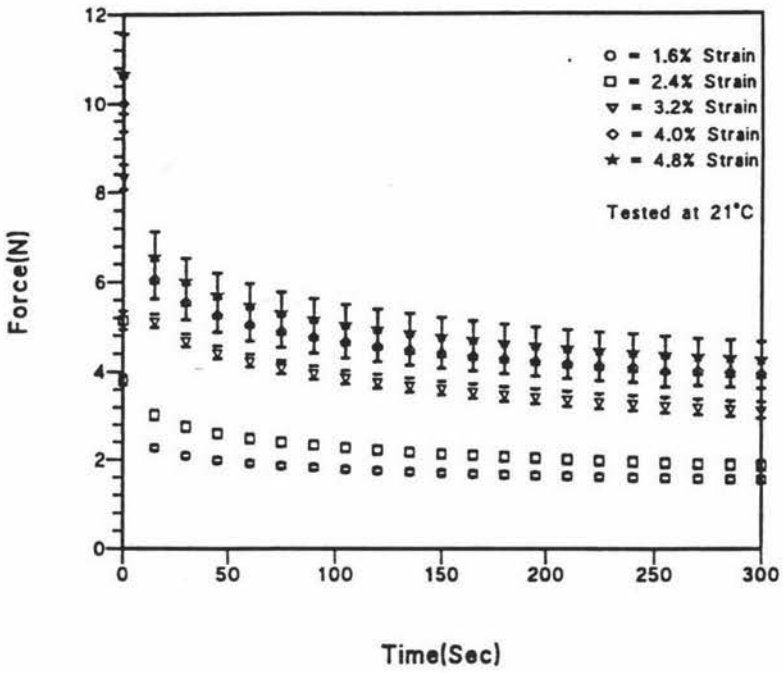


Figure 4.4a Shear Stress Relaxation Curves Showing Force versus Time for IWS Measured at Different Initial Strain Using the Instron

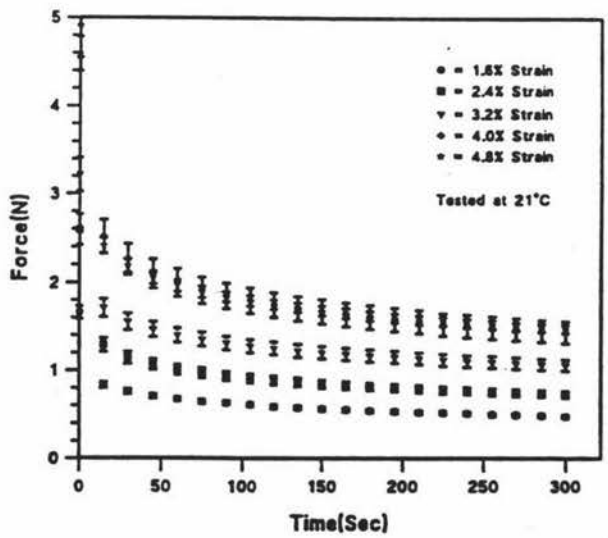


Figure 4.4b Shear Stress Relaxation Curve Showing Force versus Time for IWS Measured at Different Initial Strain Using the TA.HD

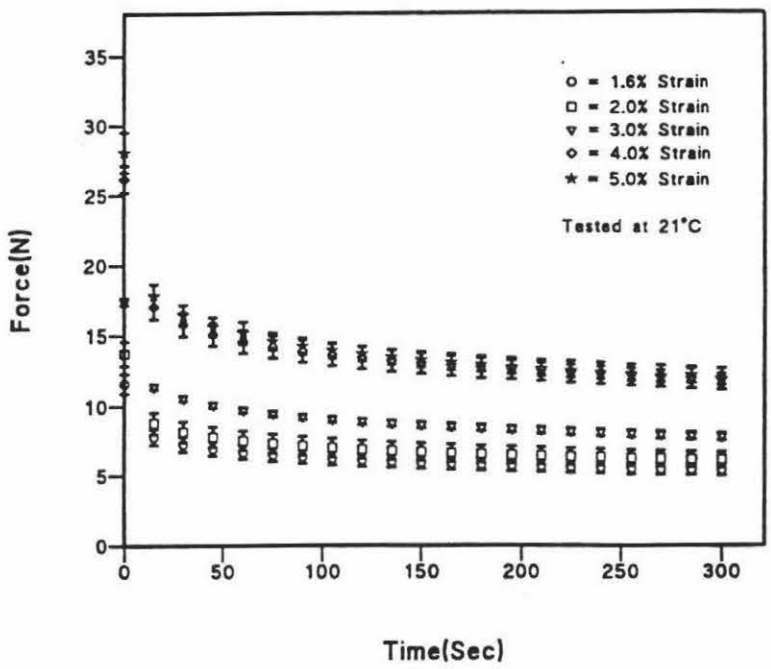


Figure 4.4c Shear Stress Relaxation Curves Showing Force versus Time for SOS Measured at Different Initial Strain Using the Instron

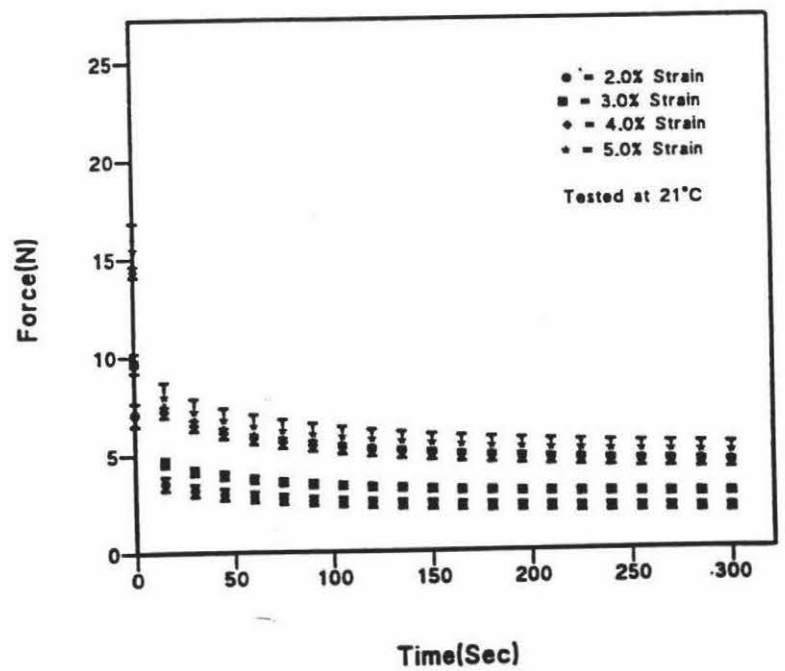


Figure 4.4d Shear Stress Relaxation Curves Showing Force versus Time for SOS Measured at Different Initial Strain Using the TA.HD

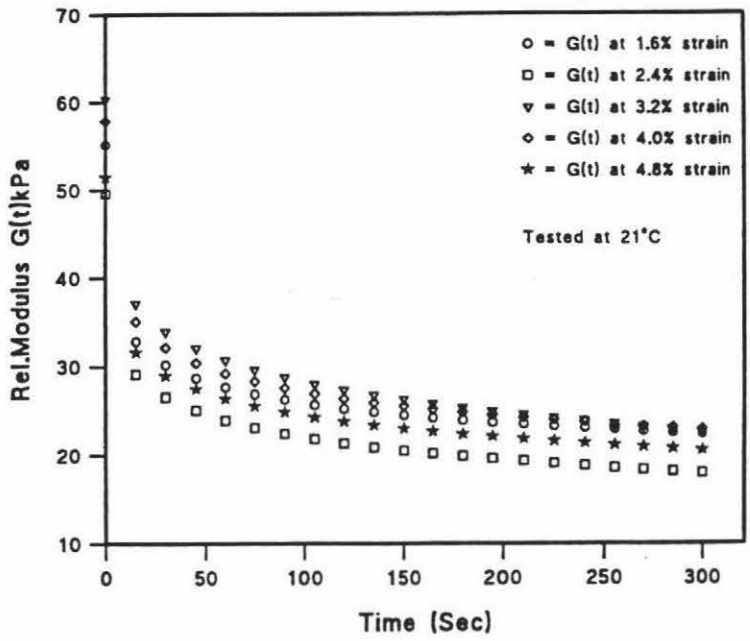


Figure 4.5a Shear Stress Relaxation Modulus versus Time for IWS Measured at Different Initial Strain Using the Instron. G(t) was Calculated Using Eq.(2.6.15)

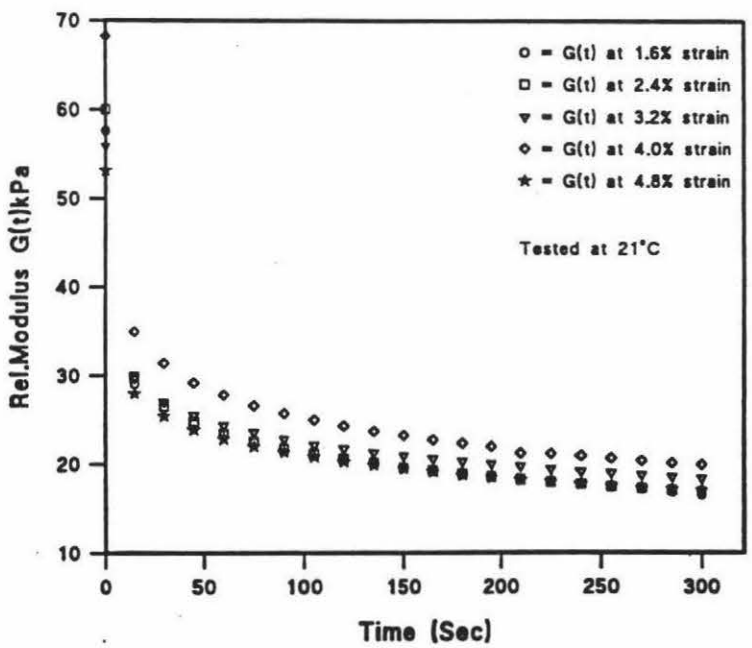


Figure 4.5b Shear Stress Relaxation Modulus versus Time for IWS Measured at Different Initial Strain Using the TA.HD. G(t) was Calculated Using Eq.(2.6.15)

