THE RHEOLOGY OF BUTTER

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Abstract.

A parallel plate viscoelastometer was built to perform creep compliance tests on butter and related fats. Creep movement was measured with a linear displacement transducer and recorded by a data logger designed and built for creep compliance experimentation.

A temperature of $10^{O}C$ was maintained by placing the parallel plate viscoelastometer in a refrigerated incubator.

A series of preliminary experiments established the creep response was linear and that the direction in which some samples were sheared was critical. The duration of creep compliance testing was also found to affect results.

Creep behaviour of butter was assumed to be viscoelastic (based on previous studies) and was modelled with a generalized Kelvin model. Elastic and viscous parameters were fitted to the data by a Marquadt non-linear least squares curve algorithm. Continuous retardation spectra were found by plotting $L(\tau)$ against ln time. Data which had been both smoothed and differentiated by the methods of Savitzky and Golay (1964) showed evidence of the existence of three or four main groups of retardation mechanisms.

On removal of stress after creep compliance testing a partial recovery of strain was observed, however, samples failed to recover as much as predicted by viscoelastic theory. A second creep/recovery cycle resulted in a responses similar in magnitude to the first recovery. All fat products tested showed the same pattern of response on repeated creep/recovery cycling.

An explanation, based on the behavior of polymers, was put forward to explain the observed pattern of response. The crystal network was thought to align in the direction in which stress was applied. The formation of new 'bonds' was then thought to lock the network in its' new position.

A number of samples were reworked, The creep curve seen on creep/recovery cycling of reworked samples was similar in shape to that seen for the original samples. However, the curves were three to four times greater than those seen for the original samples. In general, creep response was found to be inversely proportional to hardness.

The retardation spectra of reworked samples differed from those seen for the original samples in several ways. The spectra were smoother, the bulk of the spectra had moved to shorter times and they were larger than those seen for the original samples.

A survey of seasonal butter samples was also undertaken. Creep compliance parameters were found to correlate well with sectility hardness and solid fat content.

Aim of Study.

The aims of this work are:

a) To study the rheological properties of butter and related fat products by a creep compliance method.

b) To gain a clearer understanding of the relationship between rheological properties, composition and structure of butter and related products.

c) To use this knowledge to improve the rheological properties of butter.

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CHAPTER ONE

AN INTRODUCTION IN THREE PARTS

PART A: RHEOLOGY

1A.1. INTRODUCTION

Rheology is the science of deformation and flow of materials. The study of rheology encompasses many fields, from geology to medicine. Even limiting the scope of this introduction to foods presents a formidable challenge. Many good books have been written on the rheology of foods, for example, 'Industrial Rheology', by P. Sherman (1970), 'Rheology and Texture in Food Quality', by deMan, Voisey, Rasper and Stanley (1976), 'Engineering Properties of Foods', edited by Rao and Rizvi (1986), etc. These books outline the four main reasons for the study of rheological properties of foods; to gain an insight into the structure of the material, to improve quality control and predict the behaviour of new products, to correlate consumer acceptance of a product with some measurable rheological property and to design machines for handling foods.

In Part A it is proposed to survey those aspects of rheology necessary to provide a background to the topics covered, namely a brief introduction to solids, liquids and plastics, an outline of rheological models and rheology of viscoelastic materials.

1A.2. STRESS AND STRAIN

For a deformation to occur a force has to act on a body. Stress (σ) is the intensity factor of the force, expressed as force per unit area (Nm^{-2}, Pa). The various types of stress, categorized by the way in which they act, are compressive stress, tensile stress and shear stress.

Compressive stress acts at right angles and towards the plane in which it is acting. Tensile stress components also act at right angles, but are directed away from the plane in which they act, eg. stretching, while shear stresses act tangentially to the plane.

Conversely, when a body is stressed and its dimensions change, a deformation has occurred. Deformation can be expressed as strain. For example, when a body of length L is subjected to a stress (tensile or compressive), the linear deformation, ΔL, can be expressed as $\Delta L/L$, or strain (γ, unitless).

With liquids, it is more appropriate to speak of the rate of deformation ($\dot{\gamma}$), where $\dot{\gamma} = d\gamma/dt$ (s-1), the change in strain with time.

1A.3. SOLIDS, LIQUIDS, PLASTICS

Two extremes of behaviour, solid and liquid, may result when a force is applied to a material. These extremes are the basis for two broad categories into which foods can be divided, solid foods and liquid or fluid foods. Generally, solid foods retain their shape under gravity, whereas fluid foods flow under gravity and do not retain their shape. Most solid foods however, can exhibit liquid properties under some conditions.

From a rheological viewpoint the behaviour of an ideal solid is described as purely elastic and that of an ideal liquid as purely viscous.

1A.3.1. Solids

Pure elastic behaviour is defined such that when a force is applied to a material it will instantly and finitely deform, and when the force is released it will instantly return to its original form. Such a material is referred to as a Hookean solid. The amount of deformation is proportional to the magnitude of the force. A material of this nature has a rheological parameter termed the elastic modulus (E), the stress/strain ratio of the material.

Three types of moduli exist for Hookean solids, The elastic modulus, E (the force perpendicular to the area defined by stress); the shear modulus, G (the force parallel to the area defined by stress) and the bulk modulus, K, where force is applied from all directions. A fourth parameter is the Poissons ratio. On compression or stretching the ratio of lateral strain to longitudinal strain is the Poissons ratio. At small strains (less than 1%) many biological materials act as Hookean solids.

1A.3.2. Liquids

For a pure viscous material, flow begins on the application of the slightest force and the rate of flow is proportional to the magnitude of the applied force. The liquid flows until the force is removed and it has no ability to recover its original state. The magnitude of deformation depends on the time for which the force was applied. A material with these characteristics is called a Newtonian liquid.

Newtonian liquids are characterized by a rheological parameter, the coefficient of viscosity (η), the ratio of the shear stress to the resulting strain rate.

$$\eta = \sigma / \dot{\gamma} \tag{1.1}$$

The units of viscosity are Pa.s. Viscosity can be thought of as the internal friction of a liquid.

The viscosities of Newtonian fluids are influenced only by temperature and composition, whereas the flow properties of non-Newtonian fluids are influenced by changes in the rate of shear. Most foods exhibit non-Newtonian behaviour.

Non-Newtonian behaviour can be either time-independent or time-dependent. The flow properties of the former depend only on the shear rate, while the flow properties of the later also depend on the duration of the shear.

A large number of time-independent non-Newtonian foods exhibit shear thinning or pseudo-plastic behaviour, with viscosity decreasing as the shear rate increases. Foods whose viscosities increase with shear rate, dilatant or shear thickening foods, are rare, but have been reported.

An important sub group of non-Newtonian foods with time dependent properties is that of thixotropic foods. At a fixed shear rate the viscosity of such foods decreases with time, until an equilibrium is reached. This effect brought about by mechanical action breaking down structure. Foods which undergo time-dependent shear thickening, rheopectic foods, are uncommon.

Many attempts have been made to model the behaviour of non-Newtonian fluid foods. Perhaps the most relevant to this work is the power law model (Equation 1.2) for foods exhibiting time-independent flow properties. The power law model has been very widely used to describe flow behaviour.

$$\sigma = K \gamma^n \qquad (1.2)$$

where n is the flow behaviour index and K is a constant, sometimes called the consistency index. n is a measure of the degree of non-Newtonian behaviour, the lower the value of n, the more a material's properties deviate from non-Newtonian behaviour. n is dimensionless. When n = 1, K = viscosity.

1A.2.3. Plastics

In rheological terms a plastic material flows when a stress greater than a limiting value acts on it. The limiting stress is termed the yield stress (σ_o). A perfectly plastic material does not start to deform until a stress exceeding the yield stress is applied, and would continue to deform until the stress is removed. Deformation is permanent. A practical definition of a plastic often used is a material which will not flow under gravity alone.

Very few bodies are perfectly plastic. A more common type is the Bingham or plasto-viscoelastic body. When a stress below the yield stress is applied, the Bingham plastic behaves in an elastic fashion. Once the yield stress is exceeded, deformation consisting of both plastic and viscous components occurs. Upon the removal of stress, strain, representing the elastic component decreases instantly. The viscous and plastic deformation is permanent.

A Bingham plastic obeys the equation:

$$\sigma - \sigma_o = \eta' \dot{\gamma} \qquad (1.3)$$

where σ_o equals the yield stress, and η' the plastic viscosity.

Many foods approximate to Bingham behaviour. Often in practice a clear yield point may not be seen. This is illustrated in Figure 1.1. The yield stress can be taken at three different points: the lower yield value (1) where the curve deviates from the stress axis, the upper yield value (2) taken where the curve becomes straight, and the Bingham yield value which is found by extrapolating the straight line portion of the curve back to the stress axis.

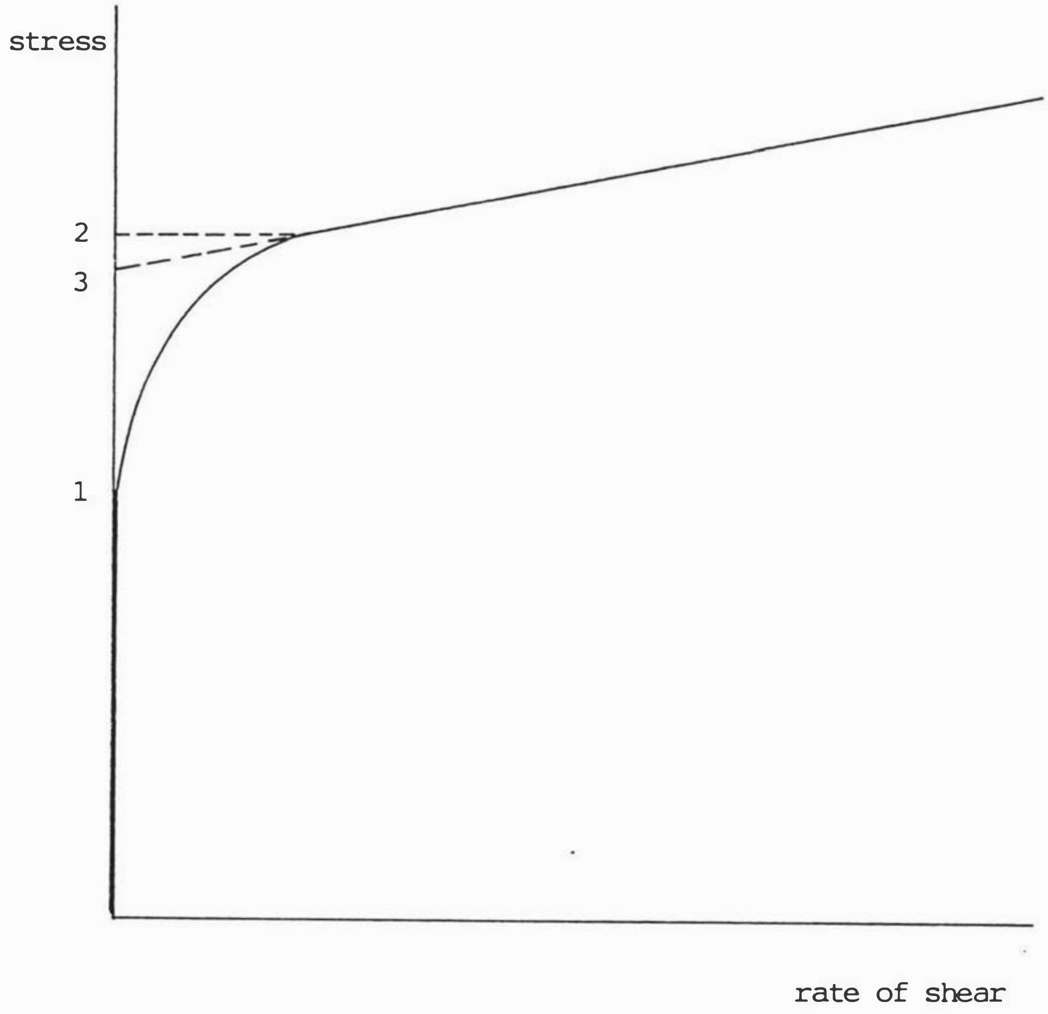


Figure 1.1: Rate of shear vs. shear for a Bingham plastic.

1A.4. VISCOELASTICS

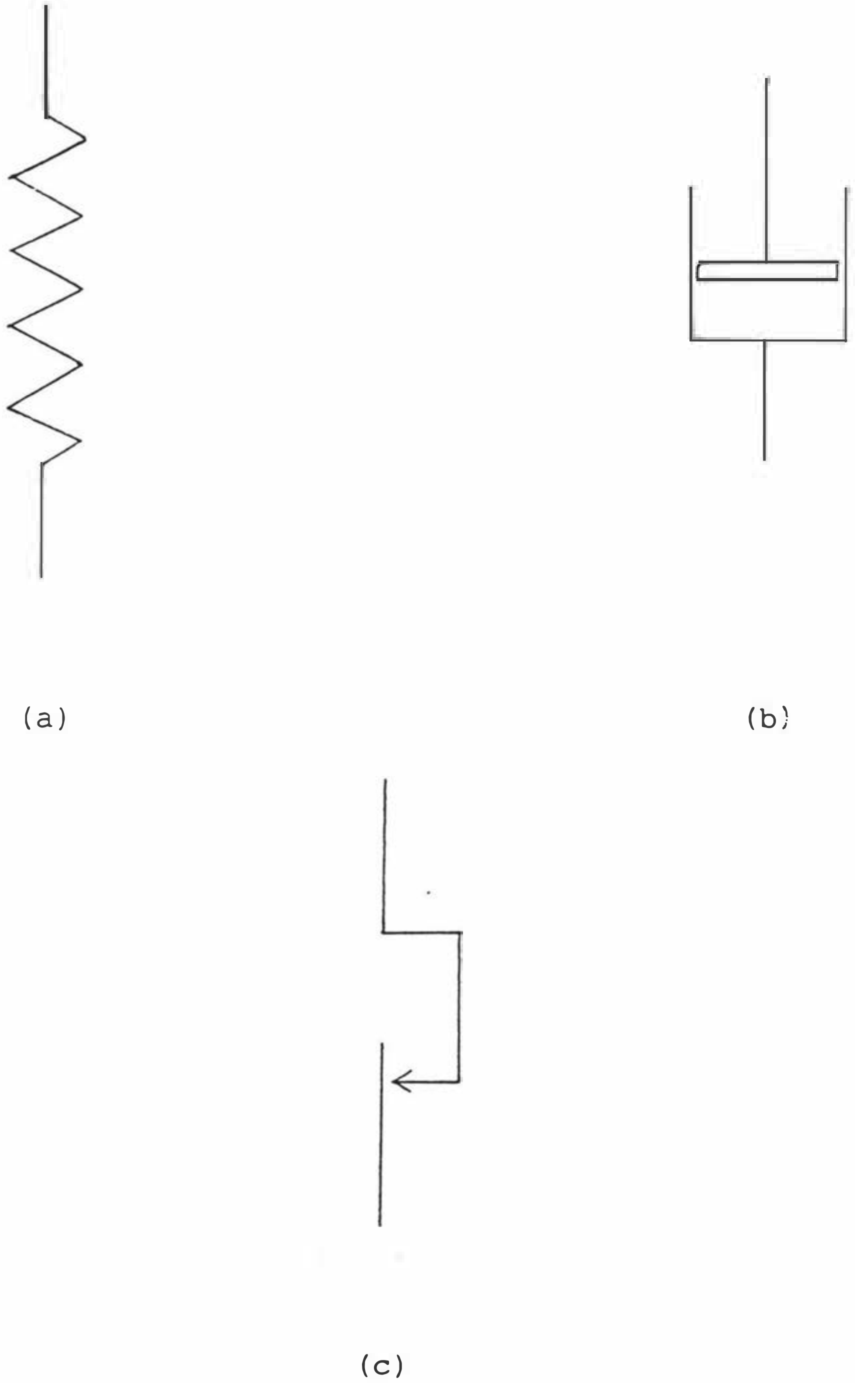
Some foods have rheological properties associated with both the elastic solid and the Newtonian fluid. These foods are referred to as viscoelastic foods. Viscoelastic materials can exhibit both solid and viscous components simultaneously during shear if sufficient time is allowed and the stress applied is large enough to prevent the sample showing pure elasticity. The materials tend to behave like solids initially and then exhibit flow. Thus the work of deformation is not completely conserved (as in solids) or dissipated (as in fluids).

1A.5. MECHANICAL MODELLING

Hookean solids and Newtonian flow can be represented mechanically. Hookean solid elements are usually represented by a spring (Fig. 1.2a) and Newtonian fluid elements by a dashpot (Fig. 1.2b). Plastic behaviour is often represented by a friction element known as the St. Venant slider (Fig. 1.2c). Viscoelastic foods are usually represented by at least one spring (as an elastic component) and one dashpot (as the viscous component). An accurate model can be used to predict changes in a material due to various stress-strain conditions, eg., harvesting, handling, etc.

The elementary models of springs, dashpots and sliders can build more complex models, the Bingham model (spring, slider and dashpot in series, Fig. 1.3a), the Maxwell model (spring and dashpot in series, Fig. 1.3b), the Kelvin model (spring and dashpot in parallel, Fig. 1.3c) and the Burger model (Maxwell unit and Kelvin unit in series, Fig. 1.3d).

The Bingham model is commonly used to represent plasto-viscoelastic behaviour. Applying stress to the Bingham model, Figure 1.3a, initially causes the spring to stretch. On reaching full extension the St. Venant slider, representing



(a)

(b)

(c)

Figure 1.2: Standard rheological models; a) Hookean spring, b) Newtonian dashpot and c), St Venant slider.