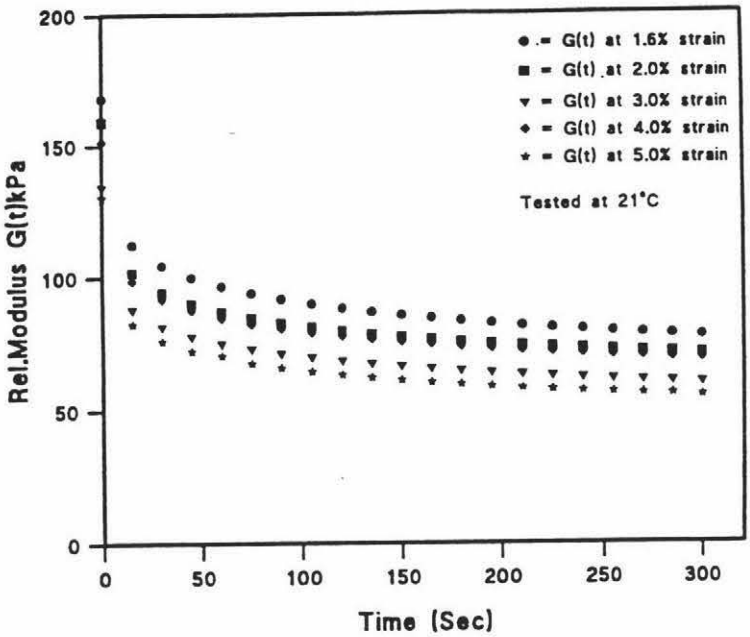


Figure 4.5c Shear Stress Relaxation Modulus versus Time for SOS Measured at Different Initial Strain Using the Instron. G(t) was Calculated Using Eq.(2.6.15)

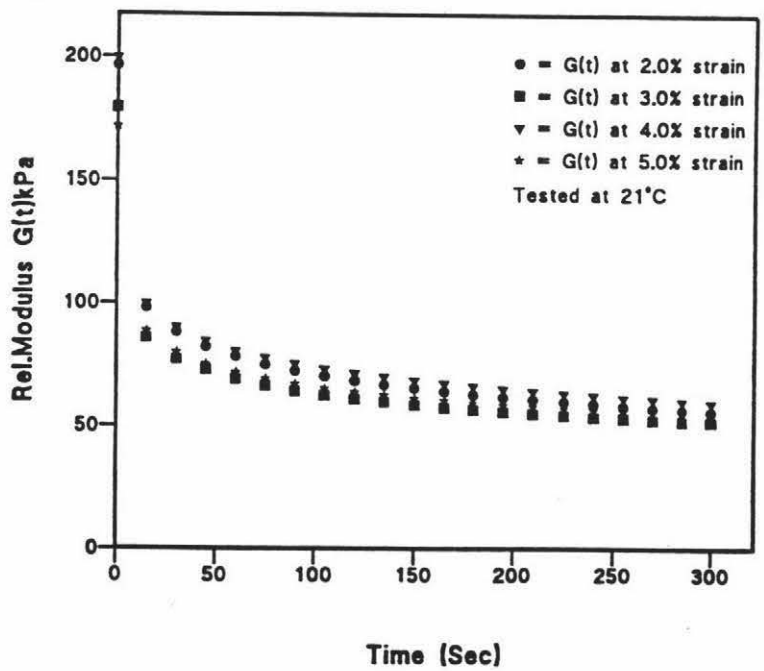


Figure 4.5d Shear Stress Relaxation Modulus versus Time for SOS Measured at Different Initial Strain Using the TA.HD. G(t) was Calculated Using Eq.(2.6.15)

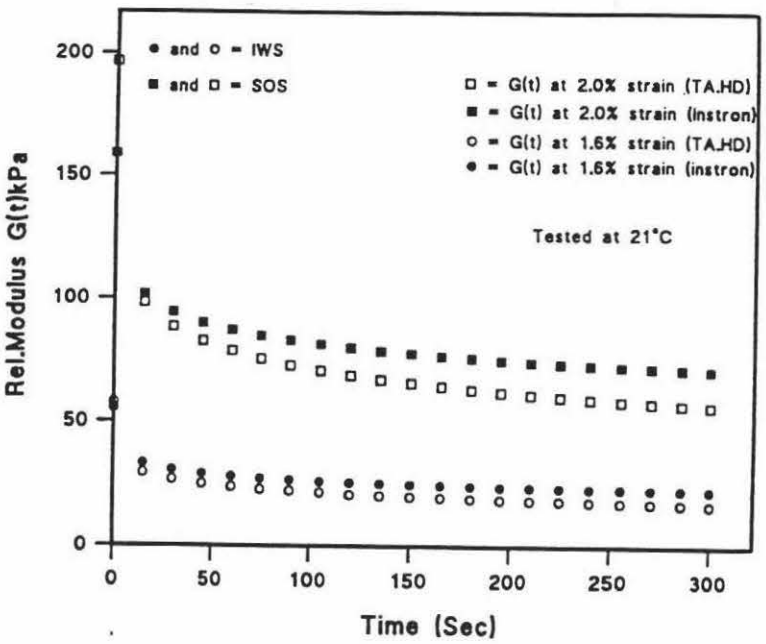


Figure 4.6 Comparison of Shear Stress Relaxation Moduli of IWS and SOS Measured at Similar Strain Using the Instron and the TA.HD

The shear stress relaxation moduli data obtained with the Instron and the TA.HD were fitted with a three element Maxwell body. The curve fitting for both cheeses and both instruments are given in Figs. 4.7a, b, c and d. The lines represent the equation while the symbols represent the experimental data points. The fitting model show good agreement between the experimental data points and the fitted line.

Fig.4.8 compares the fitted data for IWS and SOS measured using the Instron and the TA.HD. Table 4.1 gives a summary of the fitting parameters (λ_{rel} relaxation time, G_1 the decay modulus, G_e the equilibrium modulus, G_0 the instantaneous modulus and r^2 the correlation coefficient).

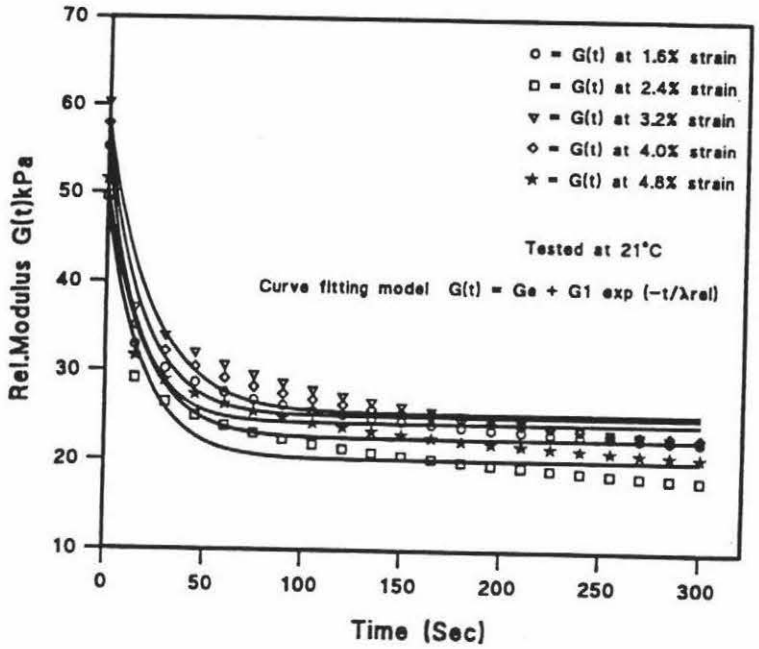


Figure 4.7a Fitted Shear Relaxation Modulus for IWS Measured at Different Initial Strain Using the Instron

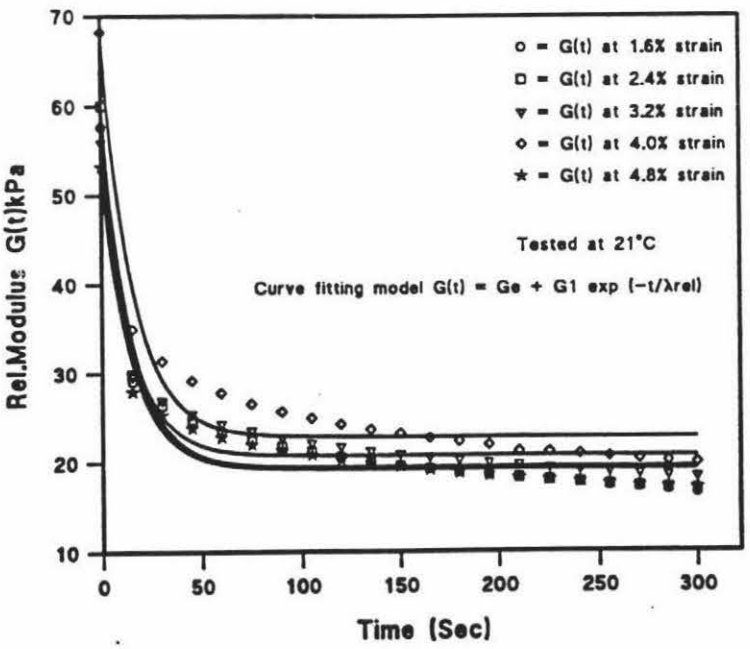


Figure 4.7b Fitted Shear Relaxation Modulus for IWS Measured at Different Initial Strain Using the TA.HD

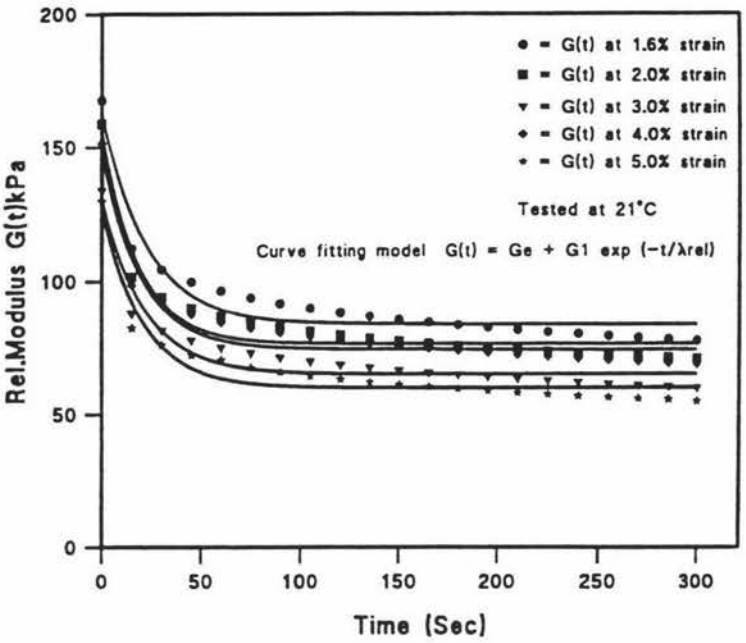


Figure 4.7c Fitted Shear Relaxation Modulus for SOS Measured at Different Initial Strain Using the Instron