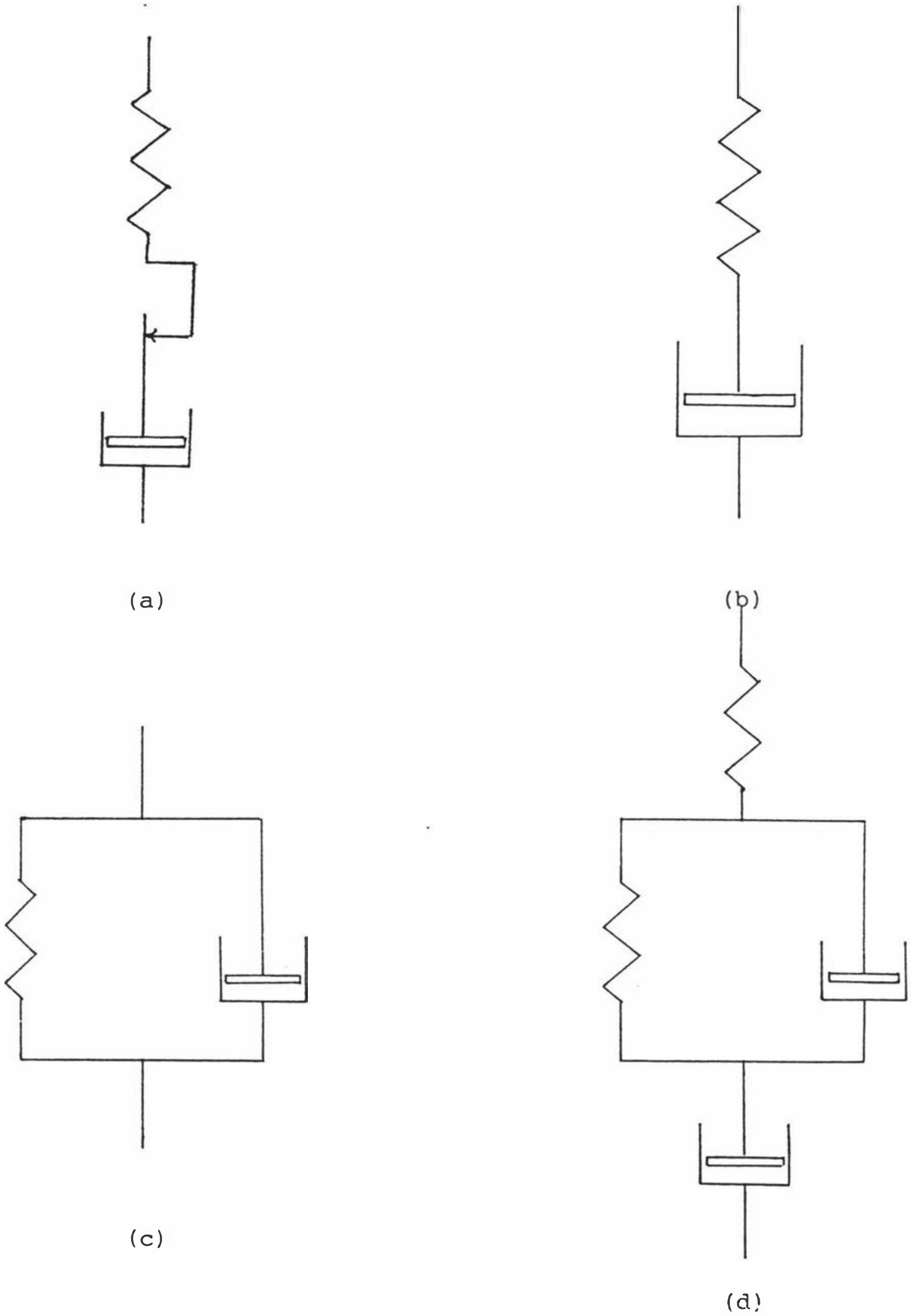


Figure 1.3: Rheological models: a) Bingham plastic, b) Maxwell unit, c) Kelvin unit and d), Burgers model.

yield stress, and the dashpot, representing viscosity, move together until fully extended or stress is removed.

The other three complex models mentioned above can represent the response of viscoelastic materials with time. Viscoelastic models can contain different combinations of springs and dashpots to represent the complex behaviours shown by different foods.

In the Maxwell model (Fig. 1.3b) the applied stress initially stretches the spring. As the spring reaches full extension all the stress goes into causing flow in the dashpot.

The Kelvin model (Fig. 1.3c) reacts to stress with both the spring and dashpot moving together at a constant rate.

The Burgers model is made up of a Maxwell and a Kelvin body in series (Fig. 1.3d). When a force is applied spring 1 deforms instantly. On reaching full extension the spring and the dashpot of the Kelvin unit move together until they are fully extended. At the same time dashpot 1 flows. The four element Burgers body is one of the best known rheological models and has been used to predict the behaviour in a number of materials

1A.6. FUNDAMENTAL TESTING

Fundamental rheological tests measure well defined properties inherent to a material. Results do not depend on sample geometry, test conditions or the apparatus used.

Fundamental rheological testing usually involves only small deformations where the distance between the structural units in the material being tested does not change significantly, ie. strain is very small. When strain is large enough to give rise to finite deformations, existing theory can no longer cope.

Fundamental techniques can be divided into two groups, those conducted under conditions of (quasi)static loading and those conducted under dynamic conditions. Static tests are really quasistatic as theoretically no test can be truly static.

The most useful tests for evaluating viscoelastic foods are creep, stress relaxation and dynamic testing. Creep tests look at strain as a function of time under constant stress. Stress relaxation examines stress as a function of time under constant strain. Creep and stress relaxation operate in the time domain. Dynamic testing operates in the frequency domain and examines dynamic moduli as a function of the frequency of a sinusoidal strain.

For linear viscoelastic materials the moduli and coefficients of viscosity from the three types of tests should be interconvertable mathematically and independent of the magnitude of the imposed force or strain.

1A.6.1. Static Testing

1A.6.1.1. Creep

Creep, the increase of deformation as a function of time, is brought about by constant shear or dynamic forces parallel to the longitudinal axis of the specimen. When the force (stress) is applied rapid deformation occurs, imposing a strain on the material. The strain then increases at a decreasing rate with time. The stress imposed must not be so large as to cause large sample deformations and a non-linear viscoelastic response. If this happens the use of rheological models to represent a material is no longer valid.

Creep has been studied using a variety of techniques. Examples include compression using a constant stress, the use of constant shear and co-axial cylinder viscometry.

Creep recovery is an alternative creep test where the constant stress is released allowing the strain to decrease, depending on sample properties.

1A.6.1.1.1. The Creep Compliance Curve

A plot of strain as a function of time is known as a creep curve. Figure 1.4 illustrates a typical creep and recovery curve for a plastic fat. Creep curves may be used to study a material's physical properties. Figure 1.5 shows a typical creep compliance/time curve, where creep compliance is the ratio of the strain to the constant shear stress at any time (t). The creep and recovery curve can be divided into five principle regions.

(1), a region of instantaneous compliance, (A-B), in which elastic deformation, J_o, occurs. It is believed bonds between structural elements are being stretched elastically. If stress is removed the sample should completely recover its original structure.

$$J_o = 1/E_o \qquad (1.4)$$

where Eo is the instantaneous elastic modulus.

(2), a time dependent retarded elastic region, (B-C), with a compliance, J_r, where it is suggested 'bonds' may be breaking and reforming at different rates. This region may be represented by the equation

$$J_r = \Sigma J_i[1 - \exp(-t/\tau_i)] \qquad (1.5)$$

(3) A linear region, (C-D), of Newtonian compliance, J_N, where flow is occurring.

$$J_N = t/\eta_N \qquad (1.6)$$

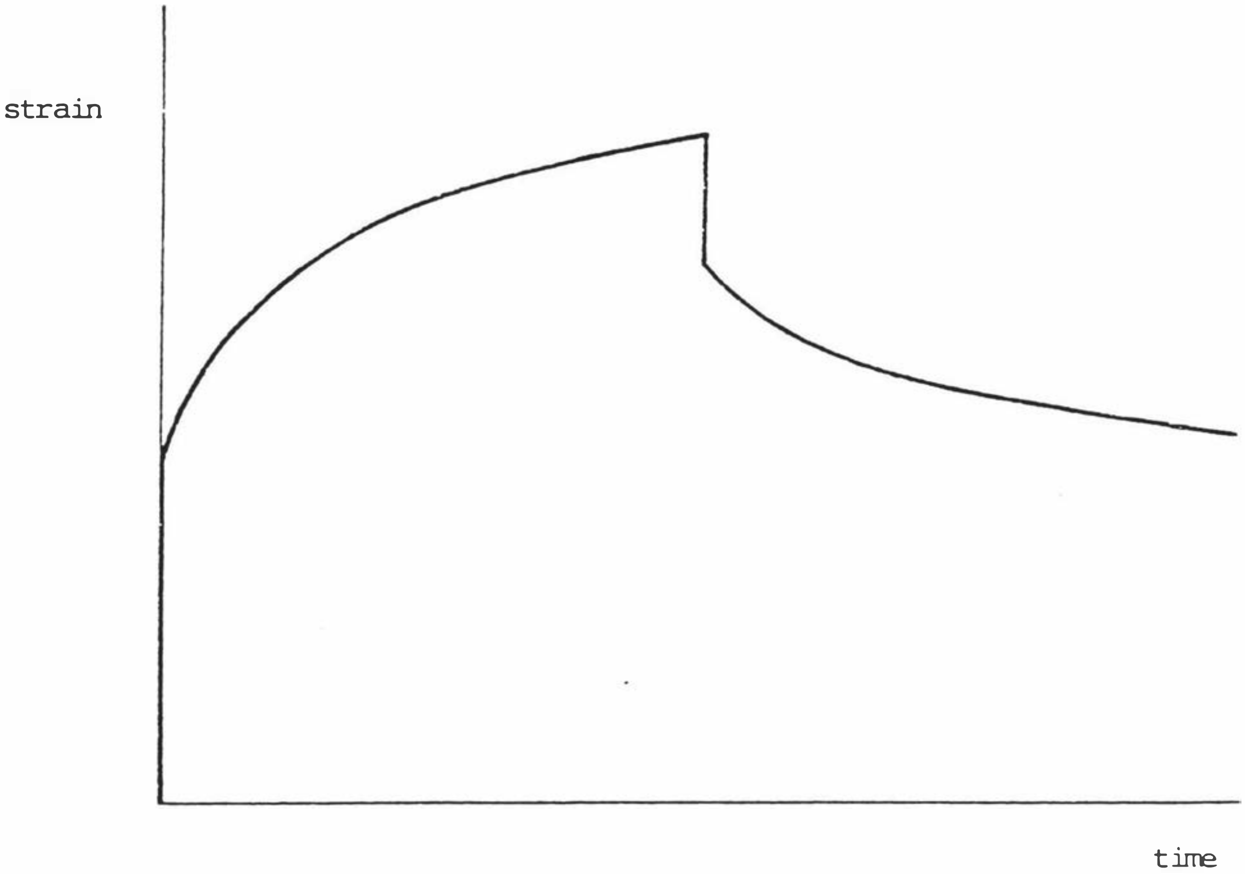


Figure 1.4: Typical creep and recovery curve for a plastic fat.

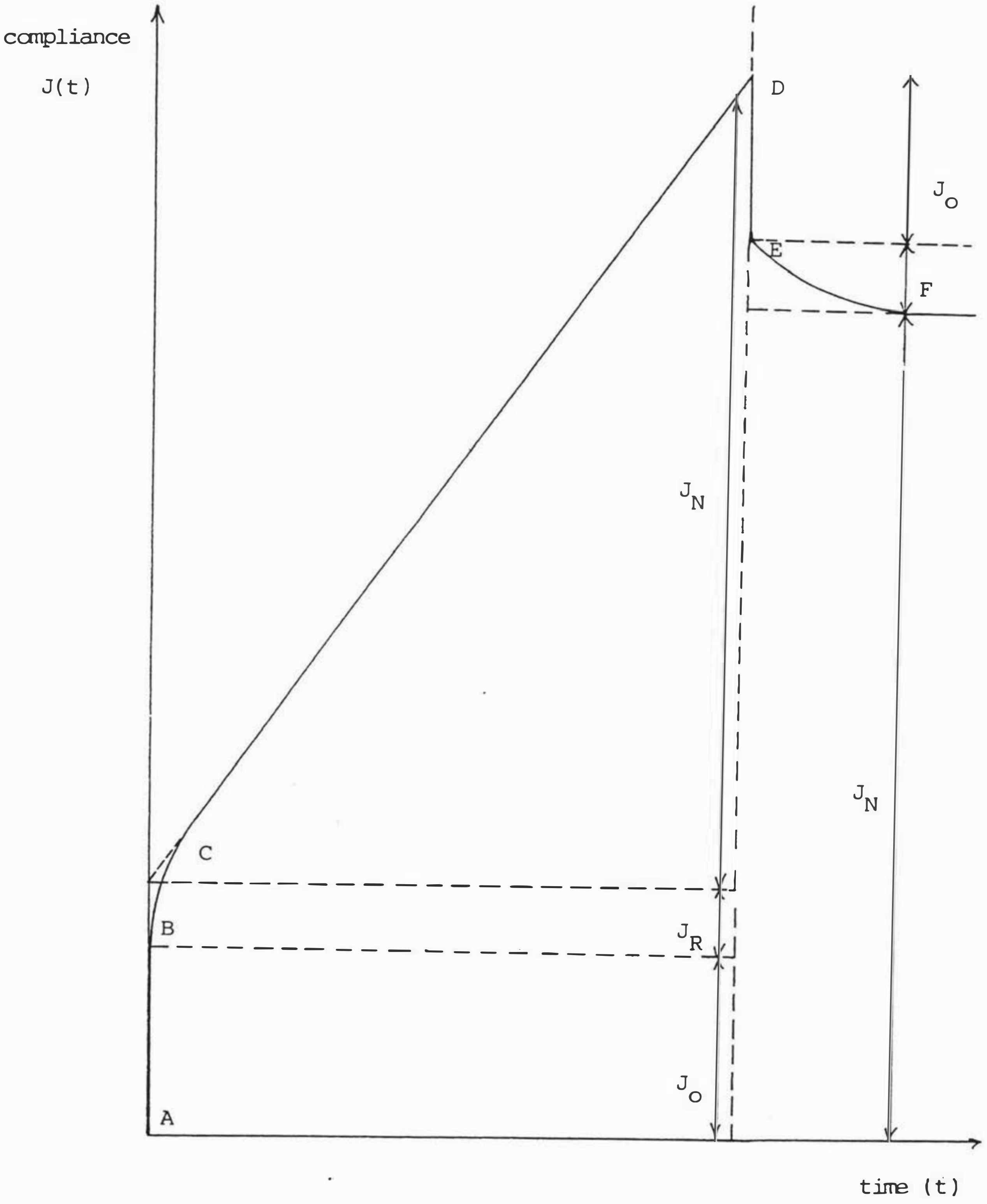


Figure 1.5: Model creep curve.

(4) On the removal of stress region (D-E) represents instantaneous recovery of elastic strain equal to the initial instantaneous strain.

(5) A region of time dependent decay of strain, (F-G), equal to the retarded elastic region. Strain does not decay to zero as permanent deformation has occurred in the C-D region.

The whole creep compliance-time plot is defined in detail by the sum of the parts.

$$J(t) = J_o + \Sigma J_i[1 - \exp(-t/\tau_i)] + \eta_N \qquad (1.7)$$

1A.6.1.1.2. The Model

The Burgers model can be used to represent the creep behaviour of a viscoelastic material. This can written mathematically as

$$\gamma(t) = \sigma_o/E_o + \sigma_o/E_r[1 - \exp(-t/\tau_{ret})] + \sigma_o t/\eta_N \qquad (1.8)$$

(Mohsenin, 1986). If a compliance function J(t) is defined as the ratio of strain to stress the above equation can be expressed in terms of compliance.

$$J(t) = J_o + J_r[1 - \exp(-t/\tau_r)] + t/\eta_N \qquad (1.9)$$

Experimental results for some viscoelastic materials have shown more than one retardation mechanism. For these materials, the complete behaviour cannot be represented by a single Maxwell or Kelvin model, or by the Burgers model. To present the viscoelastic behaviour more realistically a chain of Kelvin models, each with its own retardation time is assumed. The generalized Kelvin model, as it is known, consists of n Kelvin elements connected in series with an initial spring and a final viscous element (Fig. 1.6) described by the generalized equation

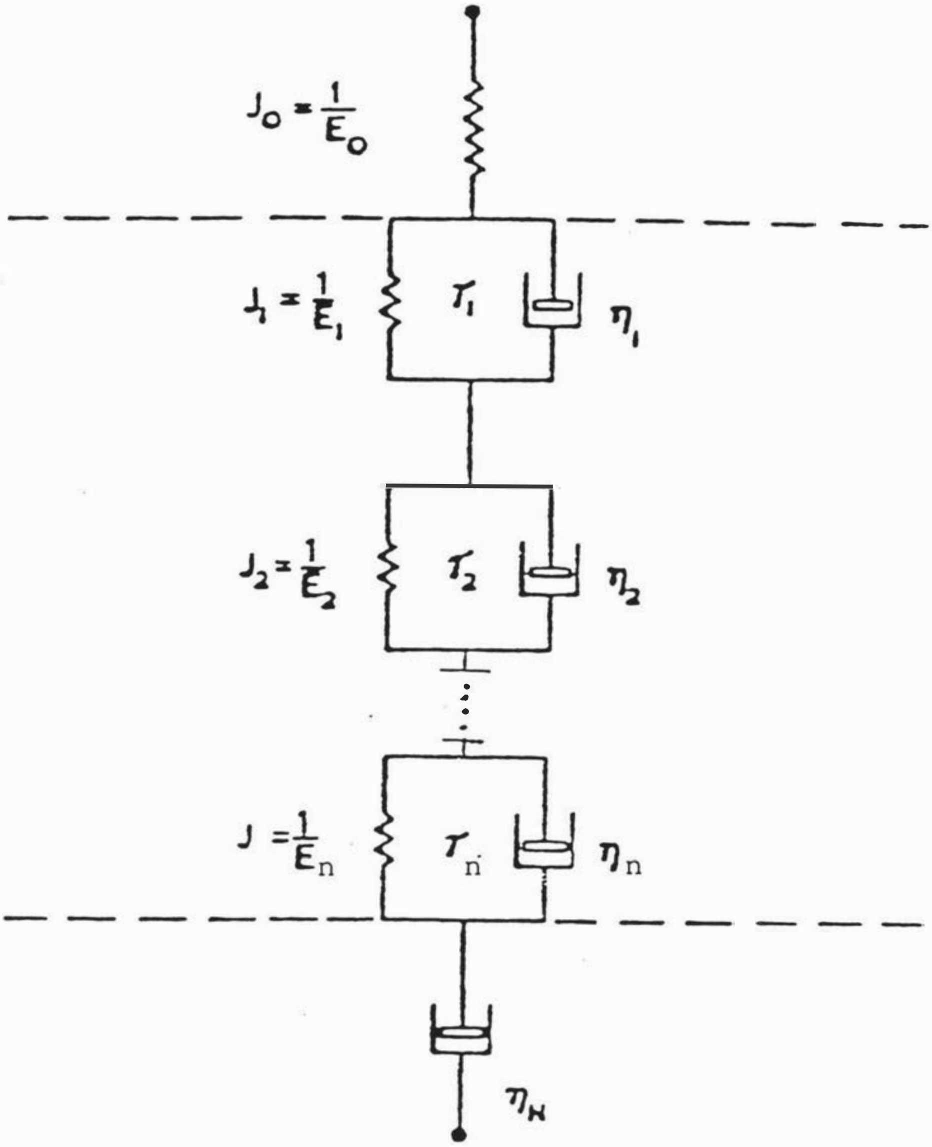


Figure 1.6: The generalized Kelvin model.

$$J(t) = J_o + \Sigma J_i[1 - \exp-t/\tau_i)] + t/\eta_N \qquad (1.7)$$

This equation is the same as that describing the creep compliance-time curve.

1A.6.1.1.3. Retardation Spectra

An alternative approach to creep curves is the use of retardation spectra.

One of the fundamental rheological parameters of a simple viscoelastic solid is the retardation time. Retardation time can be defined as the ratio of viscosity to elasticity in the sample. In a complex viscoelastic solid more than one retardation time would be present.

Experimental creep compliance data can be analysed to give either a continuous spectrum of retardation times or a line spectrum. Warburton and Barry (1968) state that the resolution of individual retardation times becomes impossible if the number is greater than ten and the smallest spacing between any two retardation times is less than five times the value of the smaller retardation time.

The number of retardation times present depends on a), the size of the molecules or particles involved, b), their shape and c), the number of molecules present. High molecular weight molecules, made up of components of widely differing molecular weights will give rise to a complicated spectrum of retardation times (Warburton and Barry, 1968). For most complex systems, such as foodstuffs, a continuous spectrum of retardation times exists.

The analysis of creep curves using Equation (1.7) assumes a finite number of retardation times.

On introducing the parameters obtained back into Equation (1.7) a theoretical creep curve can be generated. If Equation

(1.7) represents the creep behaviour adequately, the theoretical curve should approximate the experimental creep curve.

The derived compliance parameters and retardation times can be used to calculate a line spectrum of retardation times. This can be used as a check to see if the number of exponential terms or retardation times used to model a creep curve is appropriate. If the model is appropriate, the line spectrum should approximate the continuous spectrum, which is found as described below.

In the calculation of the continuous spectrum of retardation times, Equation (1.7) is first written in integral form

$$J(t) = d/d\ \ln t \int L(\tau)[1-\exp(-t/\tau)]\ d\ln t + t/\eta_N \qquad (1.10)$$

where $L(\tau)$ is the retardation spectrum. Shama and Sherman (1968) use Schwarzal's first order approximation of $L(\tau)$ to calculate retardation spectra for margarine.

$$L(\tau) = d/d\ \ln t\ [J(t) - \tau/\eta_N]_{t=\tau} \qquad (1.11)$$

Shama and Sherman (1970) use Schwarzal's second order approximation to calculate the retardation spectra of butter and margarine. The second order approximation has the advantage that the viscous flow term, η, does not have to be subtracted from J(t) before making the calculation and therefore does not have to be known accurately.

$$L(\tau) = dJ(t)/d\ln t - d^2J(t)/d(\ln t)^2\ {}_{t=2\tau}$$

or

$$L(\tau) = (d/d\ln t)[J(t) - dJ(t)/d\ln t]_{t=2\tau} \qquad (1.12)$$

1A.6.1.2. Stress Relaxation

Stress relaxation testing is frequently used to determine model components of a material. Stress relaxation is best described as the ability of a material to alleviate an imposed stress under conditions of a constant strain. Stress relaxation is usually modelled using a generalized Maxwell model comprised of a (finite) number of Maxwell units in parallel with each other.

Stress relaxation testing can be carried out in a number of different ways, for example, compression of agricultural products, stretching materials such as wheat dough and muscle fibre and cone-and-plate and co-axial cylinder viscometry for semi-solids and liquids.

1A.6.2. Dynamic Testing

Dynamic testing offers a very rapid technique causing minimal changes in chemical and physical properties. Dynamic testing methods vary stress or strain with time, usually in a sinusoidal manner.

Basic instrumentation for dynamic stress-strain testing requires a sinusoidal force provided by an electrodynamic vibrator. The specimen is held between the vibrator and a dynamic force transducer. Co-axial cylinder and cone and plate configurations such as the Ferranti-Shirley and Weissenberg Rheogoniometers have been used for semi-solid materials.

The extremely small strains imposed (less than 1%) almost assure linear stress/strain behaviour.

When a Hookean solid is subjected to a sinusoidally varying stress the strain also varies periodically in phase with the stress. Subjecting a Newtonian fluid to a periodically varying stress results in a strain 90° out of phase. A viscoelastic material, behaving in a linear fashion, which is subjected to a sinusoidally varying stress exhibits a strain response less than 90° out of phase (Fig. 1.7). If the stress is such that $\sigma = \sigma_o \sin \omega t$ the strain will vary with the same frequency but lag by an angle θ, the phase angle, ie, $\gamma = \gamma_o \sin (\omega t - \theta)$.

This behaviour results in a complex frequency dependent modulus, E^*, which can be separated into a real, in-phase component associated with the storage of energy and an imaginary, out-of-phase component associated with the loss of energy such that

$$E^* = E' + iE'' \qquad (1.13)$$

The ratio of stress to the amplitude of strain gives the value of the complex modulus.

$$E^* = \sigma_o/\gamma_o \qquad (1.14)$$

Therefore the storage modulus can be written as

$$E' = E^* \cos \theta \qquad (1.15)$$

and the loss modulus as

$$E'' = E^* \sin \theta \qquad (1.16)$$

Substituting Equations (1.15) and (1.16) into the eqation for strain

$$\sigma_o = \gamma_o [E' \sin \omega t + E'' \cos \omega t] \qquad (1.17)$$

is obtained. Equation (1.17) shows the decomposition of stress into two components, one in phase and one 90° out of phase.

At very high frequencies the storage modulus E' has a constant maximum value and materials exhibit an elastic, solid-like behaviour. At low frequencies materials exhibit a viscous type of behaviour as the storage modulus decreases.

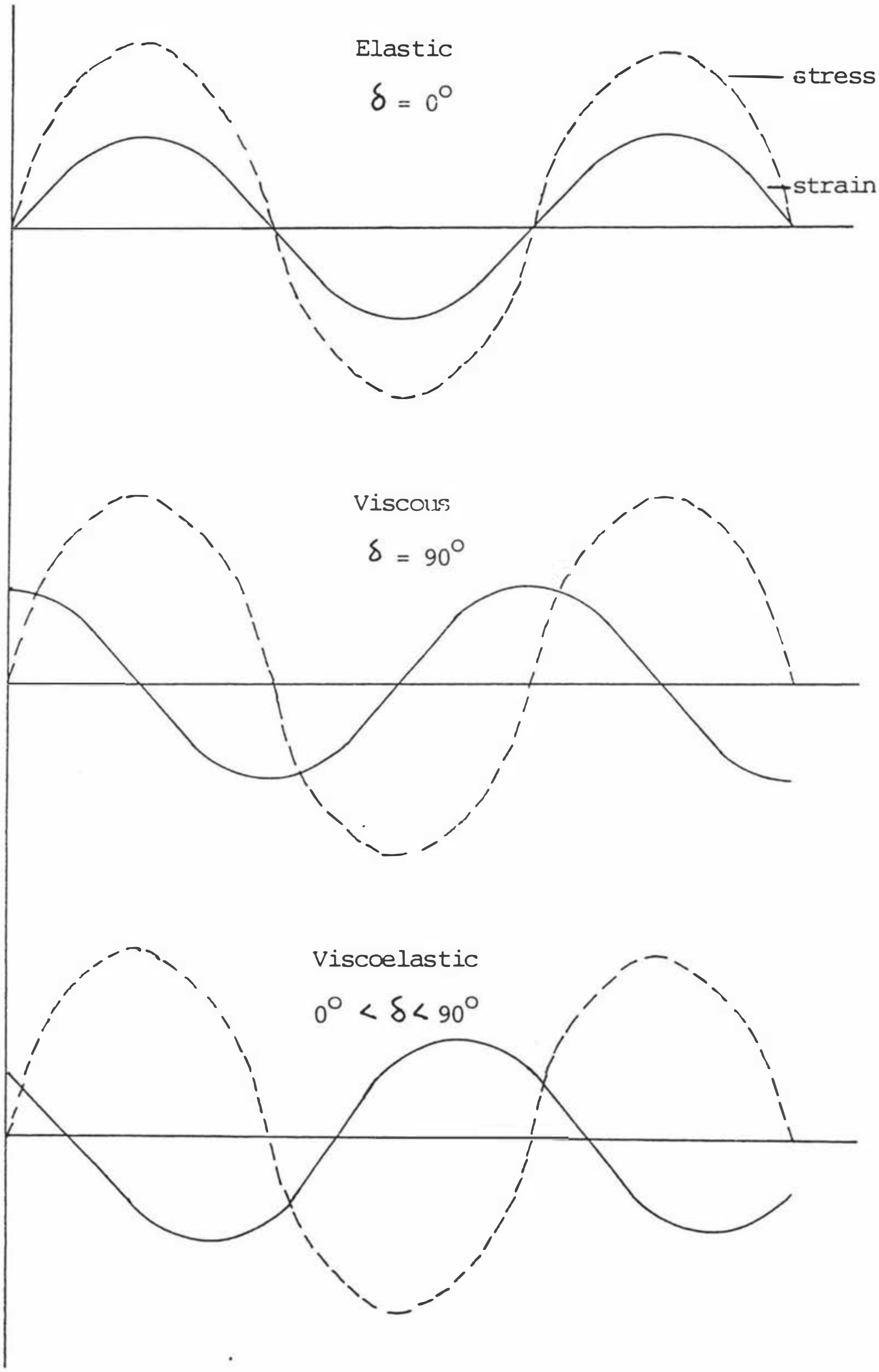


Figure 1.7: Stress response to sinusoidal strain.

The tangent of the phase angle (the loss tangent) is sometimes called the coefficient of internal friction.

In addition to the complex shear modulus, viscoelastic materials also have a complex viscosity η^*.

$$\eta^* = \eta' - \eta'' \tag{1.18}$$

where η' is the ratio of stress in phase with the rate of strain to strain and η'' is the ratio of stress out of phase with the rate of strain to strain (Sherman, 1986). The rate of strain in sinusoidal deformations is

$$d\gamma/dt = i\omega \exp (i\omega t) \tag{1.19}$$

therefore $\eta^*=E^*/i\omega$ and the two components of the complex viscosity are similarly related to the components of the complex shear modulus:

$$\eta'=E'/\omega \tag{1.20}$$

and

$$\eta''=E''/\omega \tag{1.21}$$

At low frequencies η' should approach steady state viscosity values η_o. At high frequencies G' values should approach G_o values from creep.

1A.7. EMPIRICAL TESTING

Empirical or semi-qualitative tests measure parameters that are not clearly defined. Empirical tests all tend to have specific applications in that they are usually initially developed for one product.

The majority of empirical tests involve large deformations. While such tests do not give any fundamental data, they may be more appropriate in that they mimic more closely actual conditions of usage, and often correlate well with sensory evaluations. Test conditions and apparatus also determine the magnitude of the parameter estimated. Often mechanical tests are devised to replace human sensory evaluation as a tool to appraise food texture. Empirical tests do not provide fundamental data.

PART B:MEASUREMENT OF THE RHEOLOGICAL PARAMETERS OF BUTTER AND MARGARINE

1B.1. INTRODUCTION

As mentioned above, the evaluation of the rheological properties of foods may be divided into two broad categories, fundamental testing and empirical testing. Fundamental testing measures well defined properties which, it is hoped, relate to the structure of the sample being investigated. Empirical testing is used to study textural properties which are not clearly defined. Many such techniques have been developed to study butter and other fat systems. Techniques to study both fundamental and textural properties of fats will be outlined below.

1B.2. FUNDAMENTAL TECHNIQUES

Although a number of techniques exist for evaluating fundamental rheological parameters very little work has been done on fat products. Of the three general methods of investigating fundamental parameters, creep, stress relaxation and dynamic testing, creep and dynamic testing have proved the more popular.

1B.2.1 Creep Compliance

Shama and Sherman (1968) used an automated parallel plate visco-elastometer to examine the creep compliance behaviour of margarine. Shama and Sherman analysed the creep compliance curves graphically using the method outlined by Sherman (1966) (Chapter 4, Section 6.1.1). On the basis of their results they modelled the rheological behaviour of margarine using a generalized Kelvin comprising of a Maxwell unit in series with four Kelvin units.

Shama and Sherman followed the hardening of margarine with age, observing changes in the rheological parameters. As margarine aged, viscosity term increased, indicating the margarine was growing more viscous. At the same time, the contribution of both the instantaneous and retarded elastic components decreased.

On calculating the retardation spectra, L(τ), where L(τ) is an approximation of the inverse Laplace transform of the creep function (Section A.6.1.1.3), for margarines of various ages they claimed evidence for the number of retardation mechanisms seen.

Later, Shama and Sherman (1970) used the same equipment to follow changes in viscoelastic behaviour with time after work softening margarine and butter. In contrast with the previous paper (1968) where the creep compliance response was observed for five hours, the creep compliance response of margarine after work softening was observed for 10 minutes only, due to the rapid rate margarine recovered its structure (set up) after work softening.

The behaviour of the margarine was modeled using a generalized Kelvin unit comprising a Maxwell unit in series with two Kelvin units compared with four Kelvin units used for the longer time experiments described in the 1968 paper. Also, due to the shortened observation time the viscous term obtained is not the true Newtonian viscosity, but more appropriately called the apparent viscosity.

Calculated rheological parameters for margarine are listed in both papers, and, while not directly comparable, are of the same order (Table 1.1). The viscosity term reported in the 1968 paper is ten times larger than the viscosity term reported in 1970. This is probably due to the differing durations of the two experiments. Apparent viscosity increase as the length of the experiment increases and the viscosity term approaches its true value.

The apparent viscosity term altered very little with reworking and recovered substantially after reworking. Shama and Sherman felt the apparent viscosity best characterised the consistency of margarine after working.

The results of observing the viscoelastic behaviour of butter over eight hour periods are also reported in the 1970 paper. The same number of parameters were used to characterise butter behaviour as were used for margarine after a ten minute experiment. As a result the viscous flow term will be closer to the true Newtonian flow term but the parameters for butter before and after working will not be comparable to the margarine results.

On working the elastic moduli decreased less than the viscous term and, on aging, butter consistency was felt to be characterised to a greater extent by the elastic terms.

The question arises, is it valid to compare the behaviour of butter and margarine, both before and after reworking on the basis of these experiments. The widely differing time lengths of the experiments make them very different. Short time creep experiments lead to a larger apparent viscous term and a correspondingly decreased retarded elastic contribution, while longer duration experiments give the exact opposite, a smaller

Table 1.1: Creep results reported by various workers.

Reference	Instrument	Sample	Model (a)	E_O Pa	ΣE Pa	η_N Pa.s	T ^oC	Time
Shama and Sherman, 1968.	Parallel plate	Margarine (35 days)	4 exp	$9.2\text{x}10^5$	$1.0\text{x}10^7$	$1.5\text{x}10^{10}$	15	4hr.
Shama and Sherman, 1970.	Parallel plate	Margarine	2 exp	$3.8\text{x}10^6$	$1.6\text{x}10^7$	$1.9\text{x}10^9$	10	10min
"	"	Butter	2 exp	$4.5\text{x}10^6$	$6.5\text{x}10^6$	$9.3\text{x}10^{10}$	10	8hr.
Davis, 1973.	Concentric cylinder	Lard	3 exp	$5.9\text{x}10^4$	$2.7\text{x}10^5$	$8.7\text{x}10^6$	25	15min
"	"	Shortening	3 exp	$2.1\text{x}10^4$	$1.4\text{x}10^5$	$3.4\text{x}10^6$	25	10-20m
"	Spherical indentor	Lard	3 exp	$3.5\text{x}10^4$	-	$1.2\text{x}10^8$	20	2-300m
"	"	Shortening	3 exp	$1.0\text{x}10^4$	-	$1.6\text{x}10^8$	20	2-300m
Gupta and DeMan, 1985.	Compression	Margarine	1 exp	$3.7\text{x}10^6$	$4.0\text{x}10^6$	$7.4\text{x}10^8$	10	10min
"	"	Butter	1 exp	$5.2\text{x}10^6$	$4.3\text{x}10^4$	$1.2\text{x}10^8$	10	10min

(a) The number of exponentials, referring to the number of retardation mechanisms fitted.

viscous term with retarded elastic components playing an increased part. The instantaneous elastic response is unaffected by experiment length. This trend can be seen in Shama and Sherman's results.

Retardation spectra were calculated, using a second order approximation of the Laplace transform which avoids the necessity of knowing η_N precisely (Section 1A.6.1.1.3). The retardation curves presented do not give any indication of the number of retardation mechanisms involved as they did previously in the 1968 paper.

On the basis of their creep compliance results Shama and Sherman conclude butter contains a smaller proportion of irreversibly breakable bonds as it recovers much of its original instantaneous elastic component after reworking. In contrast, margarine loses most of its instantaneous elastic response on reworking and does not recover it, indicating a far larger proportion of strong, irreversible bonds. This conclusion is unaffected by the length of the experiment as the instantaneous elastic response is not time dependent.

Davis (1973) reports the viscoelastic properties of pharmaceutical preparations have been widely studied using creep techniques. He goes on to comment on the fact few semi-solid foodstuffs have been subjected to detailed fundamental testing. In an attempt to assess available methods Davis carried out concentric cylinder and spherical indicator creep tests on lard and shortening.

Concentric cylinder tests were performed using a modified Weissenberg Rheogoniometer described by Warburton and Barry (1968). A stress was suddenly applied to the sample and maintained for a period of up to thirty minutes. The time dependent strain response was measured. Prior to testing a check for linear viscoelastic behaviour was made.

Davis observed the creep response for both lard and shortening at 25^{o}C. (Tables 1.1 and 1.2) The curves obtained were interpreted in the same way as Shama and Sherman, 1968 and 1970, ie., as classic visco-elastic curves, having an instantaneous elastic response, a number of retarded responses and eventually a region of viscous flow. The curves were analysed by the procedure described by Warburton and Barry (1968). This procedure is basically the same as the method used by Sherman (1966) and is described more fully in Chapter 4, Section 6.1.1. Three retarded elastic mechanisms were thought to be present.

Davis also experimented with creep by spherical indicator, where a sphere partially penetrates a semi-infinite sea of material (Barry and Warburton, 1968). Data in the form of penetration depths were curve fitted and analysed to give a continuous creep function. (Table 1.2).

The time scale of the indentation experiments was ten times as great as that employed for concentric cylinder testing. The indentation tests were also done at a lower temperature (20^{o}C). The same samples of lard and shortening previously used were employed in this test. Viscosity values obtained by indentation were much larger as a consequence of both the change in temperature and length of experiment, whereas instantaneous response values for the two methods were of the same magnitude (see Tables 1.1 and 1.2). The curves looked quite different, possibly as a result of differences in temperature and sample disturbance prior to testing. A disadvantage of concentric cylinder testing is the need to disturb samples during loading, in contrast with creep by spherical indicator, where sample disturbance is minimal.

Both concentric cylinder and spherical indicator tests should give approximately the same results. The difference between the two sets of results emphasizes the need to perform tests at the same temperature, for the same length of time and the

Table1.2: Results reported by Davis (1973) using a variety of rheological methods.