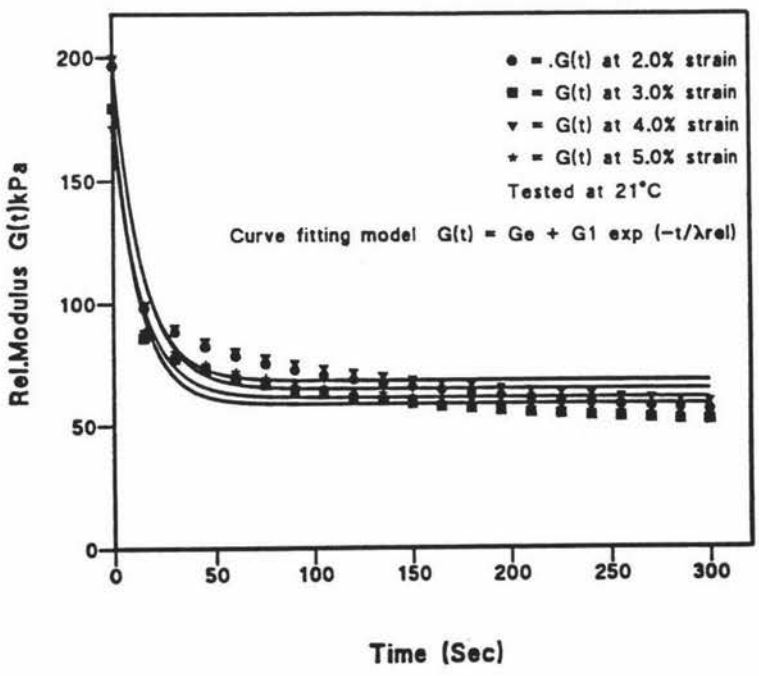


Figure 4.7d Fitted Shear Relaxation Modulus for SOS Measured at Different Initial Strain Using the TA.HD

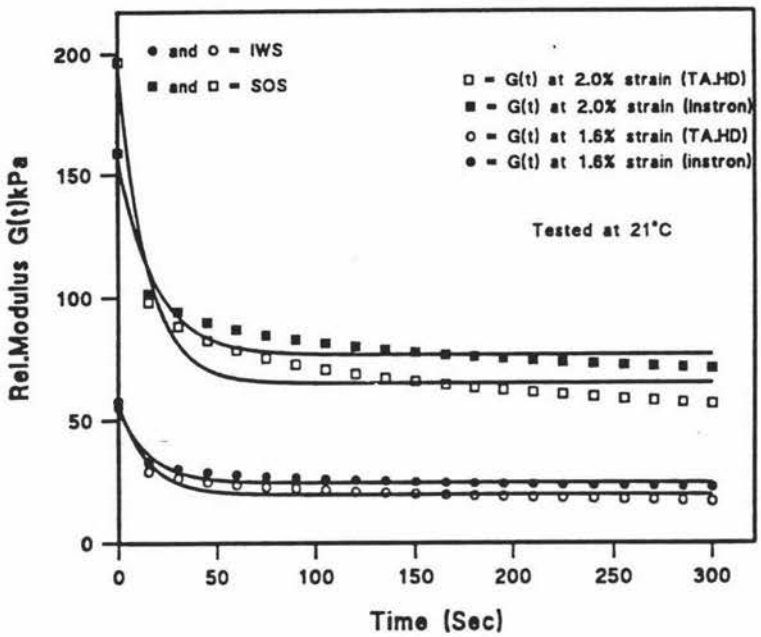


Figure 4.8 Comparison of Fitted Shear Relaxation Moduli for IWS and SOS Measured at Similar Strain Using the Instron and the TA.HD

Table 4.2 Calculated λ_{rel}, G_1, G_e and G_0 for IWS and SOS at different initial strain using the Instron and the TA.HD

Type of cheese	% strain	G_1 (kPa)	G_e (kPa)	G_0 (kPa)	λ_{rel} (sec)	r^2
	1.60	37.77	19.39	57.16	14.80	0.94
IWS	2.40	40.18	19.46	59.64	14.52	0.95
measured	3.20	34.74	20.75	55.49	14.74	0.94
using	4.00	44.64	22.86	67.49	15.64	0.94
TA.HD	4.80	33.49	19.24	52.74	14.85	0.94
IWS	1.60	30.35	24.29	54.64	16.03	0.95
measured	2.40	28.50	20.08	48.58	19.22	0.93
using	3.20	33.10	25.42	58.51	22.63	0.93
Instron	4.00	31.79	25.07	56.86	28.62	0.94
	4.80	27.86	22.55	50.41	19.52	0.94
SOS	2.00	130.39	64.76	195.16	14.57	0.94
measured	3.00	120.69	58.64	179.33	12.58	0.95
using	4.00	130.69	68.13	198.83	13.73	0.95
TA.HD	5.00	109.59	61.27	170.86	13.97	0.95
SOS	1.60	79.69	83.62	163.30	23.07	0.93
measured	2.00	79.96	76.30	156.26	18.78	0.94
using	3.00	65.84	65.13	130.97	21.61	0.93
Instron	4.00	74.49	74.22	148.71	19.74	0.94
	5.00	67.12	59.99	127.11	20.62	0.93

4.3 DYNAMIC IMPULSE HALFSQUARE

The dynamic impulse halfsquare results are given in Figs. 4.9 to 4.14. Figs. 4.9a and 4.9b show the relationship between the storage modulus (G') and loss modulus as the deformation/strain was varied at 21°C and 0.05 Hz frequency of for IWS and SOS respectively. Figs. 4.10a and 4.10b show the effects of temperature on the storage and loss moduli of IWS and SOS at the same frequency and at 0.8% and 1.6% strain respectively. Figs. 4.11a and 4.11b compares the storage moduli and the loss moduli of the two types of slices measured under the same conditions. There was a marked difference between these cheese slices as exhibited by the curves. Figs. 4.12a and 4.12b show the effects of varying temperature on the loss tangent (tan δ) to the slices while Fig. 4.13 compares the loss tangent of IWS and SOS. This also depicts a marked difference between the two cheese slices. Fig. 4.14 show the relationship between storage modulus and the loss modulus as the frequency of oscillation was varied at the same strain and a temperature of 21°C.

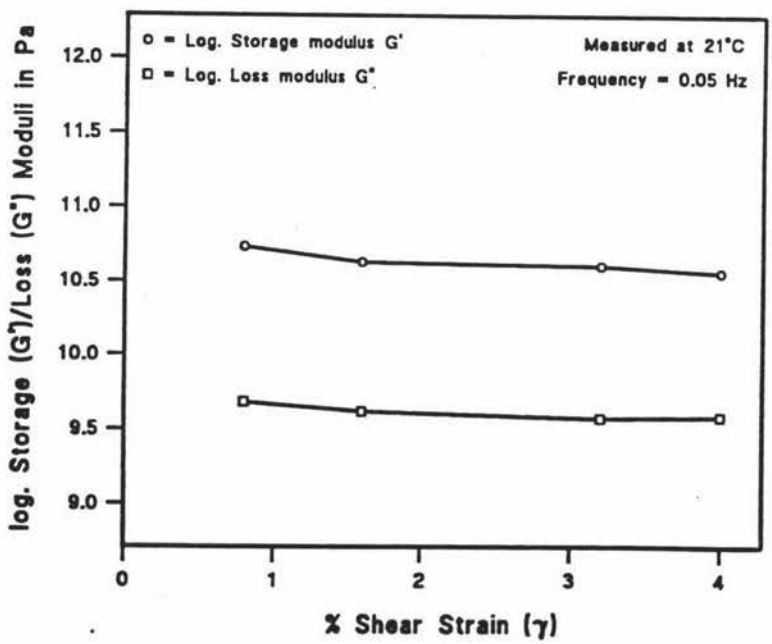


Figure 4.9a The Dynamic Storage Modulus and Loss Modulus of IWS versus Shear Strain

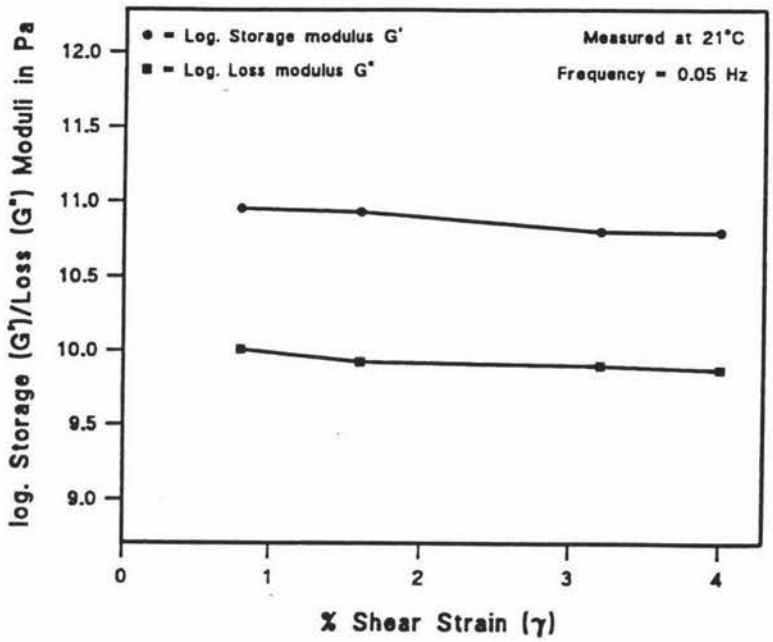


Figure 4.9b The Dynamic Storage Modulus and Loss Modulus of SOS versus Shear Strain