Method		Sample	
		Lard	Shortening
Ferranti-Shirley cone and plate Shear rate 1560/s 25^oC	Static yield value (Pa.)	$1.4x10^3$	$7.0x10^3$
	Dynamic yield value (Pa.)	$1.7x10^2$	$1.4x10^2$
	Plastic viscosity (Pa.s)	0.31	0.27
Concentric cylinder creep. Weissenberg Rheogoniometer. 25^oC.	G_o (pa.)	$5.9x10^4$	$2.1x10^4$
	η_o (Pa.s)	$8.7x10^6$	$4.3x10^7$
Creep by spherical indicator. 20^oC.	G_o (Pa)	$3.5x10^4$	$1.0x10^4$
	η_o (Pa.s) 200-300 min	$1.2x10^8$	$1.6x10^8$
	η_o (pa.s) 20-30 min	$3.0x10^7$	$5.1x10^7$
Dynamic visco-elastic testing. Parallel plate configuration, Weissenberg Rheogoniometer. 25^oC.	G' (Pa) 10 Hz	$6.0x10^4$	$1.6x10^4$
	η' (Pa.s) 2.5 x E-3 Hz	$3.2x10^4$	$1.9x10^4$

need to keep the sample in an undisturbed state, especially if a comparison is to be made between methods.

Davis also points out creep tests are limited at short times by inertial effects and the impossibility of applying instantaneous stress.

Using a simple creep analysis instrument, described by DeMan *et al* (1985), Gupta and DeMan (1985) looked at the effect working and the addition of surfactants and air had on the consistency of butter, paying special attention to changes in visco-elastic parameters.

Samples were subjected to a known compressive force and displacement was measured with a transducer. Provided compression remains very small calculating η_N from the gradient of the resultant curve is possible (Sherman, 1970).

Gupta and DeMan found a large decrease in all measured rheological parameters for butter after working. Elastic and viscous terms decreased by approximately the same amounts, in contrast with Shama and Sherman (1970), who found the viscous term reduced more than the elastic terms (Tables 1.1 and 1.3). Gupta and DeMan found all rheological parameters recovered to the same extent, once again in contrast with behaviour observed by Shama and Sherman, where the elastic terms recovered far more than the viscous terms (Table 1.3). The same changes in viscosity after working were seen by both groups of workers. Viscosity was decreased by the same extent and recovered to the same extent over similar periods of time.

Theoretically the work of Gupta and DeMan should be comparable to that of Shama and Sherman (1970). Both methods record creep compliance response under conditions of constant stress. DeMan uses an alternative method for obtaining a value for the retarded elastic term, preferring only one term to fitting one

Table 1.3: Comparison of the results reported by Shama and Sherman (1970) and Gupta and DeMan (1985).

	Shama & Sherman[a]	Gupta & DeMan[b]		Shama & Sherman[c]				Gupta & DeMan[b]	
Sample	Marg unworked	Marg unworked	Butter unworked	Butter 6 hrs	after 5 days	working 13 days	Butter 4hrs	after 7 days	working 14 days
E_o (Pa)	3.8×10^6	3.7×10^6	4.5×10^6	1.9×10^6	3.3×10^6	3.3×10^6	6.2×10^6	6.6×10^6	7.3×10^6
Er (Pa)	1.69×10^7	4.0×10^6	6.5×10^6	1.4×10^6	2.3×10^6	2.5×10^6	3.2×10^6	3.9×10^6	4.4×10^6
η_N (Pa.s)	1.9×10^9	7.4×10^8	9.3×10^{10}	1.8×10^{10}	2.5×10^{10}	3.5×10^{10}	6.4×10^8	8.7×10^8	8.5×10^8
Temp. (^oC)	10	10	10	10	10	10	5	5	5
time	10 min	10 min	8 hours	8 hours	8 hours	8 hours	10 min	10 min	10 min

(a) 1968
(b) 1985
(c) 1970

or more retardation mechanisms. His methods for calculating the instantaneous response and apparent viscosity are essentially the same.

Where experimental conditions are similar, for example, samples of margarine under constant stress for ten minutes at 10°C, differing sample composition prevents close comparison of the reported results (Table 1.3.).

No mention is made of whether or not linear viscoelastic responses were observed by DeMan *et. al.* (1985) for the stresses used (4.9 to 19.6N). From a simple plot of the instantaneous, retarded elastic and viscous response data presented for butter at 5°C, plotted against force (Fig. 1.8), it is apparent that forces greater then 14.7N produced non-linear behaviour. Viscous flow values should also be independent of the force or stress used. Viscosity parameters presented seem to be dependent on the force used.

No further indication is given of the forces used to obtain results. One can only assume some of the results presented are derived from non-linear creep responses. This results in a curvilinear relationship between stress and strain, with the creep compliance-time response being influenced by the stress. If this were the case, a different creep compliance-time curve would be generated for each stress used (Sherman, 1986). Non-linear responses cannot be analysed using the theory of viscoelasticity.

Questions of linearity aside, DeMan *et al* (1985) found evidence of an easily destroyed structural component (or components). On examining the creep compliance behaviour of butter and its recovery on the removal of stress, they found not all the instantaneous or retarded elastic strain was recovered, with the amount of strain recovered decreasing as loading times increased.

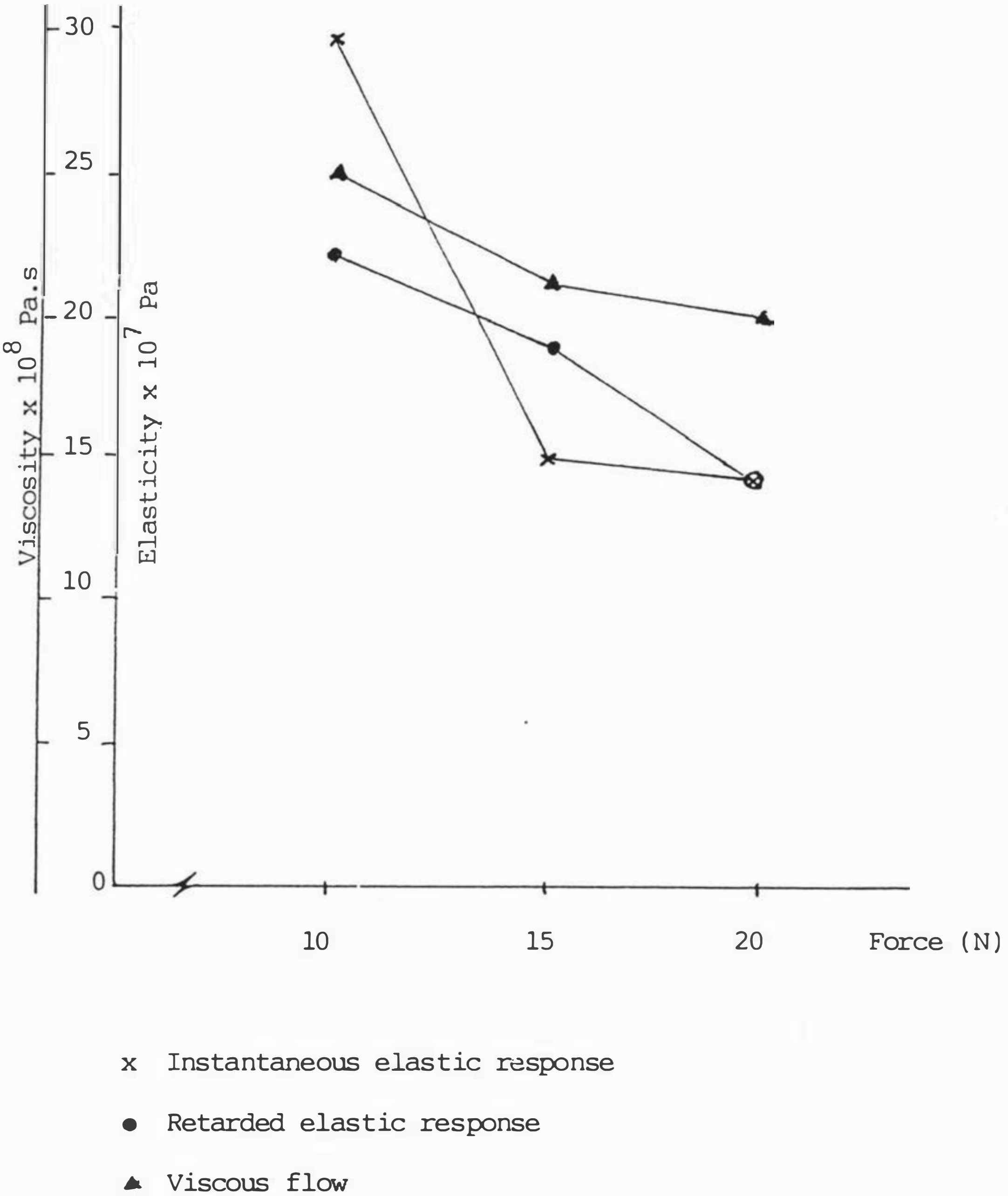


Figure 1.8: Creep parameters reported by Gupta and DeMan (1985) plotted against force used.

The creep results reported by the authors discussed here have been drawn together in Table 1.1. Owing to the diversity of samples, experiment duration and temperature very few comparisons can be made. However, the method cannot be dismissed lightly. Davis (1973) concludes creep testing offers the greatest possibilities for future testing.

1B.2.2. Continuous Shear

An alternative method of obtaining fundamental data involves the use of continuous shear. Various cone and plate configurations have been utilised for this purpose. In general, cone and plate instruments comprise a small angle cone capable of rotation and a stationary lower plate. Alternatively, the cone may be stationary while the lower plate rotates.

Parkinson *et al* (1970) used a cone and plate configuration of a Weissenberg Rheogoniometer to obtain continuous shear measurements, or rheograms, for extracted butter crystals. Testing was done at 25^{o}C.

They derived an equation which could be used in predicting the spreadability characteristics of butter and margarine. Using the equation viscosities can be calculated for high rates of shear if the viscosity of liquid fat and the mean water droplet size is known.

While the equation takes the presence of structural elements such as water droplets and liquid fat into account, the existence of any three dimensional crystal network is ignored. The initial extraction of fat crystals would have destroyed such a network. A second point of practical consideration is the test temperature. 25^{o}C is much higher than the temperatures at which the spreadability of butter is a problem.

Elliot and Ganz (1971) also used a cone and plate configuration of a Weissenberg Rheogoniometer for continuous shear measurements of butter and margarine at 'room temperature'. Describing observed behaviour as initially elastic, followed by structure breakdown and flow, with a rapid then slower recovery on the removal of stress, they proposed a modified Bingham body to model the results they observed (Fig. 1.9). The modified Bingham body differs in that two yield stresses are present in the friction element. One, σ_{or}, is the yield stress required to move the slider, but once sliding a lower stress, σ_{os}, is all that is needed to continue sliding.

Vocadlo and Young (1969), using a cone and plate Weissenberg Rheogoniometer examined the flow properties of butter, margarine and lard. On obtaining traces similar in appearance to those of Elliot and Ganz they commented on time dependent rheological characteristics being very complex and further complicated by sample slip during testing. Flow behaviour was thought to be visco-plastic, ie, have a yield term and a viscous component, and a visco-plastic model with the following equation was fitted:

$$\sigma = (\sigma_o{}^{1/n} + KG)^n$$

where σ = shear stress, σ_o = yield stress. G = shear rate and K and n = rheological parameters. When n = 1, K = viscosity, and the equation becomes that of the Bingham plastic.

Both experimental results and theoretical parameters indicated flow behaviour could not be described by a Bingham model as $n \neq 1$, (in direct contrast to Elliot and Ganz) and that a yield stress is applicable at low shear rates. Once again experiments were done at high temperatures, from 21 - 30°C.

Davis (1973) used a Ferranti-Shirley cone and plate viscometer to study samples of lard and shortening. He reports good

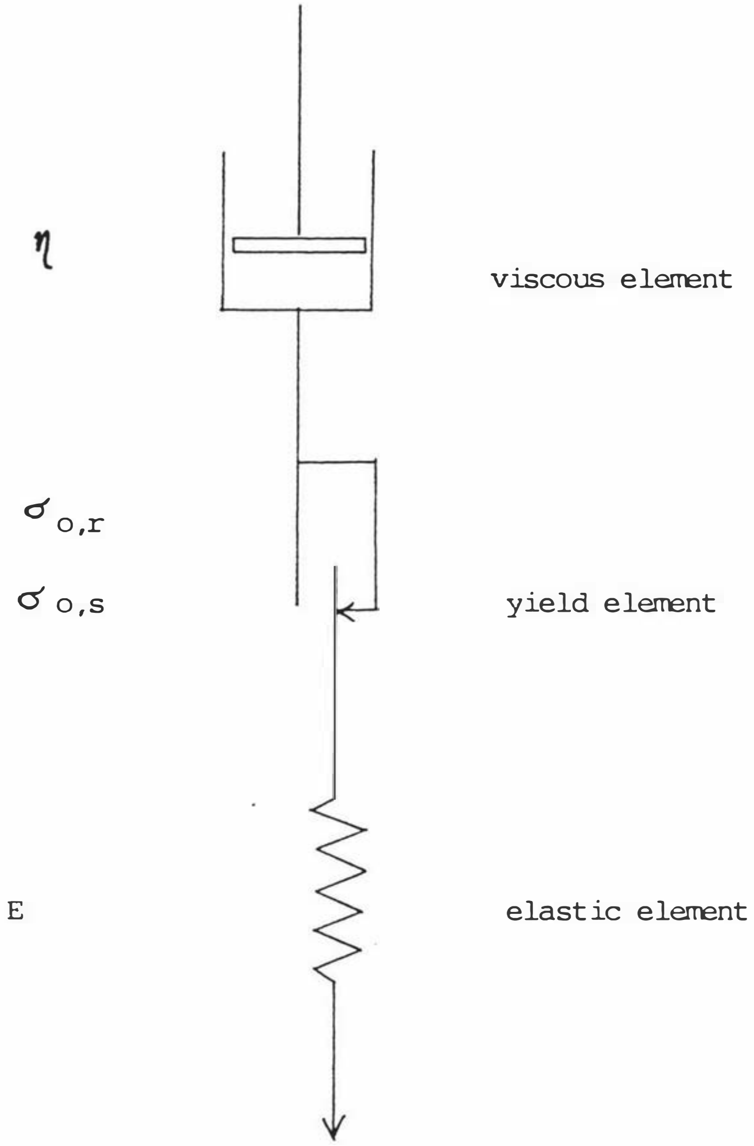


Figure 1.9: The modified Bingham body (Elliot and Ganz, 1971).

agreement between results obtained by the Ferranti-Shirley and results from a Haake-Rotovisko cone and plate attachment. Conscious of the possibilities of work softening during loading, samples were disturbed as little as possible. Testing was done at 25°C, and complex rheograms were obtained which were difficult to interpret. Davis does not propose any model other than to say typical viscoelastic behaviour is being exhibited.

Davis also comments on whether or not cone and plate shear testing is suitable for products such as fats. He expresses doubts as to the suitability of cone and plate testing due to the possibility of shear fracture and loss of material from between the cone and plate surfaces. Cone and plate testing does not seem very suitable or useful for firmer semi-solids. For a fat to be suitable for examination by cone and plate techniques it has to have a high percentage of liquid fat present. Fats such as milkfat consequently have to be at high temperatures for testing. Further, owing to the small sample size and inevitable sample disturbance on loading, it is unlikely any structural elements such as a network of fat crystals will be left intact.

1B.2.3. Dynamic Testing

Dynamic or oscillatory testing methods can also be used to investigate the fundamental rheological properties of foods. Although the method seems well suited for use on fat systems little work seems to have been done to investigate viscoelastic properties using oscillatory techniques. The theory and basic instrumentation used in dynamic testing are discussed more fully in Part A, Section 6.2.

Deiner and Heldman (1968) used an oscillating cantilever beam of butter in an attempt to investigate small strain behaviour of butter. They proposed a viscous-Maxwell-Bingham model based on their results and attempted to relate mechanical elements of the model to butter structure based on a description by

King (1964) (Fig. 1.10). They assume that stress will relax to zero if given sufficient time. From the oscillation data (not presented) the storage modulus and loss tangent were calculated. Increasing frequency caused both the storage modulus and loss tangent to increase, while increasing temperature only affected the storage modulus. No attempt is made to relate results back to the structural model presented.

Elliot and Ganz (1971) also performed dynamic tests on butter and margarine using a cone and plate configuration of a Weissenberg Rheogoniometer at 'room temperature'. The stress response wave reported was square, not sinusoidal, at strain amplitudes greater than ± 0.66. This response was in accordance with the modified Bingham model proposed above. Changes in strain direction caused an abrupt change in stress to a value similar to before but of opposite sign, causing the stress response wave to become square. In terms of the model, the displacement between these essentially constant stress levels is equal to twice the yield stress at rest.

Elliot and Green (1972) calculated the response of the modified Bingham body, proposed by Elliot and Ganz (1971), in terms of model parameters. The model should enable experimental results to be interpreted in terms of physical parameters such as viscosities and elastic moduli. They conclude generally, saying a correlation between results and subjective texture notes should make it possible to relate texture to measurable rheological properties.

Davis (1973) examined lard and shortening using parallel plates on a Weissenberg Rheogoniometer. Linear response was checked by increasing strain amplitude and monitoring the phase angle and the amplitude ratio between the stress and strain curves. When the phase angle and the amplitude ratio became dependent on strain amplitude a linear response was no longer seen. Tests were carried out at 25°C.