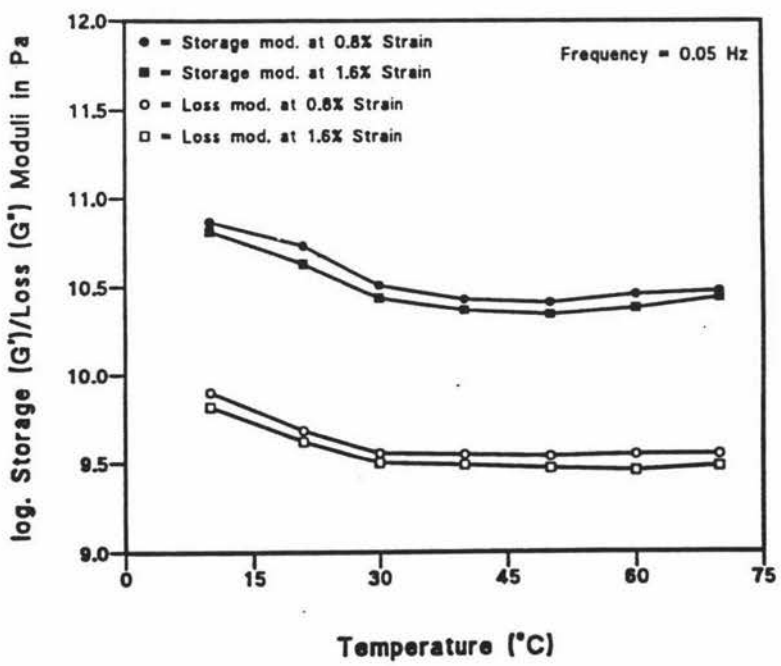


Figure 4.10a The Effects of Temperature on Dynamic Storage and Loss Moduli of IWS

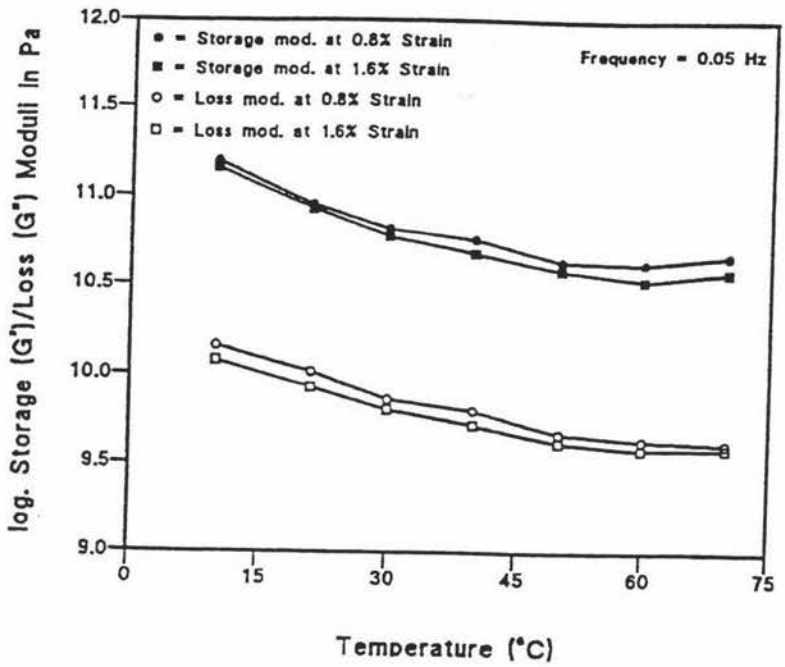


Figure 4.10b The Effects of Temperature on Dynamic Storage and Loss Moduli of SOS

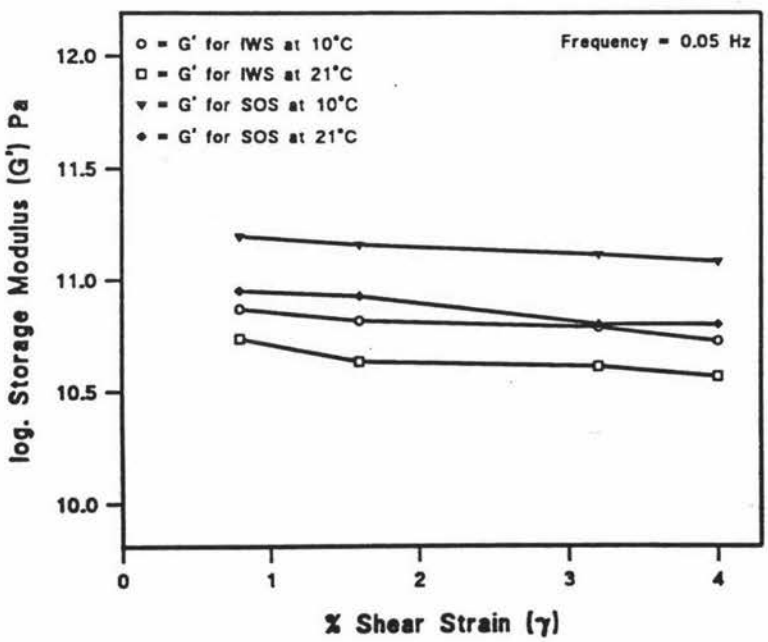


Figure 4.11a Comparison of Dynamic Storage Moduli of IWS and SOS as Shear Strain was Varied

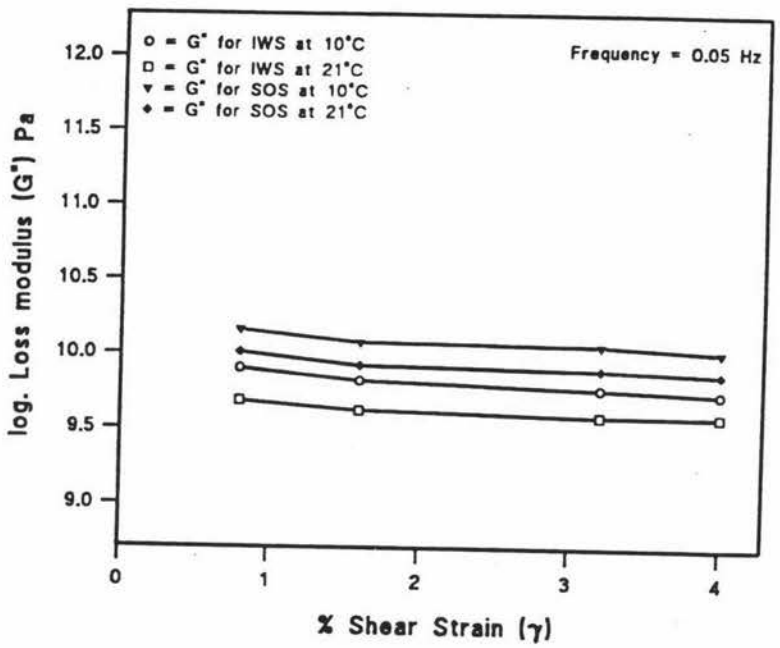


Figure 4.11b Comparison of Dynamic Loss Moduli of IWS and SOS as Shear Strain was Varied

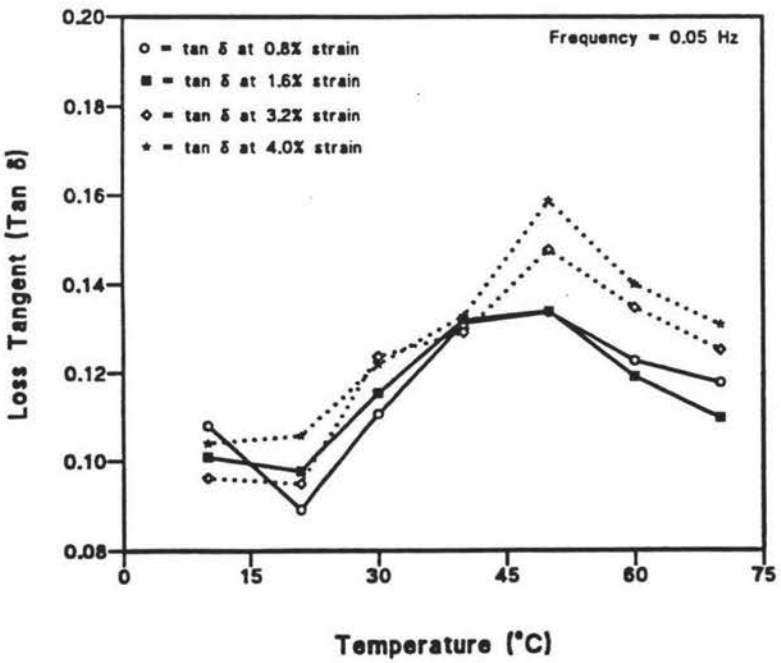


Figure 4.12a The Effect of Temperature on Dynamic Loss Tangent for IWS at Different Strain

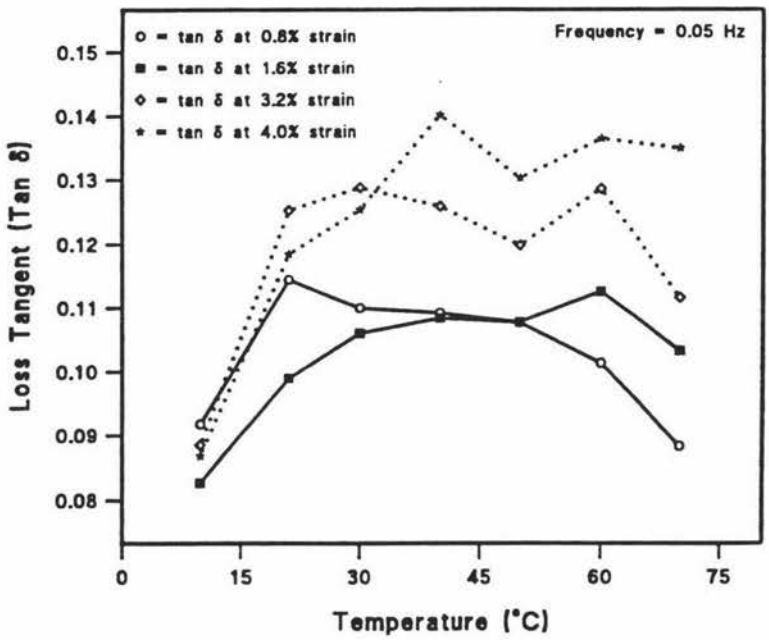


Figure 4.12b The Effect of Temperature on Dynamic Loss Tangent for SOS at Different Strain

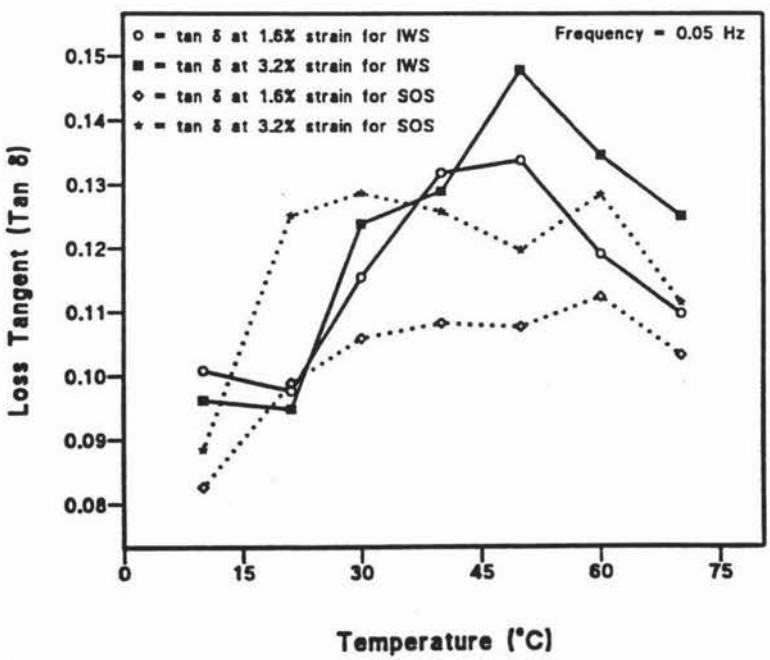


Figure 4.13 Comparison of Temperature Effects on Dynamic Loss Tangent Measured at Two Similar Strain for IWS and SOS

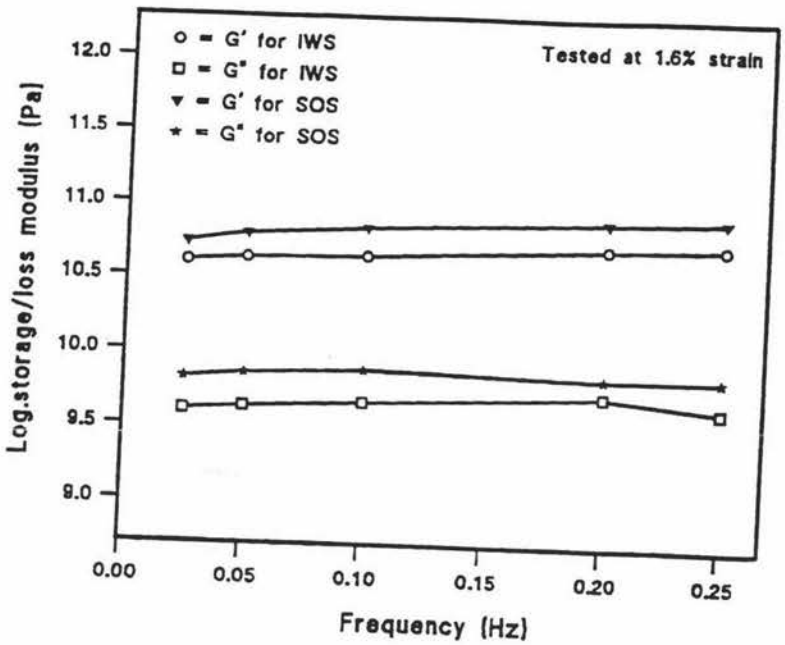


Figure 4.14 Dynamic Storage and Loss Moduli for IWS and SOS versus Frequency Sweep

4.4 THE CONFOCAL LASER SCANNING MICROSCOPY

The microscopic examination of the cheese slices revealed a marked difference in the microstructure of IWS and SOS. Fat globules were more uniformly distributed, and the globule size much smaller in IWS than in SOS. The fat globules are shown by dark spherical areas and the light areas indicate protein structures in Fig. 4.15 for IWS while Fig. 4.16a show the fat globules as dark areas. Fig. 4.16b show fat globules as light spherical areas and the protein as dark mass.

Figs. 4.17a - 4.17c show the undissolved emulsifier salt crystals indicated by spike-like light areas in IWS and SOS exhibiting a marked difference in the distribution of crystals just below the surface of the slice and their disappearance as you scan towards the middle of the slice. Fig. 4.18 show three dimensional fat globule structure as observed in SOS.

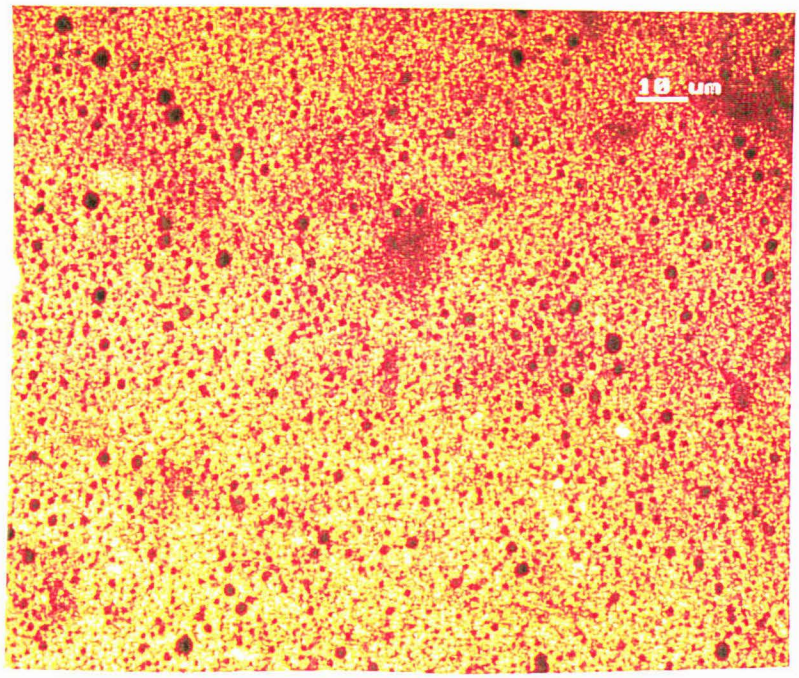


Figure 4.15 A Confocal Laser Scanning Micrograph for IWS showing fat as dark areas and protein as light continuous mass (scale of 10 μm)

Figure 4.16a A Confocal Laser Scanning Micrograph for SOS showing fat globules as dark areas and the protein structures by the light mass (scale 10 μm)

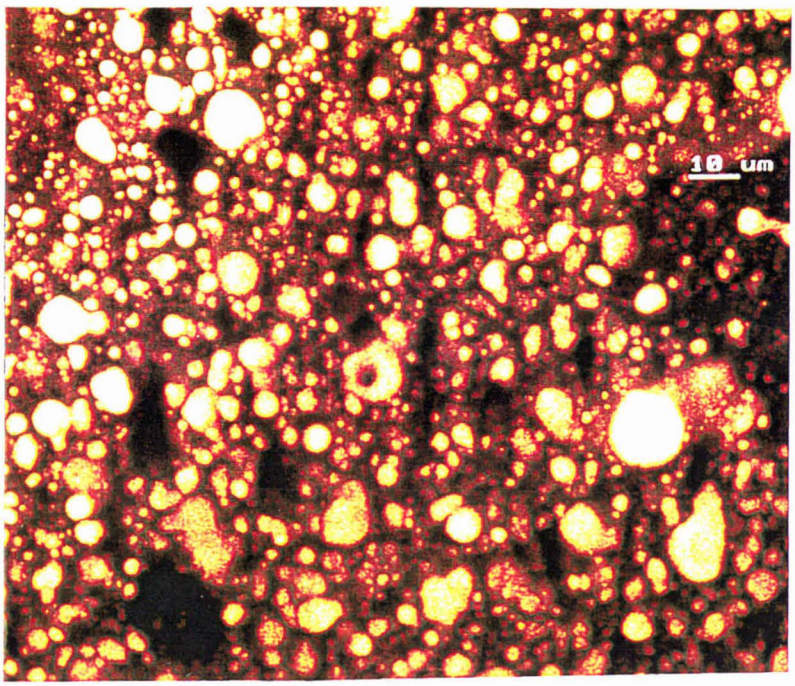


Figure 4.16b A Confocal Laser Scanning Micrograph for SOS showing fat globules as light areas and protein as dark mass (scale 10 μm)

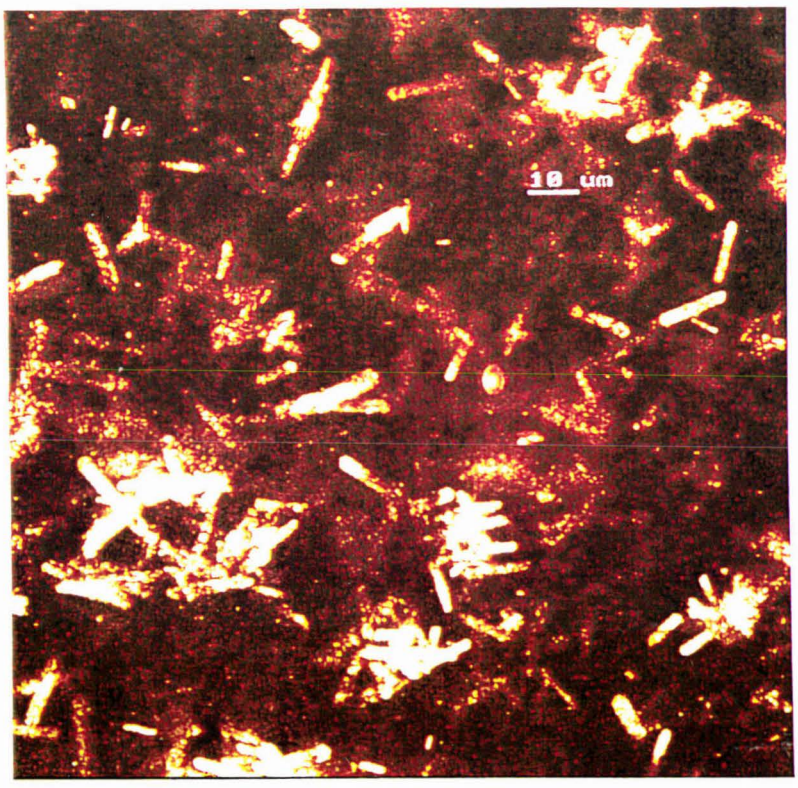


Figure 4.17a A Confocal Laser Micrograph for IWS showing fat crystals at about 15 μm below the sample surface (scale 10 μm)