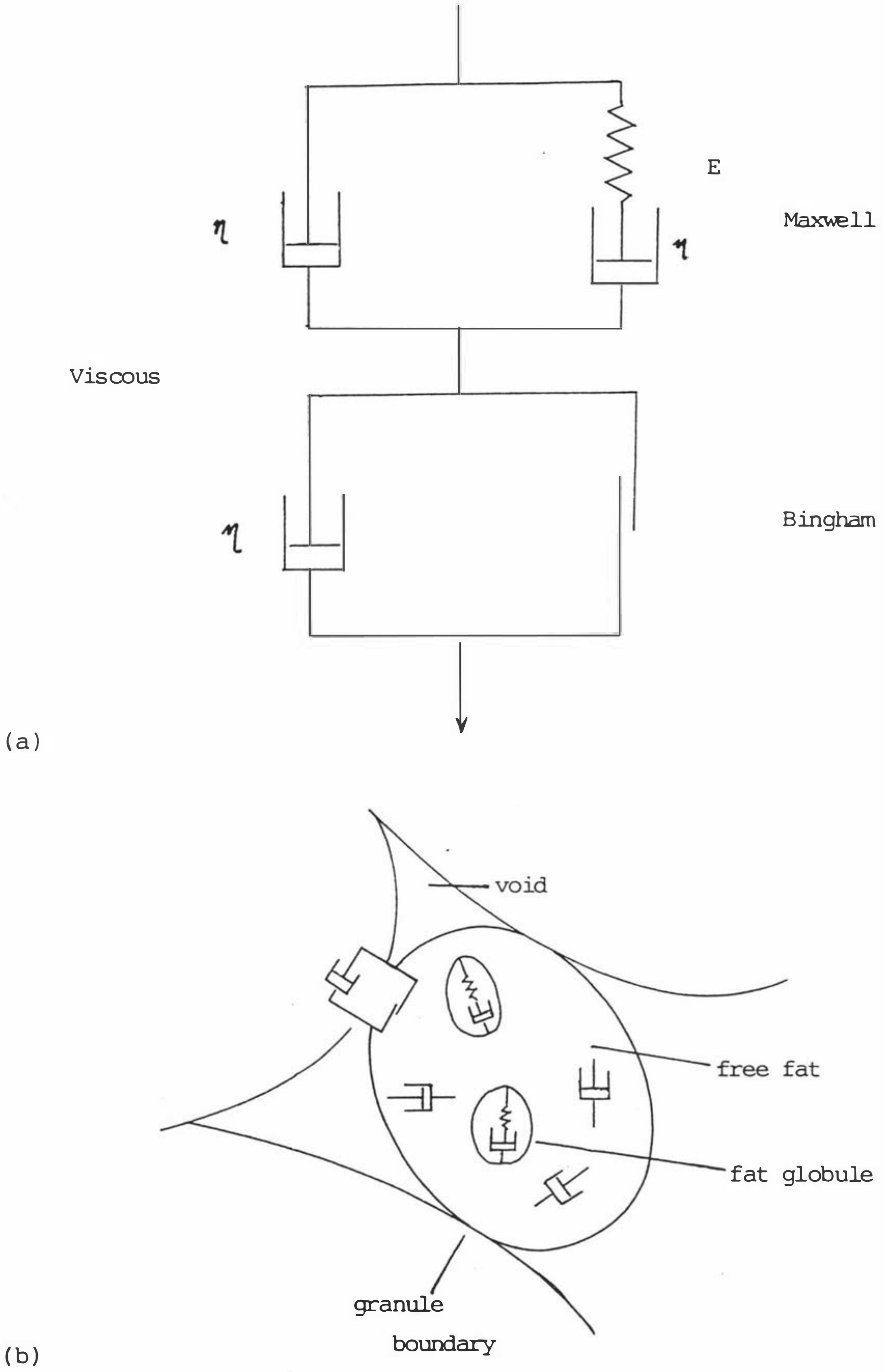


Figure 1.10: a) The Viscous-Maxwell-Bingham model (Deiner and Heldman, 1968).

b) Structural application of the model.

Samples were subjected to a variable input strain and the output response stress was measured. Both lard and shortening showed the same type of response but calculated viscoelastic parameters differed. From the similar shapes of the response curves Davis concluded the two samples had similar viscoelastic properties, possibly because the three dimensional structure is composed of components with similar frequency responses. At high shear the G′ and the G_o values from creep showed reasonable agreement (Table 1.2). At low frequencies η' values should approach the steady state η_N values obtained from creep testing (Table 1.2). This was not observed at the lowest frequency used, 2.5×10^{-3} Hertz. Davis found the calculated viscoelastic parameters obtained by oscillatory testing clearly differentiated between his two samples.

Davis feels such dynamic tests may be very useful in supplementing creep data at short times to provide more information. One drawback is the need to disturb samples during loading.

Bistany and Kokini (1983) compared the viscosity functions of four foods including a tub margarine. The viscosities were obtained by steady shear and small amplitude dynamic measurements. The experiments were carried out at 25-26°C using a cone and plate geometry. Care was taken to minimise the effect of work softening during loading. In all cases the dynamic viscosity function was larger than the steady state viscosity function. This was said to be due to structure breakdown occurring before the steady state viscosity was reached, whilst the strain in dynamic measurements is so small there is no appreciable change in the sample material. Viscometric functions of foods and corresponding linear viscoelastic results do not seem to be simply related, in contrast to classical theory.

1B.3. EMPIRICAL AND IMITATIVE TESTING

1B3.1. Sectility Testing

Sectility testing involves cutting a sample with a wire using either a constant force or a constant cutting speed.

Knoop (1972) outlines the history of sectility testing, suggesting the first workers to try this were W. Mohr and F. Oldenburg in 1933. Using a constant force they measured the time taken to cut a sample of butter in half.

Dolby (1941) devised a simple apparatus with which the resistance of a sample of butter to cutting by a wire moving at a constant rate could be measured. Dolby found the method gave reproducible results, taking the resistance measured as being an indication of the firmness of the butter.

Prentice (1972) reports Mohr et al (1951) developed a more sophisticated tester in which the wire was driven through samples at a constant speed and the counterthrust was measured.

The FIRA-NIRD extrusion apparatus (Prentice, 1954) was modified by Wood and Dolby (1965) to measure sectility. The results were found to be more reproducible than those obtained by the extrusion method.

Dolby (1941) found the flow properties of butter were similar to those of a power law fluid and not a Bingham plastic; under the smallest loads flow would occur. The maximum cutting speed used by Dolby was 0.007 mm/s.

Rebinder and Semenenko (1949) (cited by Hayakawa *et al*, 1986) used a higher rate of wire movement to obtain a value like the Bingham viscosity and a lower velocity to approximate an apparent yield stress, with force measured correlating well with spreadability.

Knoop (1972) described the plot of force vs cutting velocity as characteristic of a Bingham plastic. Knoop claims a linear relationship between velocity and force exists above a limiting velocity of 3 mm/s and that the Bingham flow limit reflects the essential property to be measured; a concept supported by Mulder and Walstra (1974). This contrasts with Dolby's (1941) suggestion butter acts more as a power law fluid. Cutting velocities used by Knoop far exceeded those used by Dolby.

Dixon and Williams (1977) looked at sectility testing using a range of cutting velocities from 0.45 mm/s - 9 mm/s to ascertain whether butter acted as a Bingham plastic or as a power law fluid. He found butter showed an exponential relationship between cutting velocity and cutting force, with excellent correlations for semilog and power law relationships, in contrast with the Bingham plastic model.

Using cutting speeds ranging from 0.33 mm/s to 10 mm/s, Mortensen and Danmark (1982) also found butter did not behave as a Bingham plastic. A good correlation between yield stress and spreadability was observed, possibly indicating the behaviour of butter is better described by a power law with a yield term. They also found a close correlation between the extrapolated yield stress based on sectility measurements at various speeds and results obtained by cone and disc penetrometer and constant speed sectility testing, indicating results obtained by the different methods are estimates of the same consistency parameter (yield stress). Sectility was felt to be more accurate in butters with a firmer consistency.

Whether or not the behaviour of butter tested by sectility is best described as that of a Bingham plastic or a power law fluid seems to depend on the speed at which the sample is cut. Knoop (1972), using high speeds, thought butter behaved as a Bingham plastic. He is supported in this view by Rebinder and Semenenko (1949). However, work done by Rebinder and Semenenko at lower cutting speeds, like that of Dixon (1977) and Mortensen and Danmark (1982), point to a power law with yield stress model as being more appropriate. This agrees with the suggestion of Dolby (1941), that butter behaves similarly to a power law fluid.

Some criticisms of sectility have been made. Prentice (1972) points out if there is any tendency in a butter towards a laminar structure, resistance to cutting will be less in the direction parallel to the laminations. Dixon (1974) compared five methods of testing butter and expressed the opinion that as sample preparation was elaborate, sectility would rank low as a preferred method. However, the method was not used routinely.

In sectility's favour, Sherman (1970) reports on comparisons between penetrometry, sectility and extrusion showing sectility to correlate better with spreadability and firmness than penetrometry. Knoop (1972) favoured sectility testing for its precision.

1B.3.2 Extrusion

Extrusion testing of butter involves measuring the force required to extrude a plug of butter through an orifice. The force measured can be used as an index of spreadability.

Prentice (1954) describes an instrument for this purpose, produced commercially as the FIRA-NIRD extruder. The force required by the FIRA-NIRD to extrude a sample declines as extrusion progresses. The friction of the sample against the extruder walls decreases proportionally to the amount of sample in the extruder. At the point of emptying the closest approximation of the force needed to maintain extrusion can be ascertained.

Two empirical parameters can be calculated; the minimum thrust at the moment of emptying, which can be used as a measure of resistance to extrusion, and secondly, the friction element, giving an indication of properties such as 'stickiness'.

Prentice reports a good correlation between the perceived spreadability of butter, as determined by a trained panel, and the force required for extrusion. Reproducibility was thought to be good, with confidence levels of ± 0.23 kg at the 5% significance level. Much of the variance in instrument readings was said to be due to variability of samples. The small amount of work done during extrusion was thought to be insignificant and obscured by the lack of homogeneity in the butter.

Naudet and Sambac (1959), cited by Sherman (1970) also found a good correlation between FIRA-NIRD extrusion results and spreadability for margarine, with sectility less highly correlated.

In contrast, Knoop (1972) argues against extrusion. He points out it is not very reproducible, and the fall off in force observed towards the end of measurement is partly from a change in the viscosity of the sample as a result of structural change and partly a result of sample softening as a great part of the mechanical work is changed to frictional heat, and not just due to declining frictional effects.

Taylor *et al* (1971) mention extrusion gave results which were not as reproducible for butter as those obtained using sectility hardness testing. This is probably due to sectility being more suited to samples with a firmer consistency (Mortensen and Danmark (1982)).

Dixon (1974) found good temperature control was necessary to prevent samples warming during extrusion. He found extrusion measured similar properties to the disc penetrometer but that these were not highly related to such properties as shear strength and plasticity.

Vasic and DeMan (1968) examined conventional churn butter and butter manufactured in a manner similar to margarine. They found work softening occurred during extrusion and that a direct relationship existed between hardness and extrusion pressure for the same type of butter. However, even though butters manufactured by different methods, possibly having different crystal structures, have the same hardnesses they may require different extrusion pressures. Vasic and DeMan thought the determination of the work of extrusion was useful for comparing plastic fats with the same hardness but possibly different crystal structures for this reason.

Kawanari *et al* (1982) describe an extrusion viscometer in which the sample is forced through a capillary tube to determine flow characteristics. Both the Casson equation and power law fitted the data well. However, the flow equation derived did not correlate well with spreadability or texture notes. This is at variance with results reported for instruments such as the FIRA-NIRD extruder, for example, Prentice (1954). The differences between correlation with spreadability for the two extrusion methods could be accounted for as the difference in forces needed to move butter through an orifice (FIRA-NIRD) and through a small diameter tube.

1B.3.3. Compression

Compression is the study of butter behaviour under a load, usually applied along the vertical axis of the sample.

Davis (1937) loaded a cylindrical sample of butter axially at 16 - 17^{o}C. Using a basic rheometer (made out of Meccano) and a 100g load, load/deformation curves were generated. The deformation was found to be non-linear and a slow but incomplete recovery was observed when the load was removed. From data obtained Davis calculated viscosity and moduli of elasticity for various butters. He defined to ratio of viscosity to elastic modulus as 'springiness'.

Using similar techniques Scott Blair (1938) and Dolby (1941) attempted to express the firmness of butter as a viscosity. Scott Blair pointed out the values obtained were highly dependent on the conditions of the experiment and valid only for those particular conditions. Both Scott Blair and Dolby found the crumbling of samples under compression a problem. Dolby felt this was due to some samples having a laminated structure. Dolby found the reproducibility poor for the same reason. As results from compression were directly correlated with sectility hardness results Dolby concluded the two tests measured the same property of butter.

Prentice (1972), commenting on the above results, points out the calculation of any viscosity or elasticity term from such data is spurious as there is no way of knowing what proportion of energy is being stored (elastic) or dissipated (viscous) at any particular instant. Prentice also comments that the Burgers model, a four component rheological model (Section A.5) which has been proposed to approximate the viscoelastic behaviour of samples compressed and then allowed to relax, does not predict behaviour on subsequent loading, nor does it allow for a yield value, real or apparent.

Dixon (1966) developed a triaxial compression tester where a cylindrical sample is confined by a constant lateral stress and subjected to an increasing major principle stress. At each confining stress the principle stress is increased until equal to the shear strength of the butter and the sample collapses. Dixon described the behaviour of butter under these conditions in terms of apparent plasticity, apparent elasticity and total strain. Two parameters were derived from the stress/strain relationship; shear strength as a measure of firmness and plasticity, and percentage deformation at maximum shear stress.

Later, Dixon (1974) compares compression testing with a number of other empirical tests. Compression testing was found to be less precise than other methods such as cone penetrometry.

1B.3.4. Penetrometry

Penetrometry was developed for measuring the firmness or yield point of semi-solid foods. A cone, needle, sphere etc. is allowed to come down either under the force of gravity or at a constant rate. As it contacts the material being tested penetration depth or, if penetration is occurring at a constant rate, the force necessary to penetrate the sample is measured.

1B.3.4.1. Disc Penetrometry.

Kruisheer *et al* (1938) measured the force necessary to push a circular block 4cm^2 cross sectional area into a sample of butter at a constant velocity. Kruisheer suggests the value obtained was slightly in excess of the yield value. Results from the instrument correlated well with the texture assessments of professional Dutch graders. The Kruisheer den Herder penetrometer was manufactured commercially and received official acceptance in Holland.

DeMan and Wood (1958) used a modified Kruisheer den Herder penetrometer, commenting that it was not suited to hardness measurements at low temperatures. Wood and Dolby (1965), using the apparatus described by DeMan and Wood, also comment on the instrument performing unsatisfactorily at temperatures below 12.5^{o}C, with samples cleaving as the force applied exceeded 5 kg. Conversly, Mortensen and Danmark (1982) found the Kruisheer den Herder penetrometer to be most accurate for taking measurements in soft butters

1B.3.4.2. Cone penetrometry.

Cone penetrometry uses a cone shaped probe instead of a disc. This is probably the most common type of instrument presently in use to assess the rheological properties of butter

(O'Conner *et al* (1983)). Various standard cones are in use, for example, a 20^{o} angle cone is the present standard of the American Oil Chemists Society (AOCS, 1960). In normal operation the depth of penetration is measured, with cone angle, dropping assembly mass, sample temperature and penetration time remaining constant.

Penetrometry values are not linearly related to hardness or softness due to cone shape. This makes it impossible to compare data obtained by using cone assemblies of different mass. There have been a series of proposals to overcome this problem, several investigators suggesting converting readings to yield values.

The International Dairy Federation (Walstra (1979)) proposed the following relationship:

$$AYS = gW/\pi \tan^2(\alpha/2)p^2$$

where AYS = apparent yield stress, g = acceleration due to gravity, W = weight of cone assembly, α = the cone angle and p = the penetration depth.

Hayakawa *et al* (1986) suggest all attempts can be related to one general equation:

$$H = CW/p^n$$

where H = hardness or yield value, C = a constant depending on cone geometry, W = weight of cone assembly, p = penetration depth and n is an exponent. This equation can be simplified to

$$H = W/p^n$$

for the AOCS cone (AOCS, 1960). The problem of the value of the exponent remains, Hayakawa and DeMan (1982) proposed a value of one.

The principle of cone penetrometry has been used by many workers. Haighton (1959) used a constant weight cone penetrometer to obtain yield values for margarines and other fat products. Table margarines with yield values between 200-1000 g/cm^2 (2x10^5 - 1x10^6 dyne/cm^2) were thought to be 'usable'. Temperature was not specified.

Tanaka *et al* (1971) used a constant speed cone penetrometer to measure textural properties. Using force/penetration data, apparent viscosity and yield values were calculated. Assuming butter exhibited visco-plastic behaviour, they proposed a Kelvin unit as a mechanical model. Yield values agreed quite closely with those obtained using the constant weight penetrometer. For example, yield values of the order of 5x10^5 dyne/cm^2 were obtained for margarine using constant speed penetrometry. These are in good agreement with yield values obtained by Haighton (1959) using constant mass pentrometry. Apparent viscosity at 10^{o}C was of the order of 4.6 x 10^6 poise, a number which appears rather unrealistic when compared with a Newtonian material of similar viscosity, e.g. bitumen.

Kawanari *et al* (1982) found the yield value obtained by cone penetrometry useful for predicting spreadability and firmness. Equipment cost and convenience were also found to favour the use of penetrometry as a routine quality control test.

Mortensen and Danmark (1982) examined cone and disc penetrometry and sectility as methods of evaluating consistency. They found all three methods measured the same consistency parameter, the yield stress. Comparison of the three methods found cone penetrometry to be the least accurate, especially for firm butters. A comprehensive survey of New Zealand butters also confirms this finding for harder butters (McLennan and MacGibbon, 1987). McLennan and MacGibbon also found a very poor correlation between cone penetrometry and sectility hardness results (r = 0.18).

Many variations on the general theme of penetrometry have been reported. One such example is a sliding pin consistometer (Davey and Jones (1985)) which measures average force resisting a cylindrical cutting pin moving through a prescribed path. The force measured correlates well with perceived hardness. Ease of use, minimal sample preparation and portability are features of the method and of penetrometry in general.

Another variation is thermopenetrometry (DeMan *et al*, 1984). The temperature of a sample is raised from 5 to 25^{O}C while an AOCS specification cone rests on the sample continuously. The penetration of the cone into the sample with changing temperature is continuously recorded by a linear displacement transducer.

1B.3.5. Spreadability Simulation

Spreadability simulations imitate the actual use of butter by mechanical or instrumental means in an attempt to determine the factors involved the spreading of fats.

Mohr and Hassing (1949) described an apparatus which scraped a layer 2mm thick from a sample of butter with a knife held at 90^{O} to the surface and moving across it at a constant velocity. At temperatures below 15^{O}C the instrument gave reasonable reproducibility and good differentiation between samples. Results were almost linearly related to measurements made by sectility.

Later, Huebner and Thomsen (1957) repeated this work with the knife blade inclined at 45^{O} to the surface. Defining the characteristics measured with this instrument as spreadability and those measured by sectility as hardness they concluded from the close correspondence between the two tests that hardness was the principle factor affecting spreadability.

Kokini and Dickie (1981) suddenly imposed a constant shear rate on samples of butter and margarine at 25°C using a cone and plate apparatus. They showed transient stresses in butter played an important role in the assessment of spreadability. The use of the Bird-Leider model was proposed for predicting shear stress development in foods. The model can be used to provide a crude prediction of spreadability in foods with strong transient shear stresses.

The model proposed by Kokini and Dickie was further developed by Mason *et al* (1982) to give better prediction of the growth of transient shear stresses at the inception of steady shear flow.

PART C: BUTTER AND MARGARINE

1C.1. INTRODUCTION

In order to gain a better understanding of the way in which fat systems such as butter and margarine respond to rheological testing method of manufacture, fat composition, structure and other factors must be considered. An introduction to those factors considered most relevant is given below.

1C.2. BUTTER

1C.2.1. Manufacture

Four basic steps are required to convert cream into butter: a), the crystallization of milkfat, b), the concentration of milkfat, c), phase inversion and d), the dispersion of moisture. In New Zealand the continuous Fritz process is normally used to make butter.