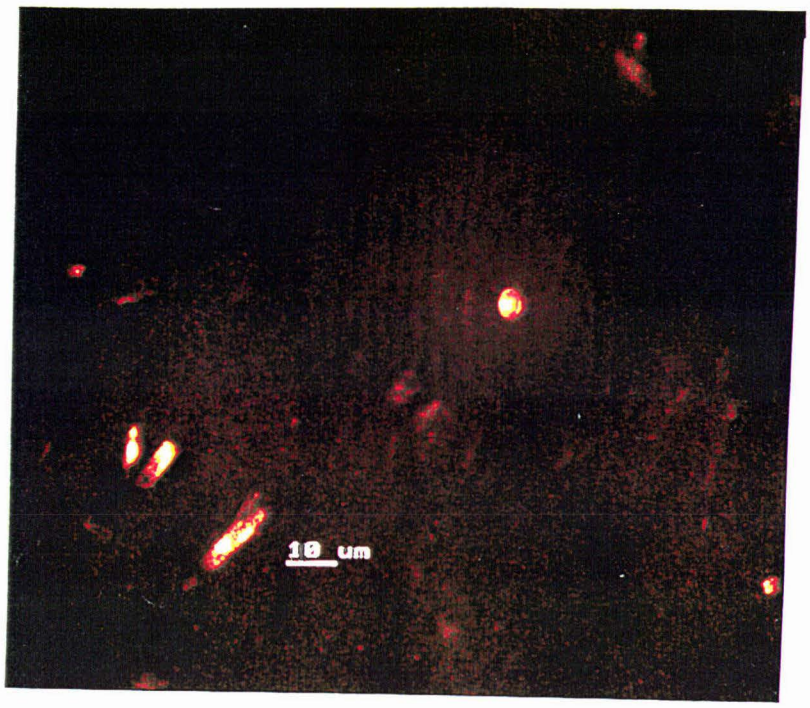


Figure 4.17b A Confocal Laser Scanning Micrograph of IWS showing fat crystals at about 120 μm below the surface of the sample (scale 10 μm)

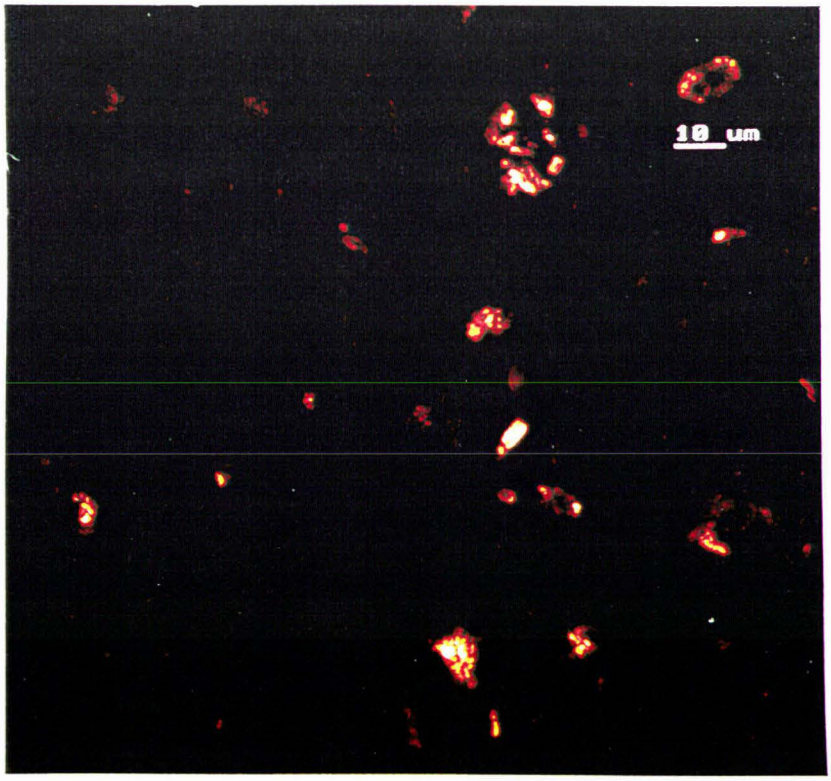


Figure 4.17c A Confocal Laser Scanning Micrograph for SOS showing fat crystals at about 15 μm below the surface of the sample (scale 10 μm)

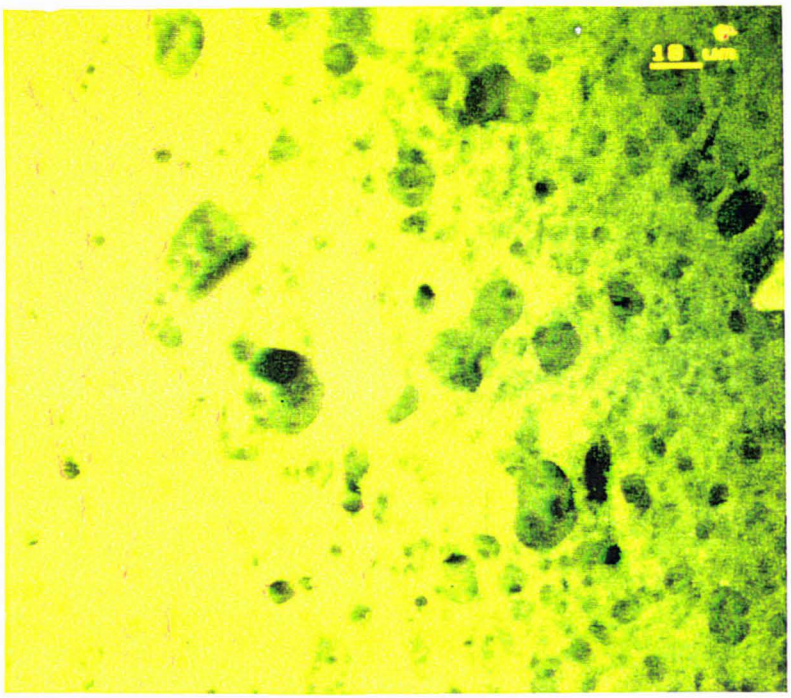


Figure 4.18 A three dimensional Micrograph of SOS showing the spherical structure of fat globules (scale 10 µm)

CHAPTER 5

DISCUSSION

5.1 INTRODUCTION

The experimental results given in chapter 4 are discussed here under shear creep, shear stress relaxation, dynamic impulse halfsquare and the confocal laser scanning microscopy sections. A general discussion is given to relate the different methods used to determine the rheological properties of processed cheese slices produced using different processing conditions.

Section 5.2 and 5.3 focuses on the determination of the linear viscoelastic range in both shear creep and shear stress relaxation. Section 5.4 focuses on the dynamic measurements which were carried using small amplitude impulse shear. The dynamic viscoelastic properties were resolved into the storage (elastic) modulus G' and loss (viscous) modulus G" and the phase difference between strain and stress δ. This was used to determine the melting characteristics of cheese slices made under different processing conditions as the temperature was varied from 10^0C to 70^0C.

Section 5.5 focuses on the cheese microstructure examined using a Confocal Laser Scanning Microscope. The microscopic structure was then related to different process conditions under which the cheese slices were made. The findings from the above sections were then related in the general discussion (5.6). This section also includes problems encountered during this project.

5.2 SHEAR CREEP

5.2.1 Establishment of Linear Viscoelastic Region and the Instantaneous Speed

The standard procedure used to establish the linear viscoelastic region was by increasing the initial applied force and determining if the resulting displacement/deformation increases by the same proportion. It was found out that at lower forces as the force was doubled, the resulting displacement doubled. For IWS cheese with applied forces ranging from 2.14 to 4.24 N, the resulting displacement increased from 2.03×10^{-5} m to 4.0×10^{-5} m which is essentially proportional to the increase in the applied force. Increase in the force above 4.24 N caused a 26% displacement above the expected value. It was deduced therefore that the applied forces for IWS to obtain linear viscoelastic behaviour should vary between 0.0 N and 4.5 N.

The increase in force from 3.37 N to 6.73 N for SOS cheese indicated a linear viscoelastic behaviour. The displacement increased proportionately from 1.62×10^{-5} m to 3.21×10^{-5} m. Above 6.73 N, any increase in the applied force did not show a proportional increase in the resulting deformation.

The maximum displacement within the linear viscoelastic region correspond to 1.61% strain for IWS cheese and 1.60% strain for SOS cheese with the applied forces corresponding to a shear stress of 890.79 Pa and 1557.41 Pa respectively. The applied stress on the two cheese slices exhibit marked differences though the resulting strain was basically the same. It is inferred that these differences were a result of different process conditions used to process the IWS and SOS cheese.

The crosshead speed of 30 mm per minute was used throughout the creep measurements. This was assumed to be the most suitable speed with respect to the magnitude of applied stress and the sample thickness. The maximum applied force was reached between 0.03 to 0.2 second. This time range was considered short enough to avoid any significant creep to occur before the specified force was reached. This complied with the prerequisite of creep measurements as reported by Ferry (1980), Steffe (1992), Rao and

Steffe (1992) and Whorlow (1992).

5.2.2 The Stress-Strain Relationship

The displacement or the strain increased sharply on the onset of the force. As force was kept constant, there was a gradual increase in the displacement. Results show (Figs. 4.1a and 4.1b) the instantaneous displacement (y-intercept) followed by a non-linear increase of the displacement from t = 0 to t = 30 seconds followed by an approximately linear increase in the displacement from t = 30 to t = 300 seconds. The trend was observed at all applied forces and in both IWS and SOS cheeses. However, at higher force there was an increase in the standard errors of the mean and the ill-defined regions (the regions of instantaneous displacement, non-linear displacement and linear displacement) of the responses become more noticeable. This conforms with reports by Whorlow (1992).

5.2.3 Creep Compliance

Creep compliance J(t) is the strain per unit stress of a viscoelastic material (cheese) giving the fundamental material property. The increase of the compliance with time signifies the deformation or flow experienced by the cheese slice due to the applied stress. The magnitude of deformation or flow depends on the elastic (solid) and viscous (liquid) components of the cheese slice. A solid material will exhibit lower compliance while a liquid material will exhibit higher compliance. In molecular terms, solid materials have their molecules more intertwined therefore require higher stress to deform whereas, the liquid materials have their molecules less closely intertwined requiring less stress to deform. It was deduced from above that the IWS cheese was more liquid-like and less elastic than SOS cheese. This is depicted by a higher shear creep compliance for IWS cheese than SOS cheese.

The calculated retardation times for IWS cheese varied between 22.31 seconds and 33.99 seconds whereas those of SOS cheese varied between 27.64 seconds and 38.61 seconds

(Table 4.1). Under the same strain, the retardation times of IWS cheese were lower than those of SOS cheese. The longer retardation times for SOS would indicate a more internal resistance to deformation in SOS than in IWS cheese. This conforms with the above findings that SOS cheese is more elastic than IWS cheese.

The two types of cheese slices have essentially similar composition. The rheological differences can only be explained to have resulted from different processing conditions. IWS cheese was cooked at 83°C for 3.5 minutes while SOS cheese was cooked at 75°C for 2.5 minutes. The combination of higher cooking temperature and longer time aids better emulsification of fat and protein hydration therefore less protein-protein interaction resulting in a weaker structure. The IWS was cooled rapidly whereas the SOS was cooled at a slower rate. Rapid cooling stops further protein-protein interaction whereas slow cooling facilitate protein-protein interaction. This is indicated by SOS cheese being more elastic than IWS. This is in agreement with the reports by Rayan et al (1980), Lee et al (1981), and Heertje et al (1981).

5.3 SHEAR STRESS RELAXATION

5.3.1 The Establishment of Linear Viscoelastic Region and the Instantaneous speed

It was observed that the resulting forces on imposition of given strain were higher for the Instron than the TA.HD for both cheeses. The resulting forces from Instron measurements were higher than those from TA.HD measured under the same condition. The reasons for this behaviour are discussed later in this section.

Results show a proportional increase in force responses as the applied strain is increased between 1.6% and 4.0% strain. This trend is observed with both cheese slices and pieces of equipment. The increase of strain above 4.0% resulted into lower increase in force than the expected values. This indicate that strain above 4.0% are beyond the linear viscoelastic range.

As the applied strain was increased, the accuracy or reproducibility of data was better at lower strain, the standard error of the mean was lower than 0.02% but this increased with increasing strain to about 0.08% as the applied strain reached about 5.0%. The trend was the same with the measurements carried out using the Instron and the TA.HD and for IWS and SOS cheeses.

The time to reach a given deformation in regards to sample thickness (shear strain) was established from the displacements to be imposed. Within the linear viscoelastic region of 1.6% to 4.0% strain the displacements corresponding to these strain were calculated using equation (3.5.3) and these were from 0.032 mm to 0.10 mm for SOS cheese and 0.04 mm to 0.125 mm for IWS cheese. The crosshead speed used for both the Instron and the TA.HD was 30 mm per minute. At this deformation rate, the maximum applied strain was reached within 0.064 to 0.24 seconds. It was considered that these strain rates were rapid enough for any significant relaxation to occur before the specified deformation is reached. The application of strain using higher crosshead speeds introduced artifacts such as strain overshoot. It was generally considered that this speed was rapid enough to conform with findings by Hedegard et al (1970), and Shama & Sherman (1970).

5.3.2 Stress Relaxation Modulus

Shear stress relaxation modulus is the shear stress per unit strain. This was calculated using equation (2.6.15). The shear stress relaxation modulus decay as time measured within the interval 0 to 300 seconds. Responses from both samples measured using the Instron and the TA.HD shows similar trends.

The resulting forces after the imposition of a given deformation were higher for Instron than those of TA.HD at all deformations. However, the calculated stress relaxation modulus from the Instron data and that from the TA.HD showed that the modulus from TA.HD was higher than that of the Instron measured at the same deformation. These differences might have been caused by differences in sample dimensions. The Instron's sample area was 4.32×10^{-3} m^2 whereas that of TA.HD was 1.8×10^{-3} m^2. The area of

the samples for the Instron are more than twice those of TA.HD samples. A load cell capacity of 100 N was used for the Instron while the TA.HD had a 50 kg load cell. With the use of the same deformation rates in both pieces of equipment, the differences could result from different inertial forces on the specimen resulting into different stress relaxation moduli.

However, for both instruments there was a marked rheological difference between the IWS and SOS cheeses. Higher relaxation moduli were observed at all strains for SOS cheese than IWS cheese at the same measurement conditions. In other words, it is observed that the stress relaxation moduli of the two types of processed cheese slices were dependent on their rheological properties rather than the measuring equipment as long as similar conditions were used. This is in agreement with reports by Voisey (1971) and Masi (1989).

5.3.3 Fitted Stress Relaxation Modulus

Experimental stress relaxation modulus was fitted using a three element Maxwell model. From the fitted stress relaxation data the equilibrium modulus G_e, the elastic element modulus G_1, the instantaneous modulus G_0 and the relaxation time λ_{rel} were derived.

It was found that there was good agreement between the experimental data and the fitted data with correlation coefficient of 0.93 to 0.98 (Table 4.2). The comparison of fitted data indicate that there was better fitting of IWS cheese than in SOS cheese. However, there was no noticeable difference in fitting Instron data as compared to TA.HD data. This might be explained by the difference in sample dimension as described in section (5.3.2) above. These findings are in agreement with reports and recommendations by Peleg (1977), and Luyten (1988).

The relaxation time for both cheeses were calculated using equation (2.6.15) and tabulated in Table 4.2. There was a difference in the relaxation times for the same cheese when the Instron results were compared to those of TA.HD at the same strain.

The possible explanation is the difference in sample area and different load cell used as explained earlier. It was found out that the relaxation times for IWS cheese were approximately the same as those of SOS ranging from average of 13.7 seconds to 20.8 seconds. This closely relates to the findings by Masi and Addeo (1984 and 1987).

The comparison of the stress relaxation moduli for IWS cheese and SOS cheese indicated lower moduli for IWS cheese at all strains measured using both pieces of equipment. The moduli for SOS cheese were about three times higher than those of IWS cheese measured at the same strain.

The different relaxation phenomena shown by the two cheeses indicate the different relaxation behaviour owing to protein-protein interaction, hydrophobic and hydrophillic attractions and van der Waal's forces which have to be overcome during the stress relaxation experiments. The magnitude of stress relaxation modulus depicts how elastic and or liquid the material is behaving. Energy is dissipated (lost) and stored during the stress relaxation experiments. The magnitude of stored energy is indicated by the magnitude of the equilibrium modulus of a three element Maxwell body. The higher relaxation modulus of SOS cheese depict more interaction of molecules especially he protein-protein interaction. The IWS cheese depicts lower relaxation modulus therefore less interactions within the network and the molecules are further apart and move more independently. This infers therefore that IWS processed cheese has a more liquid-like behaviour than SOS processed cheese owing mainly to different process conditions. This conforms with the theories put forward and suggestions by Ferry (1980), Shama and Sherman (1979) and Masi and Addeo (1984b and 1986).

5.4 DYNAMIC VISCOELASTIC AND MELTING CHARACTERISTICS

5.4.1 The dynamic Linear Viscoelastic Region

The relationship between the dynamic storage (elastic) modulus and the dynamic loss (viscous) modulus for IWS cheese as strain is increased from 0.8% to 3.2% show that

both moduli were essentially constant at 21°C. However, there was a slight decrease of both the storage and the loss moduli above 3.2% strain. This indicate a linear region of up to a 3.2% strain at 21°C for IWS cheese.

The dynamic storage and loss moduli of SOS cheese as strain is varied from 0.8% to 4.0% at 21°C show that both moduli were essentially constant up to a strain of 3.2%. There was a slight decrease of both the storage and loss moduli above 3.2% strain. This indicate the linear viscoelastic region was up to 3.2% strain at 21°C for SOS cheese.

There was a gradual decrease in both the dynamic storage and loss moduli as the temperature was raised from 10°C to 70°C. Although the magnitude of decrease of moduli varied with cheese type, the same general trend appeared in both cheeses. The storage modulus for IWS cheese seems to decrease more gradually between 10°C and 50°C and slightly increases or remain constant between 50°C and 70°C, whereas the decrease in loss modulus was more rapid between the same temperature range and a corresponding increase in dynamic modulus above 50°C.

Similar responses were observed with SOS cheese but the rate of decrease of the dynamic moduli were slower as compared to IWS cheese. The storage modulus decreased between 10°C and 60°C and then slightly increased while the loss modulus decreased for the same temperatures range but the rate of decrease became even slower especially above 60°C.

This phenomena could be explained in terms of breakage of intermolecular forces such that molecules are sufficiently separated and move independently as strain is applied and the temperature is raised. At above 50°C for IWS cheese and 60°C for SOS cheese, the molecules are much separated without much interaction resulting to more movement/flow rather than reformation of bonds. This is in agreement with reports by Ferry (1980).

5.4.2 The Comparison of Storage and Loss moduli of IWS and SOS Cheese

The storage modulus indicate the magnitude of the elastic (solid) component of the material. It was observed that the storage modulus of IWS was lower than that of SOS cheese measured under similar conditions. Results show that the difference in the storage moduli of IWS cheese measured at 10°C and 21°C with varying strain was about one log.-cycle lower than that of SOS cheese measured under similar conditions. This indicate that IWS cheese is more liquid-like than SOS cheese.

The comparison of loss moduli of the two cheeses indicate that the loss modulus for IWS cheese to be lower than that of SOS cheese. There was more pronounced differences between the storage moduli of the two cheeses than the corresponding loss moduli. This exhibit the closeness of the viscous components of the two cheeses. The two cheeses have approximately the same composition depicting that these rheological differences are a result of different processing conditions. This conforms with findings by Meyer (1973), Ben Naim (1980), Rayan et al (1980), Lee et al (1981), Heertje et al (1981) Kinsella (1982), and Caric & Kalab (1987).

5.4.3 The dynamic Loss Tangent (tan δ) for IWS and SOS cheese

The dynamic loss tangent is the ratio between the loss modulus and the storage modulus. Higher ratio depict more liquid-like materials while lower ratio depict more elastic materials. As temperature is scanned for example between 10°C and 70°C, the magnitude of the loss tangent indicate the onset of flow of the melting cheese as the temperature is raised.

A drop in the loss tangent between 10°C and 21°C, a gradual rise of loss tangent from 21°C to 50°C and finally a sharp drop between 50°C and 70°C for IWS cheese was observed. The SOS cheese on the other hand show different responses in that there was a sharp increase of loss tangent between 10°C and 21°C, then a gradual increase up to 40°C, followed by a slight decrease up to 50°C and a sharp rise between 50°C and 60°C

and finally a sharp drop at 60°C. These behaviour could be explained by fat melting as the temperature approaches 21°C for IWS cheese, and 30°C to 40°C for SOS. This could be explained by the difference in fat distribution in IWS and SOS. The fat globules in IWS are more uniformly distributed than in SOS. At temperatures above 40°C, there is onset of protein mobilization but sufficient energy had to be dissipated for flow to occur. However, at 60°C the dissipated energy was high enough to cause flow in SOS and 50°C for IWS cheeses.