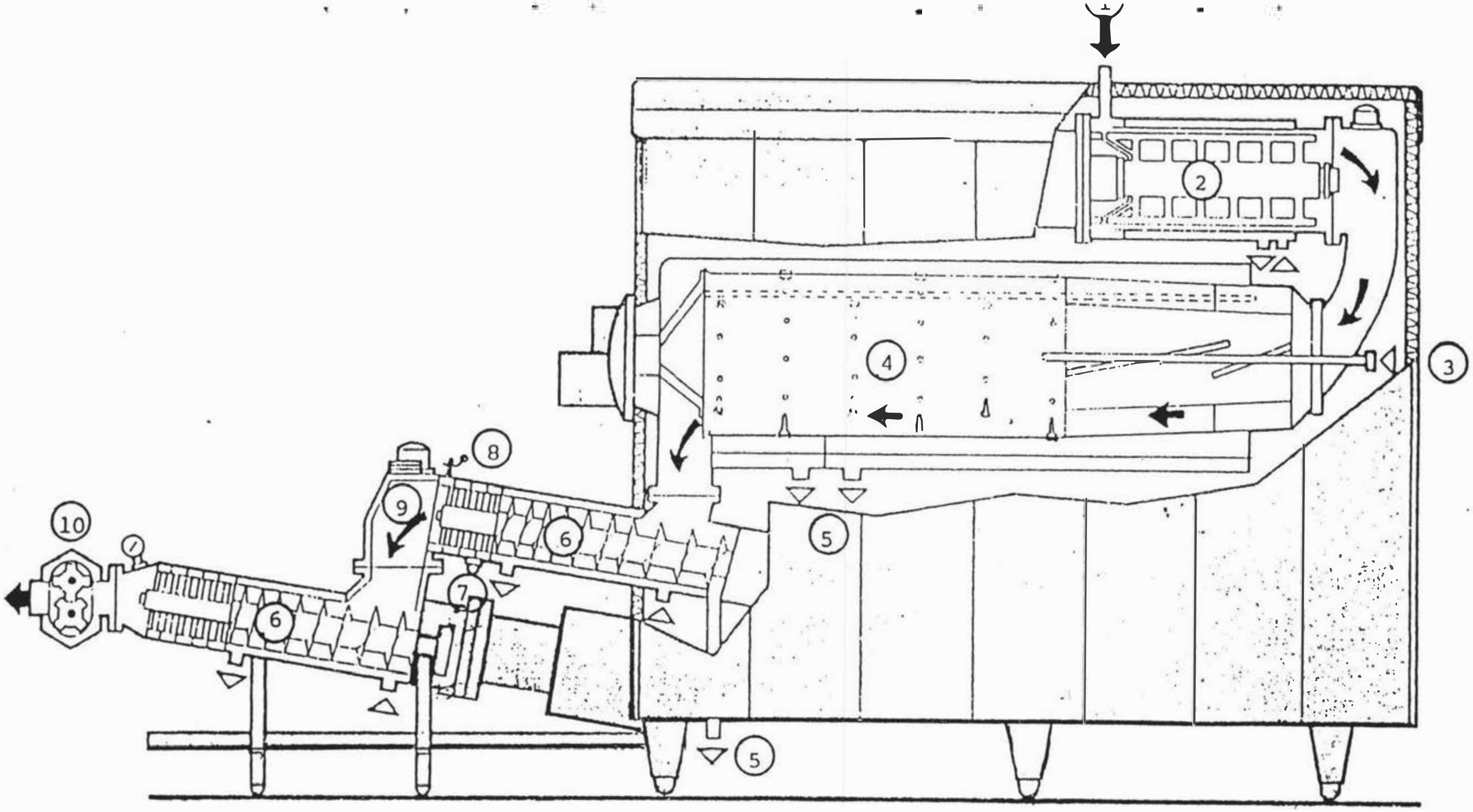
In this process the milkfat is crystallized by holding the cream at low temperatures in silos overnight. Phase inversion occurs during the churning of the cream and the concentration occurs in the draining off of the buttermilk. The moisture is finely 'dispersed' in the fat phase by shearing or working as the butter is forced through a series of spaghetti plates.

Cream to be made into Fritz butter is pasteurized on reception at the factory. Pasteurization is usually done in a high temperature, short time vacuum pasteurizer or Vacreator, which is effective in the removal of undesirable odours and taints. After pasteurization a variety of cream tempering treatments may be used. An example is slow cooling, where the cream is cooled to slightly above churning temperature and left to cool to churning temperature overnight.

All continuous buttermaking machines comprise the following basic elements: a), a primary churning section b), a separating section to separate butter granules and buttermilk and c), a working section designed to distribute moisture, salt etc. evenly throughout the butter. A schematic diagram of a continuous buttermaking machine, the Pasilac HCT, is given in Figure 1.11.

The machine has a four bladed beater driven normally between 1000-2000 rpm in the primary churn. Cream enters the primary churn on a tangent from the side and has to pass around a distributor to the beater blades. Buttermilk and granules flow through a closed chute to the horizontal separating section.

The separating section is a cylinder revolving between 15 and 20 rpm driven by an electric motor and expanding pulley. The buttermilk and granules are moved by paddles to the draining section, which is a perforated cylinder lined with fine stainless steel gauze. The buttermilk is drained off into a tray and then to a balance tank to be pumped away. The granules are washed with a fine spray of chilled water before dropping into the first working compartment of the working section.



1. Cream inlet
2. Churning section water cooled
3. Chilled buttermilk 'wash'
4. Separation section
5. Buttermilk drains
6. Texturising sections water cooled
7. Injection point
8. Throttle gate
9. Vacuum section
10. Butter pump

Figure 1.11: The Pasilac HCT 2 continuos buttermaker.

This compartment has a pair of auger screws which force the granules through four orifice plates, each followed by a four bladed beater. This system shears or works the butter. The diameter of the orifices in each plate controls the degree of working. Salt slurry is injected in between the second and third plates through two fine tubes from the top of the working section. Following salting the butter emerges as 'spaghetti' into the second working compartment where it is moved along by screws and forced through a second series of orifice plates each followed by a four bladed beater. The butter emerges as a well worked mass and is packed.

1C.2.2. Structure

Butter consists of liquid fat, crystalline (solid) fat, intact fat globules, globule fragments, water droplets and air cells. Butter has a continuous liquid fat phase in which these particles are dispersed.

During churning some of the original milkfat globules are damaged, liquid fat may be lost from globules, some globules are completely disrupted and many globules clump and coalesce. Subsequently, working destroys more globules releasing the fat contained within. The proportion of intact globules in butter is only 5 - 20%. Different pasteurization techniques can affect this proportion, plate pasteurization gives about 20% intact globules whereas vacreation gives less than 5%.

The crystalline fat released from the fat globules is a major component of the disperse phase. The fat crystals can flocculate together. They attract each other by van-der-Waals forces and, as repulsive forces are absent, the crystals form a lasting network (Tempel, 1961). Touching crystals can slowly grow together by further crystallization, giving rise to a strong, solid network. It is probable the strong bonds do not easily reform when broken, whereas formation of the van-der-Waals type bonds is completely reversible, with bonds forming in a short time (Haighton, 1965). The presence of a crystal network formed and maintained by a mixture of reversible and irreversible bonds adequately explains the phenomenon of (i), setting, the increasing firmness after manufacture, (ii), the effect of work softening and (iii), the increase in hardness after work softening (see below).

Solid fat remaining inside globules also forms limited crystal networks. However, the presence of fat globules and water droplets has the effect of decreasing firmness, possibly by physically preventing flocculation and limiting the extent of the crystal network.

Butter also has the remnants of a continuous water phase consisting of buttermilk droplets, globule membranes and possibly some protein. Experimental observations such as the diffusion of salt into butter and the rate of water evaporation from butter support the presence of an (almost) continuous water phase (Mulder and Walstra, 1974). The continuous aqueous phase represents only a minor portion of the moisture in butter and may only be present in localized patches. The majority of the water will be present as discrete droplets. Legal requirements restrict the amount of moisture to 16% by weight.

1C.2.3. Factors Affecting Rheological Properties

1C.2.3.1. Components of the Disperse and Continuous Phases

The most important rheological characteristics of butter are hardness and ease of spreadability. Mulder and Walstra (1974) state that generally the rheological properties of a dispersion such as butter depend on the size, shape and volume of the disperse phase and the viscosity of the continuous phase.

The viscosity of the continuous phase (liquid fat) is unlikely to alter butter consistency as the viscosity of the liquid phase is low and that of butter as a whole is about 10^6 times larger (Mulder and Walstra, 1974).

The presence of water droplets may influence the rheological properties of butter. However, because the amount of water present is so consistent (15.6 ± 0.2%) variations in hardness are not considered to be due to water droplets. Non-traditional products with deliberately high water contents, lowfat spreads for example, will have altered textures and rheological responses.

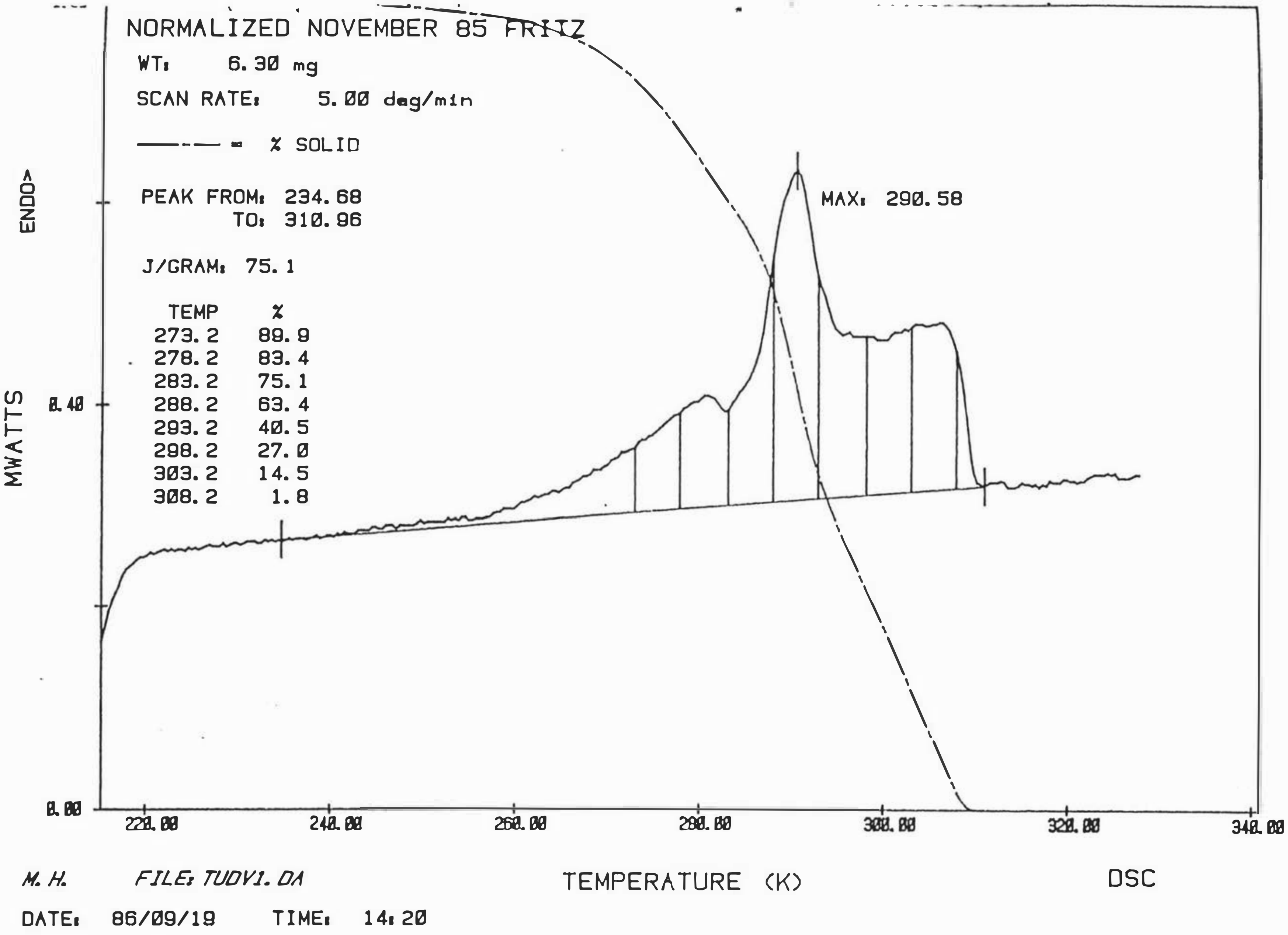
The proportion of fat crystals (solid fat) and the type of crystal network markedly affects the final hardness of butter.

The solid fat content is affected by temperature, milkfat composition, and thermal treatment of cream. The extent and type of crystal network is influenced by the amount of non-globular fat and the setting process.

The shape and size of the fat crystals would also be expected to have an effect on hardness. However, in normal butters the difference in crystal sizes are small (Mulder and Walstra, 1974).

1C.2.3.2. Butter Temperature

The temperature at which butter is held profoundly affects factors such as hardness and ease of spreading. The fat crystals in butter melt over an extremely wide range, from -40 to +35°C, with most melting between 0 and 35°C. This is well illustrated by a differential scanning calorimetry melting thermogram (Fig. 1.12) of milkfat extracted from butter. It can be seen that the solid/liquid fat ratio changes very quickly as temperature increases from 5-20°C. It is this change in the solid/liquid fat ratio which alters the rheological response of butter as temperature increases, ie. as temperature increases butter becomes softer and easier to spread.



TEMP	%
273.2	89.9
278.2	83.4
283.2	75.1
288.2	63.4
293.2	40.5
298.2	27.0
303.2	14.5
308.2	1.8

Figure 1.12: Differential scanning calorimetry melting thermogram of a Fritz butter.

1C.2.3.3. Milkfat Composition

The fatty acid composition of the triglycerides of butter markedly affects the amount of crystalline fat at a given temperature. Many factors can affect the fatty acid composition of milkfat triglycerides. Among these are season, feed, state of lactation, genetic variation, age, milking interval and health and nutritional status of the cow.

In New Zealand there is a marked seasonal variation in fatty acid composition (Gray, 1973). This produces changes in solid fat which in turn affects butter hardness. This is illustrated by typical solid fat and sectility hardness values for spring butter at 10°C of 48 - 56% and 1530 - 1870g respectively and for summer butter at 10°C of 56 - 62% and 1870 - 2250g respectively (MacGibbon and McLennan, 1987). Other workers, eg. Knightsbridge and Black (1978) and Cullinane *et al* (1984) have found similar seasonal trends for Australian and Irish butters respectively.

MacGibbon and McLennan (1987) found that by no means all the variation in butter hardness could be explained by the solid fat content. Mulder and Walstra (1974) state factors other than solid fat content can influence the firmness of butter by often as much as a factor of two.

Fatty acid composition can be deliberately manipulated. Cows can be fed supplements containing protected lipids. This results in increased levels of unsaturated fatty acids, leading to a softer product. Such products may be spreadable at refrigerator temperatures (Taylor and Norris, 1977). Alternatively, low melting milkfat fractions can be used to manufacture a softer product, for example, the 'Soft Butter' mentioned by Taylor and Norris, 1977.

1C.2.3.4. Cream Treatment

The treatment of cream prior to churning plays an important role in determining the final consistency of butter.

Rapid cream cooling to, and holding at churning temperature results in the formation of small, mixed crystals containing lower melting triglycerides (Vasic and DeMan, 1965). Butter made from such rapid or shock cooled cream gives a harder butter with a higher solid fat content. An alternative cream cooling regime is the 'Alnarp' or 'Swedish' method which employs an initial rapid cooling to low temperature which initiates crystallization, followed by tempering at 17.5 - 21^{O}C. Prior to churning the cream is cooled to churning temperature. This procedure allows recrystallization of the higher melting triglycerides, resulting in fewer mixed crystals, a lower solid fat content and a softer butter (Erickson, 1985).

The 'Alnarp' method is thought to result in a thicker, stronger layer of crystal fat building up within the fat globule. This would lead to more globules surviving churning intact and fewer fat crystals in the continuous phase which would reduce the hardness of the butter. Alternatively, shock cooling fat is thought to result in the formation of free fat crystals forming throughout the fat globule. (Precht and Peters, 1981a, 1981b)

Cream tempering can be used to give either a softer product, eg. in summer in New Zealand, when the solid fat content is high; or to give a firmer product, eg. in the early New Zealand spring when the butter tends to be soft.

The type of pasteurization can also affect butter consistency. Butter made from cream which has been Vacreated sets at a faster rate and reaches a greater final hardness than butter made from cream which has been plate pasteurized (Taylor *et al*, 1973). This is probably due to the smaller proportion of intact fat globules in butter made from Vacreated cream (see above). Consequently, in butter made from Vacreated cream there are more fat crystals in the liquid fat and hence the setting rate is faster.

1C.2.3.5. Manufacturing Variables

The manufacturing process determines the structure of the butter. The range over which machine variables can be altered is limited in practice because of requirements to meet specification. Cream flow to the churning section and beater speed are important variables, primarily affecting fat losses in the buttermilk and moisture content (Bloore *et al*, 1985). The flow of chilled water through the jackets of the working section and the auger speed affect the effectiveness of working, which in turn influences moisture distribution and hardness. However, the effect on hardness is minor.

1C.2.3.6. Product Handling

The handling of the finished product also affects consistency. The hardness of butter continues to increase for several days after manufacture. This phenomenon is called setting. Butter sets rapidly initially, reaching perhaps 70% of its final hardness in five hours, but the rate decreases, approaching a final value asymptotically, attaining 95% of its final hardness after 30 days.

Setting is thought not to be caused by further fat crystallization (DeMan and Wood, 1958), but rather by the formation of a crystalline network held together by van-der-Waals forces. Once crystals are in close contact they can also grow together. Setting has been described as similar to a reversible, isothermal, sol-gel transformation, involving changes in the spatial arrangements of particles (DeMan and Wood, 1958). The disperse particles are thought to form a scaffold type structure.

Processing conditions can affect the setting rate of butter. Butter made from Vacreated cream set approximately twice as quickly as that made from plate pasteurized cream. Taylor *et* *al* (1973) thought this was due to vacreation reducing the stability of the fat globules. This would increase the number of fat globules broken up during churning, leading to an increase in the number of small fat crystals in the continuous phase and consequently an increase in the rate of setting.

Butter made from rapid or shock cooled cream sets faster than butter made from slow cooled cream which sets faster than butter made from 'Alnarp' treated cream. These butters all have different hardnesses. It is assumed harder butters have higher solid fat contents and therefore have more fat crystals to take part in the setting process.

Temperature also affects setting rates. Butter sets more quickly at higher temperatures, possibly because the smaller fat crystals have greater mobility in the increased volume of liquid fat. Setting ceases altogether at temperatures below -20°C (DeMan and Wood, 1958) but resumes once the temperature is increased.

The temperatures to which butter is exposed after setting is complete can also alter hardness. Increases in temperatures beyond those reached during manufacture will result in fat crystals melting, and recrystallization occurring on any subsequent cooling will generally have the effect of increasing hardness. This is demonstrated by Taylor and Jebson (1974), who cause the hardness of 'Alnarp' butter to increase by temperature cycling.