At strain above 1.6%, these responses were more pronounced indicating that at higher strain the materials act more liquid-like as depicted by the increase in the loss modulus/storage modulus ratio. However, the temperature transition point for both cheeses remained at 50°C and 60°C for IWS and SOS cheese respectively. The transition point exhibit the melting temperature or the phase change from solid-like to liquid-like behaviour of the cheese.

The comparison of the loss tangent for IWS cheese and SOS cheese show that the IWS cheese has a generally higher loss tangent. This is evidence that IWS cheese is more liquid-like than SOS cheese although they have essentially the same composition. The differences can be explained as being a result of different process conditions used to manufacture these cheeses. IWS cheese was cooked at a higher temperature and at a longer time resulting in better emulsification and more protein hydration. This was followed by rapid cooling which stops further protein-protein interaction resulting in a weaker matrix. On the other hand, SOS was cooked at a lower temperature and shorter time. Cooling was slow allowing protein-protein interaction, hydrophillic and hydrophobic bonding and van der Waal's forces resulting in firmer matrix. This is in agreement with the findings by Carter (1989).

5.4.4 The Relationship Between the Storage and Loss Moduli and the Frequency

The dynamic storage modulus and the dynamic loss modulus are frequency dependent. However, results show that the dependence of the dynamic moduli was very slight

showing that both IWS and SOS cheeses are very solid-like materials at the measured temperature of 21°C. It was shown that both the dynamic storage moduli for IWS and SOS cheeses increase slightly as the frequency of oscillation was increased between 0.025 Hz and 0.25 Hz. The dynamic loss modulus of IWS cheese increased slightly between 0.025 Hz and 0.2 Hz and then dropped suddenly while that of SOS cheese increased between 0.025 Hz and 0.1 Hz and decreased slightly from 0.1 Hz up to 0.25 Hz. This would be indicating that above 0.1 Hz there are artifacts that could affect the results. It was also observed that at 0.5 Hz the loss moduli for both cheeses became negative hence the loss tangent. No reason could be found as to why this happened but as discussed above the presence of artifacts could not be ruled out.

5.5 THE CONFOCAL LASER SCANNING MICROSCOPY

The fat distribution within the protein matrix of IWS cheese indicated small round globules with size ranging from 0.1 μm to 1.0 μm with more protein-fat interaction than protein-protein interaction. The fat distribution in SOS cheese is not as uniform as that of IWS cheese. The fat globule size is larger mainly ranging from about 0.5 μm to 5.0 μm with a more continuous protein phase.

There is abundant crystals close to the surface (about 20 μm) of IWS cheese but these decrease as you go to the centre of the sample (about 120 μm). Fewer crystals were observed in SOS cheese throughout the sample. Crystal formation is associated with the cooling rate. Rapid cooling results in fat crystallization, and also crystallization of undissolved emulsifier.

The microscopic structural differences between IWS cheese and the SOS cheese was a result of processing conditions, whereas the IWS cheese was cooked at 83°C for 3.5 minutes and cooled rapidly, the SOS cheese was cooked at 75°C for 2.5 minutes and cooled slowly. Variations in the cooling rate had significant effects on the matrix buildup and therefore the cheese microstructure. This indicate therefore that the IWS cheese resembles a soft type processed cheese while the SOS cheese resembles a hard type

processed cheese. This is in agreement with the findings by Templeton & Sommer (1936), Kimura et al (1979), Taneya et al (1980 and 1981), Rayan et al (1980), Heertje et al (1981) and Shimp (1985).

5.6 GENERAL DISCUSSION

It is important to point out problems encountered during this work and the way they were remedied without causing significant errors to the experimental results.

It was observed during the experiments that high crosshead speed (from 50 mm per minute and above) caused sample failure (fracture) and overshoot of the desired/set values both of force in the creep test and displacement in the stress relaxation test. This caused difficulty in the setting of inputs such that the measurements were within the linear viscoelastic region. By trial and error a speed of 30 mm per minute was determined and the maximum stress or strain reached within 0.2 second or less. It was assumed that this deformation rate was basically rapid enough with insignificant relaxation or creep during loading.

The temperature control during the dynamic tests was difficult because of the long and lighter extension used with this geometry. This problem was magnified especially during the injection of carbon dioxide which caused vibration. The vibration cause artifacts especially at small amplitude deformation making the results unreliable. The CO_2 injection was briefly stopped during the crosshead movement to solve this problem and this did not cause any significant temperature variations. At above 60°C and at very small deformations (below 0.01 mm), noise occurred rendering the results unreliable. This resulted in the use of deformations of 0.016 mm (0.8% strain) to 0.1 mm (4.0% strain) which were essentially within the linear viscoelastic region. The samples tend to flow to the bottom at times especially if held at 70°C for long periods of time. It was therefore necessary to hold the sample at this temperature for as short a time as possible.

Despite the above shortfalls, the results were accurate and there was a high degree of

reproducibility.

It is important at this point to qualitatively relate the viscoelastic properties obtained from different measurements used in this project. The exact interrelations among the viscoelastic functions and the mathematical models to relate these functions could not be developed during this thesis and will not be discussed here.

Viscoelastic materials such as cheese show elastic recovery after deformation whether the measurements were static or dynamic. The difference might be the application of stress or strain and the strain rate or a frequency of oscillation such that these have different values therefore causing different responses on the material's elastic and viscous components.

It was observed that at the same temperature and strain, the relaxation modulus G(t) of IWS cheese is approximately equal to 1/J(t) of the same cheese. The plot of G(t) is approximately a mirror image of those of J(t) especially in the region of equilibrium modulus G_e and equilibrium compliance J_e. The relaxation time appears to occur at shorter time than the corresponding retardation time of the same material. For example the retardation time for IWS cheese is about 28 seconds while the corresponding relaxation time is about 17 seconds. This is in agreement with the theory put forward by Ferry (1980).

The high magnitude of compliance indicate the presence of configurational rearrangement or realignment of the molecules within the interval of the experiment. In other words, it is the relationship between the energy dissipated as heat and the energy stored in the elastic component of cheese. On the other hand, the magnitude of the relaxation modulus depicts the relation between the energy dissipated and energy stored in the three element Maxwell body during the interval of the experiment. The two measurements therefore measure the same properties although different modes are used.

The dynamic tests basically gives the stress strain relationship and differentiate the elastic component from the viscous component of the material. The elastic component or the

storage modulus is a measure of energy recovery and storage during a circle of deformation. Since both the equilibrium relaxation modulus G_e and the dynamic storage modulus $G'(\omega)$ are a measure of stored elastic energy and therefore the rigidity, their measurement would be qualitatively equivalent if the loading rate/strain rate were equivalent with the frequency used in the dynamic. While the linear viscoelastic region was between 0.8% to 4.0% strain in dynamic and stress relaxation measurements, this region was only up to a strain of 1.6% with creep test. A good explanation regarding this difference in behaviour could not be found.

The results from the above three experimental methods agree in that the IWS cheese is more liquid-like and less elastic than the SOS cheese. Relating these results to the cheese microstructure revealed that there was better fat distribution in IWS cheese than SOS cheese. There is more protein-protein interaction in the SOS than IWS cheese. This is shown by lower stress relaxation modulus, dynamic storage modulus, lower melting temperature and higher creep compliance in IWS cheese than in SOS cheese. These differences were attributed to the different process conditions the two cheeses were subjected to. This is in agreement with findings by Rayan et al (1980), van Vliet & Dentener-Kikkert (1982) and Walstra & van Vliet (1986).

This work has established the fundamental rheological test methods to characterize the mechanical and melting properties of different processed cheese slices produced under different process conditions. The dynamic impulse halfsquare is a useful method to determine the melting properties of processed cheese slices under small deformation. Simple inexpensive instruments could be accurately used to measure the static rheological properties of processed cheese slices. The microscopic examination gave a useful means of comparing the cheese microstructure to its mechanical properties. The combination of the tests methods used in this work give a better understanding to the relationship of process conditions, the texture and the rheological properties of the product.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1 CONCLUSIONS

It is concluded that:

1) The linear viscoelastic region for processed cheese slices is extended to a strain of 4.0% measured by shear stress relaxation method at 21°C. The linear viscoelastic range for shear creep is 1557 Pa for SOS cheese and 891 Pa for IWS cheese at 21°C.

2) Mechanical models are a useful means to conceptualize the static measurements of foods such as processed cheese. A three element could be used to fit relaxation data which would enable the stress to be categorized in instantaneous, equilibrium, and the decay components from which relaxation time could be calculated. The Kelvin/Voigt body could also be used to fit shear creep data and equilibrium compliance, instantaneous compliance and retardation time could be calculated.

3) The dynamic impulse halfsquare method could be used to determine the mechanical properties of processed cheese slices and could accurately show the loss (viscous) modulus and the storage (elastic) modulus components of the cheese. The relationship between these moduli gave the loss tangent which depicts how solid-like or liquid-like the cheese behaves.

4) The dynamic impulse halfsquare measurements were used to determine the melting characteristics of processed cheese slices. It was found that the melting properties depend on the process conditions used to manufacture the two cheeses.

5) The microstructure of cheese slices showed a marked differences which were

attributed to different processing conditions. The mechanical properties were found to depend on the microstructure of the slices and therefore the process conditions.

6) Simple and inexpensive equipment like TA.HD (Texture Analyser) could give accurate results when used for static measurements such as stress relaxation. The TA.HD could not be used for dynamic measurements because it cannot generate/perfect halfsquare waveforms necessary to perform dynamic tests. However, if a connection between eqs. (2.6.14) or (2.6.15) with eqs. (2.8.34 & 2.8.35) is derived to take into account the finite speed to reach the peak of the shear impulse, the texture analyser could be also used to carry out dynamic measurements.

6.2 RECOMMENDATIONS FOR FUTURE WORK

It is recommended that:

1) Further research shoud be done to determine the linear viscoelastic strain for cheese slices using shear creep experiments.

2) More research work should be carried out to establish the effects of high frequency on the dynamic impulse viscoelastic properties. This could be achieved by comparing the standard techniques such as sine waveforms with the impulse waveform technique at similar frequencies.

3) To establish mathematical models and direct relationship between the creep, stress relaxation and the dynamic impulse measurements.

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