1C.2.3.7. Reworking

Mechanical working after manufacture (reworking) has the effect of permanently lowering the hardness of butter. This is known as work softening. Reworking can be carried out on a continuous reworker similar to a continuous buttermaking machine (Section 1C.2.1), except the churning and separating sections are replaced with a shiving section. The shiving section contains rotating knives which reduce butter blocks to small pieces. The pieces are then conveyed to the working section.

Reduction in hardness depends on the extent of setting prior to reworking and also on the hardness of the original butter (Taylor *et al*, 1971).

Reworking is thought to break down the fat crystal network by disrupting the forces holding the network together. The network can be easily reestablished by the formation of new, van-der-Waals forces between crystals, thus leading to an increase in hardness after reworking. However, only a portion of the original hardness is recovered. The breakdown of other types of 'bonds' has been proposed to account for the permanent reduction in hardness seen. These 'primary bonds' are thought to be stronger, and once broken, very slow to, or unable to reform (Haighton, 1965). The breaking and failure of these strong bonds to reform could account for the permanent decreases in hardness observed.

1C.3. MARGARINE

1C.3.1 Manufacture

In general, margarines are manufactured from a fat blend of liquid oil and hydrogenated fat, and an aqueous phase which may or may not contain milk, salt, emulsifiers, preservatives, etc. A wide range of formulations are used in the manufacture of margarine. Both fats used, and processing parameters can be tailored to suit desired specifications.

The basic process of margarine manufacture can be broken into four or five operations; emulsification, cooling, working, holding and/or packaging.

The initial emulsion may be formed in a batch or continuous process. In a continuous process the oil and aqueous phase ingredients can either be metered into a line feed or simply mixed in line. On mixing the two phases form an oil-in-water emulsion. Emulsifiers are added to reduce the surface tension between the phases, helping the emulsion form with minimal work. Emulsifiers also stabilize the finished product, preventing the aqueous phase from leaking or coalescing.

Once the emulsion is formed it is cooled in a series of scraped surfaced heat exchangers. In a scraped surface heat exchanger the product passes through the annulus between a rotating shaft and an outer insulated jacket containing a refrigerant. Blades attached to the mutator shaft scrape the inner jacket wall continuously to achieve maximum cooling. Shaft speeds range from 300 - 700 rpm, scraping the surface clean as many as 1500 times per minute. The high internal pressures and shearing forces generated by the blades cause rapid crystal nucleation and further emulsification. Figure 1.13 illustrates diagrammatically a scraped surface heat exchanger.

Margarine is only partially crystallized during cooling, in many processes further crystallization takes place in a 'working unit'. A common working unit is the pinworker which has pins arranged in a helical pattern on a variable speed shaft which intermesh with stationary pins positioned on the cylinder wall. Product passing through the pinworker is then worked by the pins, causing rapid crystallization to occur.

If a stiffer consistency is required for packaging, the product may be allowed to rest, and partially set, in some sort of holding tube before being packaged. The holding or resting tube is a jacketed cylinder that may contain baffles or perforated plates to keep the product from setting up on the walls.

A typical equipment configuration for the continuous manufacture of table margarine is shown in Figure 1.14. The emulsion is formed, cooled in the scraped surface heat

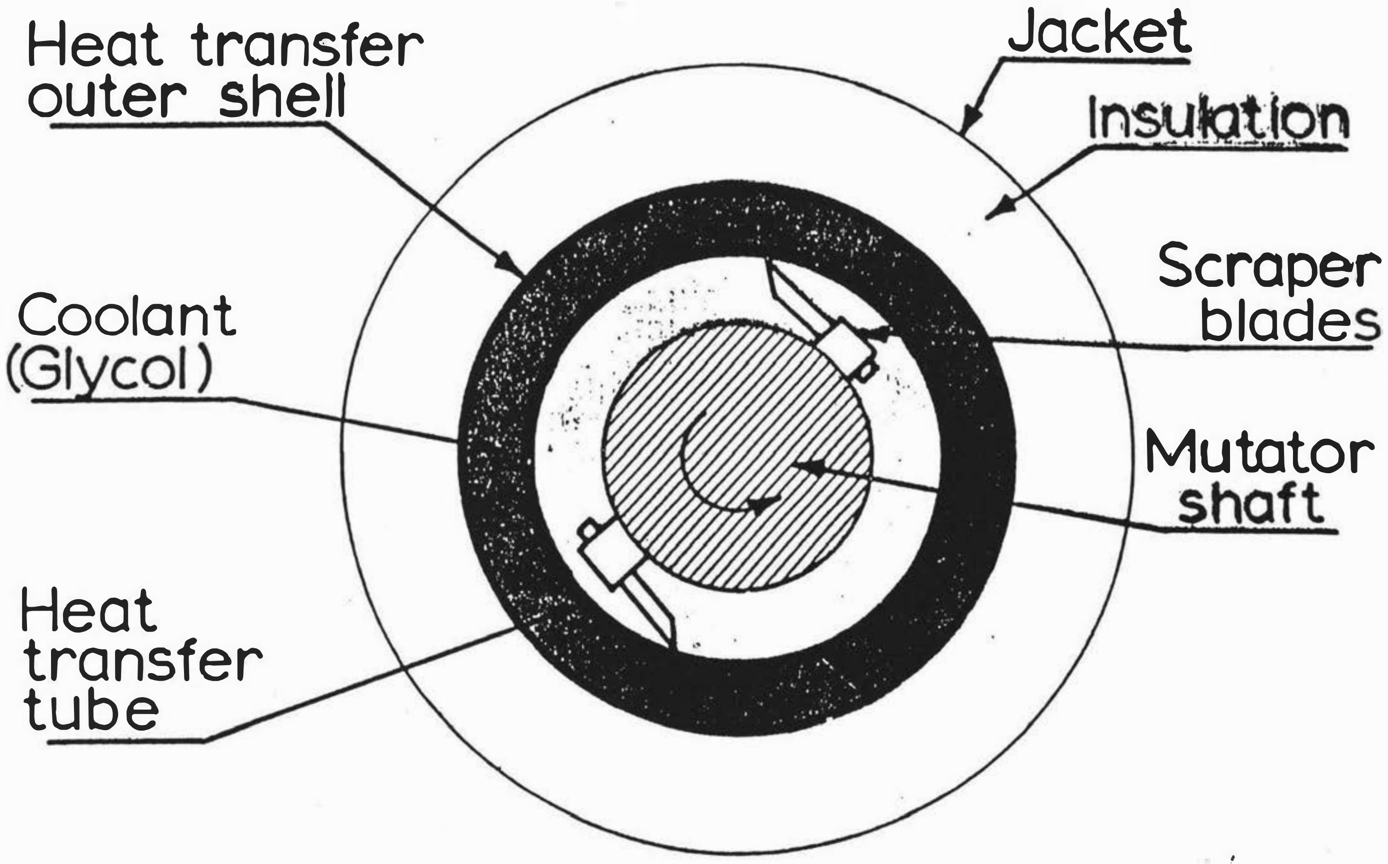


Figure 1.13: Diagram of a section through a scraped surface heat exchanger.

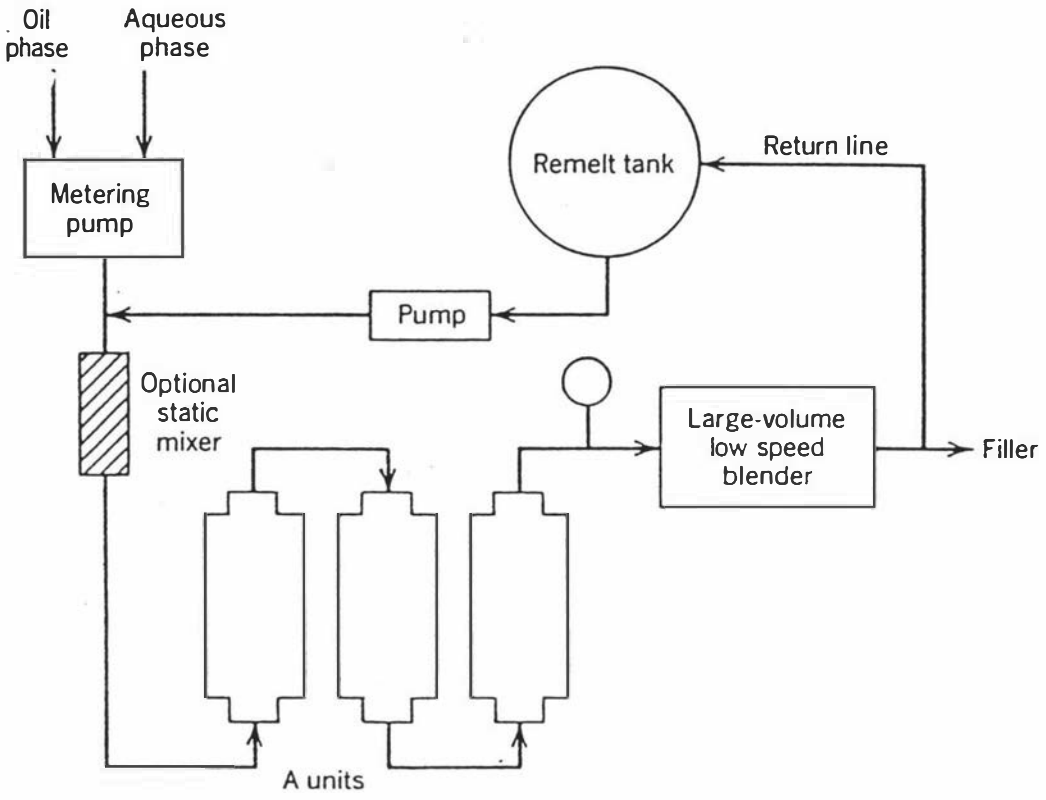


Figure 1.14: Continuous soft margarine production (Erikson, 1985).

exchangers, then worked, in this case, in a large blender. As the product must be quite fluid to fill packaging containers, there are no holding tubes.

In a closed system such as is illustrated, some overfeeding must be present to maintain sufficient product to the filler. The remelt line allows excess product to be returned to a tank where it is remelted and pumped back into the product stream to be reprocessed.

The manufacture of margarine differs markedly compared to traditional butter manufacturing. While the raw materials of butter are limited to milkfat alone, margarine can, and does, have a wide range of formulations. The formulations can be varied to make products for specific end uses, for example, pastry margarines and soft table margarines. Formulations can also be varied to take into the changing cost of ingredients.

The margarine manufacturing process is also more flexible than that of traditional buttermaking. The two manufacturing processes differ fundamentally in the way in which water-in-oil emulsions are formed. In buttermaking a phase inversion from oil-in-water to water-in-oil occurs during churning, whereas the emulsion is formed in margarine manufacturing by simply mixing the two phases together.

1C.3.2. Structure

Margarine is a water-in-oil emulsion consisting of liquid fat, crystalline (solid) fat and water droplets. The fat crystals and water droplets are dispersed in the continuous liquid fat phase, with the water droplets being kept separate by the fat crystals.

Crystalline fat is the major component of the disperse phase. The fat crystals can vary in size and shape, from 0.1 µm - 30 µm needles and platelets to 100 µm diameter spherulites. As with butter, the fat crystals also form a three dimensional network held together by van-der-Waals forces, or else show a tendency to form tiny clusters (Haighton, 1976). Crystals in direct contact with other crystals in the network may grow together to form stronger bonds, thus reinforcing the network. Margarines in which crystal networks form tend to be harder than those in which networks do not occur (Haighton, 1976).

Shama and Sherman (1970) considered the crystalline fat in margarine to have fewer van-der-Waals reversible type 'bonds' and more irreversible 'strong bonds' than butter.

Other fat systems are thought to form three dimensional networks similar to butter and margarine, for example, lard and shortenings. Nederveen (1963) found suspensions of fat particles in oil had strong mutual attractions and felt some sort of crystal structure was formed.

The structure of butter and margarines have similarities and differences. Both fat products have, as their major structural component, crystalline fat which can form three dimensional networks, with liquid fat intermeshed between the fat crystals. Both products contain water in the form of water droplets. In addition, butter has the remnants of a continuous water phase, which is absent in margarine. Butter also contains intact fat globules and globule fragments, which are not found in margarine.

1C.3.3. Factors Affecting Rheology

A comparison of the factors affecting the consistency of margarine and butter reveals the amount of solid fat, and the way the solid (crystalline) fat can form networks is equally important for both products. Similarly, it is found the continuous liquid fat phase and the presence of water droplets does not influence the consistency of margarine or butter to any great extent.

1C.3.3.1 Temperature

As with butter, the rheological characteristics of margarine change with temperature. In contrast to butter, the solid/liquid fat ratio does not change rapidly in the 5-20°C range. Figure 1.15 shows a differential scanning calorimetry melting thermogram of a poly-unsaturated margarine. Two major melting peaks at -27°C and -10°C can be seen, with relatively little melting occurring after 5°C.

A comparison of the differential scanning calorimetry melting curves for margarine (Fig. 1.15) and butter (Fig. 1.12), shows 60 - 70% of the solid fat in margarine has melted by 5°C, while most of the solid fat in butter melts between 5 and 20°C. This illustrates changing temperature has little effect on margarine, in direct contrast with butter. As temperatures increase over 20°C the solid fat contents of both products become similar. The two figures also show graphically the difference in fat composition of the two products.

1C.3.3.2. Fat Composition

The consistency of margarines and shortenings depends heavily on solid fat content of the products and hence the oils and fats used in manufacturing. Marked variations in fat content are therefore possible for margarine products, unlike butter. Examples of this are pastry margarines, with high solid fat contents and poly-unsaturated table margarines, which have low solid fat content at temperatures above 5°C.

Poly-unsaturated margarines are much softer than butters, with sectility hardness values of about 110g at 10°C, compared with 900g for the softest spring butters. Above 20°C the hardness of both products tends to be the same, due to similar solid fat levels.

1.3.3.3. Manufacturing Variables

Margarine and shortenings are much more susceptible than butter to changing process conditions. The rate and extent of

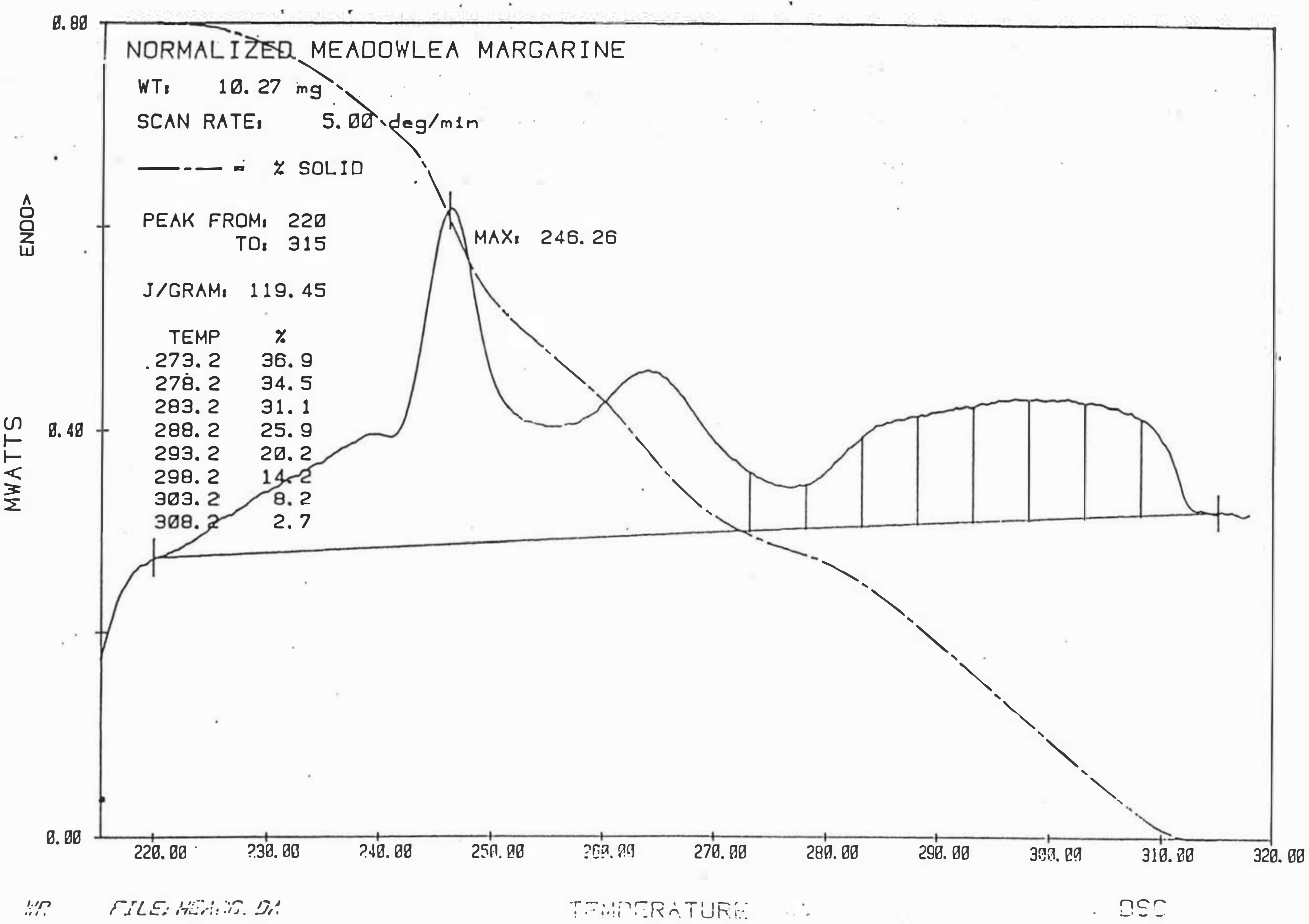


Figure 1.15: Differential scanning calorimetry melting thermogram of a table margarine.

cooling can be controlled by changing scraped surface heat exchanger variables. The number of scraped surface heat exchangers used can be varied, usually two or three. Rate and extent of cooling can be controlled by the rate of product throughput and shaft speed.

Controlling cooling in the scraped surface heat exchangers and thus crystal nucleation and crystallization can affect solid fat content and hardness. For example, rapid cooling would lead to a large number of small crystals and a harder product. Different cooling regimes can be used to imitate such processes as 'Alnarp' cooling, with the effect of lowering the hardness of a product.

A choice of whether or not to work a product after cooling exists. Working units can be placed between or after scraped surface heat exchangers, or in both positions. A choice of type of worker is also possible, for example, pinworker or blender.

Working produces a product with a more plastic body, compared to unworked products. This is probably achieved by a), increased fat crystallization, preventing to some extent further crystallization after packing, which would contribute to a harder, more brittle product and b), breaking crystal - crystal bonds and disrupting any van-der-Waals bonds which may have already formed as part of a crystal network.

Another option available in margarine manufacture is recycling. Some of the product leaving the scraped surface heat exchangers is mixed back into the emulsion before it enters the scraped surface heat exchangers. This is a form of precrystallization which helps achieve earlier crystallization and enlargement of higher melting glycerides (Erickson, 1985) leading to a greater distribution of crystal sizes and improved consistency.

1C.3.3.4. Reworking

Margarines and shortenings can be reworked in the same fashion as butter, with the same results, a permanent reduction in hardness. This can be explained in the same way as for butter (Section 1C.2.3.7).

In general, margarines seem to show a greater permanent reduction in hardness, than butter. This is perhaps due to margarine having a greater number of 'strong' bonds than butter, which are not reformed after reworking (Shama and Sherman, 1970).

1C.3.3.5. Polymorphism

Crystal size and form also influence consistency. Fats exhibit polymorphism, the ability to crystallize in more than one form, one of which is stable for a given set of conditions. Long chain hydrocarbon compounds like triglycerides can pack together in a number of different ways which are almost energetically equivalent (Norris, 1977). In the case of triglycerides, three main polymorphic forms exist, α, β and β', each with a different melting point.

Fats with fatty acid chains of varying lengths are more stable in the β' form, while fats in which chain lengths show little variation are stable in the β form. The β' form, consisting of a very fine network of crystals is desirable in margarine as it is capable of immobilizing large amounts of liquid oil and aqueous phase droplets. In some cases if a margarine oil has strong β tendencies, even though produced in the β' form, it may transform to the β crystalline state. This is accompanied by a change in texture (to coarse and sandy) and consistency with the development of large crystals.

1C.4. AMMIX BUTTER

1C.4.1 Manufacture

A new commercial buttermaking process, termed the Ammix process, has recently been introduced in New Zealand. The process utilizes technology developed for the manufacture of margarine. In the Ammix process the four basic steps in converting cream to butter, crystallization, concentration, phase inversion and moisture dispersion, are carried out in a different order, compared to Fritz butter.

The 'concentration' occurs in a separator in the AMF plant, where a 75% fat cream is produced. The phase inversion occurs in the homogenizer in the AMF plant. Crystallization and the dispersion of moisture occur in the scraped surface heat exchangers and pinworkers.

In the process, anhydrous milkfat (AMF) is produced from fresh pasteurized cream in a Westfalia direct-from-cream plant without neutralization of free fatty acids. The crude AMF is Vacreated to remove any tainting substances and residual moisture and then held in a silo at a temperature of 40°C until required.

Cream for blending is Vacreated, cooled to 8°C and held in a silo. Cream is used as the principle source of moisture and non-fat milk solids in order to ensure the presence of some unbroken fat globules in the butter. Unbroken globules are thought to improve flavour and texture.

A mixture with the same composition as butter is formed by continuous blending of AMF, cream, and salt slurry (if required). The temperature of the cream is raised to 40°C *en route* to blending.

The blend is passed through two scraped surface heat exchangers where it is shock cooled, with crystallization being initiated. The cooled product is then worked in a pin worker, where further crystallization takes place. The product then passes through two further scraped surface heat exchangers and a second pinworker. The butter may be packed in bulk at this stage, or held in a holding or resting tube to allow it to set partially and become firm enough to be patted. Figure 1.16 illustrates the equipment configuration described. A remelt line, as for margarine, is also included.

From the above description of the Ammix process it can be seen to be very similar to the margarine manufacturing process. As with the margarine process, the Ammix process has greater flexibility than traditional buttermaking processes. A variety of products can be produced on an Ammix plant. For example, milkfat/oil blends such as the product made by Taylor and Norris (1977) which consisted of 80% milkfat and 20% oil.

1C.4.2 Structure

Ammix butter consists of liquid fat, solid (crystalline) fat and water droplets. Intact fat globules and globule fragments are also present, but in smaller numbers than in traditional butter.

As with traditional butter and margarine, solid fat forms the major structural component. A network of fat crystals, initially held together by van-der-Waals forces is formed, with stronger bonds forming later.

Other methods similar to the Ammix process have been developed. Perhaps the most discussed is the Cherry-Burrell 'Gold-n-Flow' method. Vasic and DeMan (1968) feel the structure of Cherry-Burrell butter is similar to that of margarine. Cherry-Burrell butter is usually much firmer than butter made by traditional methods.

Kawanari *et al* (1982) felt butter manufactured by the Cherry-Burrell method to be stronger and less spreadable than that made by traditional methods. However, further working of

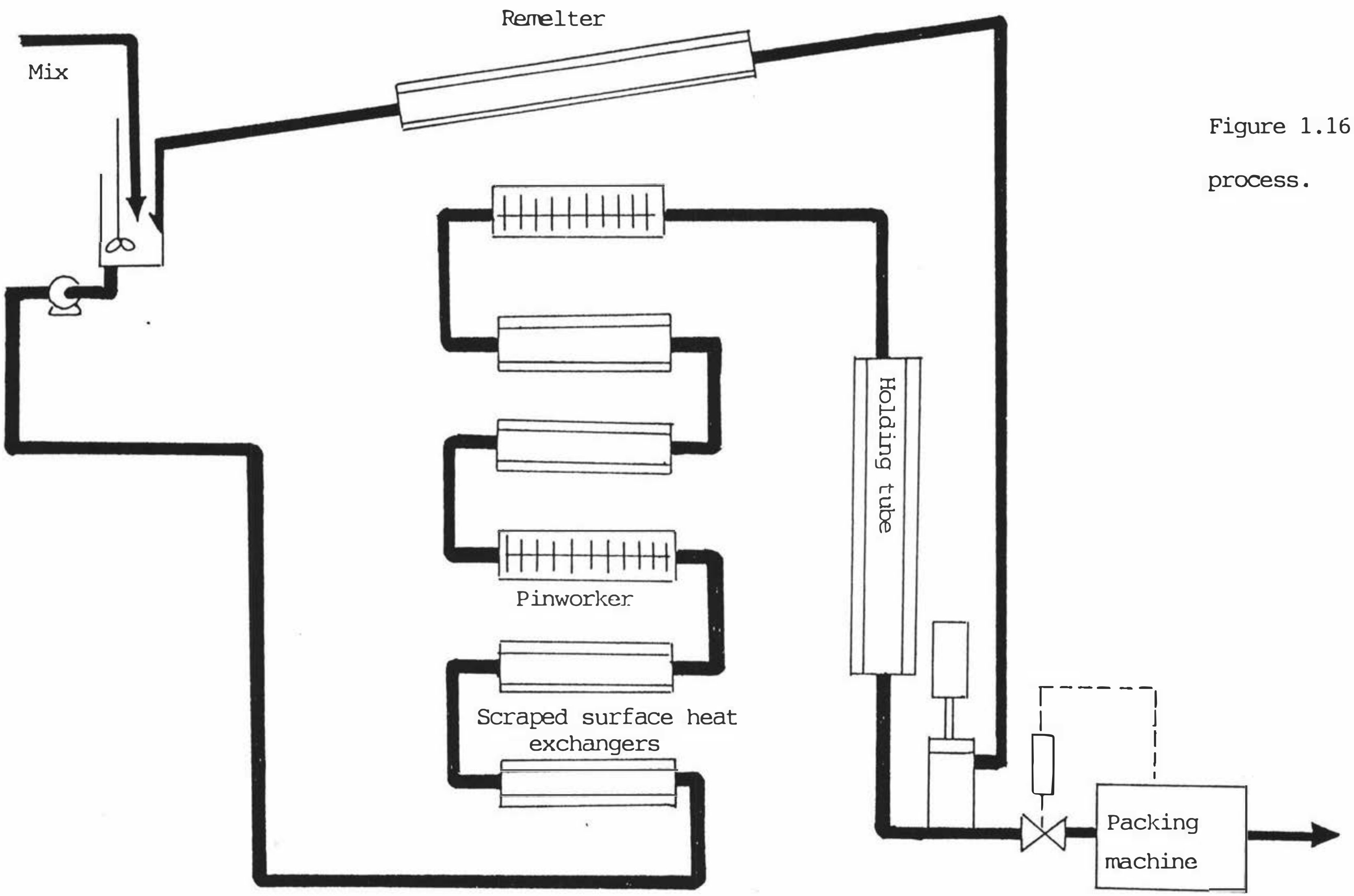


Figure 1.16: The Ammix process.

conventional and Cherry-Burrell butters made from the same cream resulted in butters of approximately the same hardness (Vasic and DeMan, 1968). Butter manufactured by the Cherry-Burrell method receives very little working. In contrast, Ammix butter is pinworked twice, resulting in a softer butter with a more plastic body (Munro, 1985).

1C.4.3. Factors Affecting Rheology

The solid fat content of Ammix butter, as with traditional butter and margarine, has a major effect on firmness. The amount of solid fat, and type of crystal network formed will affect the final hardness of the butter. In general, the hardness of Ammix butter has been found to be similar to that of Fritz butter. An Ammix butter compared with a Fritz butter made from the same cream was harder, but the difference in hardness disappeared after working.

1C.4.3.1. Components of the Disperse and Continuous Phases

The continuous liquid fat phase and the presence of water droplets have very little effect on the rheological behaviour of Ammix butter.

Ammix butter contains fewer fat globules than comparable traditional butter. As a result less fat will be confined in globules and a greater number of fat crystals will be free to participate in crystal networks. This could lead to a stronger or harder product than traditional butter.

Cherry-Burrell butter contains no or very few fat globules. As more fat crystals would be available to form crystal networks and the presence of fat globules prevents the formation of the network of crystals to some extent, both factors could contribute to a harder product. Cherry-Burrell butter may also contain large, roughly spherical bodies of clustered crystals. Larger crystals would have a softening effect, however this effect is not seen (Vasic and DeMan, 1968).

1C.4.3.2. Temperature

A differential scanning calorimetry meting thermogram (Fig. 1.17) of a Ammix butter shows the same melting curve as that of a traditional butter (Fig. 1.12). Melting thermograms and solid fat contents determined by NMR are obtained from extracted milkfat. The extraction process erases the thermal history of the milkfat. Thus, two butters which may have the same melting curves and solid fat contents may have different hardnesses at the same temperature.

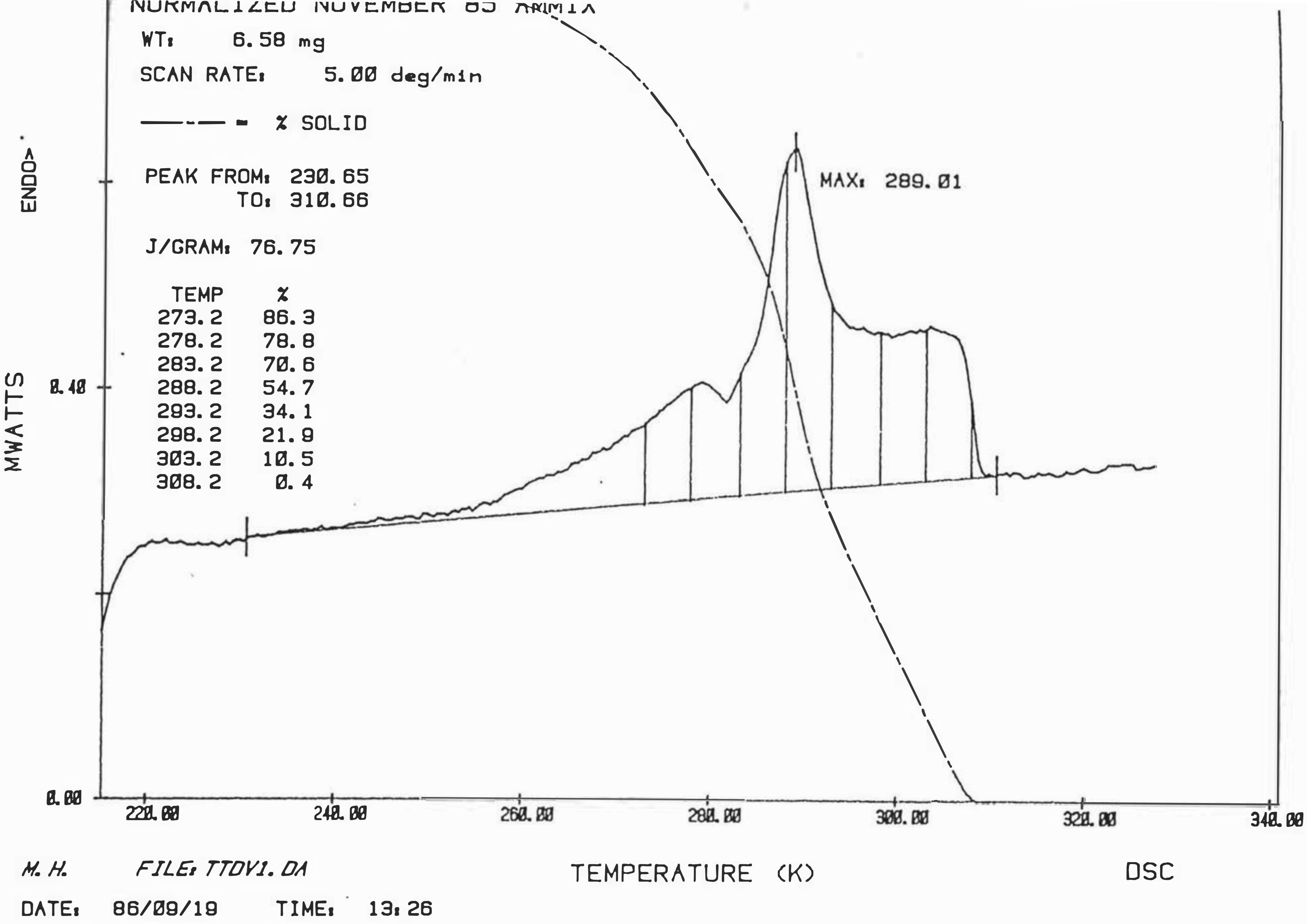
Ammix butter has been found to soften more quickly as temperature increases, compared to traditional butter, especially at temperatures above 20°C (Bissell, 1987). As a direct result, Ammix butters do not stand up as well as traditional butters at higher temperatures.

1C.4.3.3. Manufacturing Variables

As with margarine, the Ammix process offers a wide variety of processing variables.

The rate of cooling would affect the product hardnesses in the same way as for margarine, with shock cooled products being harder. Different cooling treatments such as 'Alnarp' cooling are possible, leading to softer products. In practice, however, it has been found to be difficult to isolate and gauge the effect of cooling as altering cooling regimes often means other variables are also altered (Bissell, 1987).

Experimentation on pilot plant scale has shown there is no significant difference in hardness between pinworked products and products allowed to rest before packing (Bissell, 1987). A lower throughput resulted in a softer product, perhaps due to either increased crystal nucleation occurring in the scraped surface heat exchangers, or increased holding times or both (Bissell, 1987).



TEMP	%
273.2	86.3
278.2	78.8
283.2	70.6
288.2	54.7
293.2	34.1
298.2	21.9
303.2	10.5
308.2	0.4

Figure 1.17: Differential scanning calorimetry melting thermogram of an Ammix butter.

The recycling of product is also an option in the manufacturing of Ammix butter. Bissell (1987) reports products made using the recycling technique to be softer, and to have lower solid fat contents than controls manufactured without recycling.

1C.4.3.4. Reworking

On reworking, the hardness of Ammix butters is reduced more than the hardness of traditional butter. In this respect Ammix butter is behaving more like margarine. The reason for the greater reduction in hardness found is probably the same. Ammix butter seems to contain a higher number of strong 'bonds', compared to traditional butter. A large proportion of these bonds may be broken on reworking and not reformed, contributing to a greater permanent reduction in hardness.

1C.5. AFTERWORD

The three products, traditional butter, Ammix butter and margarine share the same basic structural elements and differ in raw materials and manufacturing method. Ammix butter seems to hold a middle ground betwen traditional butter and margarine. Manufactured from the raw materials of butter, using margarine technology, structure and behaviour on reworking fall between the two extremes, with the advantages of a desireable product and a flexible manufacturing method.

CHAPTER TWO

MATERIALS

2.1. BUTTER FROM COMMERCIAL DAIRY FACTORIES

Samples of commercially produced Fritz and Ammix butters were collected over two and a half dairying seasons. Forty 500g pats of Fritz butter, all from one day's production during the first week of the month, were obtained each month from Tui Co-op. Dairy Co. Ltd., Pahiatua. Similarly, Ammix butter produced by Tai Tapu Central Co-op. Dairy Co. Ltd, now Alpine Dairy Products Ltd., Christchurch, was also obtained. Samples were also taken prior to packing at the Manawatu Co-op. Dairy Co. Ltd, Longburn.

2.1.1. Commercial Sample Identification

Commercial butter samples have been identified by factory of origin, month and year. Samples from Tui Co-op. Dairy Co. Ltd. are prefixed TUI, samples from Tai Tapu Central Co-op. Dairy Co. Ltd. are prefixed TT and samples from Manawatu Co-op. Dairy Co. Ltd. are prefixed MAN. For example, a sample of 1986 November butter manufactured by Tui Co-op. Dairy Co. Ltd. would be referred to as TUI November '86.

2.2. BUTTER MADE USING DIFFERENT CREAM COOLING TECHNIQUES

Butters were manufactured from creams subjected to different cream cooling techniques at the New Zealand Dairy Research Institute, Palmerston North.

Six hundred kilograms of cream was vacreated using normal operating conditions. The cream was divided into three batches and each cooled in a different way.

(1) Shock cooling. The cream was cooled in a plate heat exchanger to 5°C and pumped to a holding vat. Cream

temperature was allowed to rise slowly to 11.5°C, held overnight and churned at this temperature. The final temperature of the butter was 16°C.

(2) Slow cooling. The cream was cooled to 13°C in a plate heat exchanger, pumped to a holding vat and cooled to 11.5°C in the vat. The cream was held overnight and churned at this temperature. The final temperature of the butter was 16.3°C.

(3) Alnarp cooling. The cream was cooled in a plate heat exchanger to 4°C and held at this temperature for four seconds. The cream was then warmed to 21°C in a plate heat exchanger, pumped to a holding vat and held for four hours. The cream was then cooled in the vat to 11.5°C, held overnight and churned at this temperature. The final temperature of the butter was 15.7°C.

Each batch of cream was churned in a cubical Silkeborg batch churn using normal operating conditions. The temperature of butter leaving the churn was to be no more than 16°C.

From each churning two 25 kg boxes and twelve 500 g pats were packed.

2.3. BUTTER AND ANHYDROUS PRODUCTS MADE FROM THE SAME FAT.

A butter, plasticized milkfat and a milkfat/oil blend were manufactured from the same milkfat at the New Zealand Dairy Research Institute, Palmerston North, using a Gerstenberg and Agger Pilot Plant Perfector Type 3-57 R22 (Gerstenberg and Agger A/S, Copenhagen, Denmark).

The plant was set up in the configuration indicated in Figure 2.1. Three production runs were carried out using the production conditions listed in Table 2.1. The product was recycled through the plant until steady state conditions were reached. The recycled product was melted down and added back

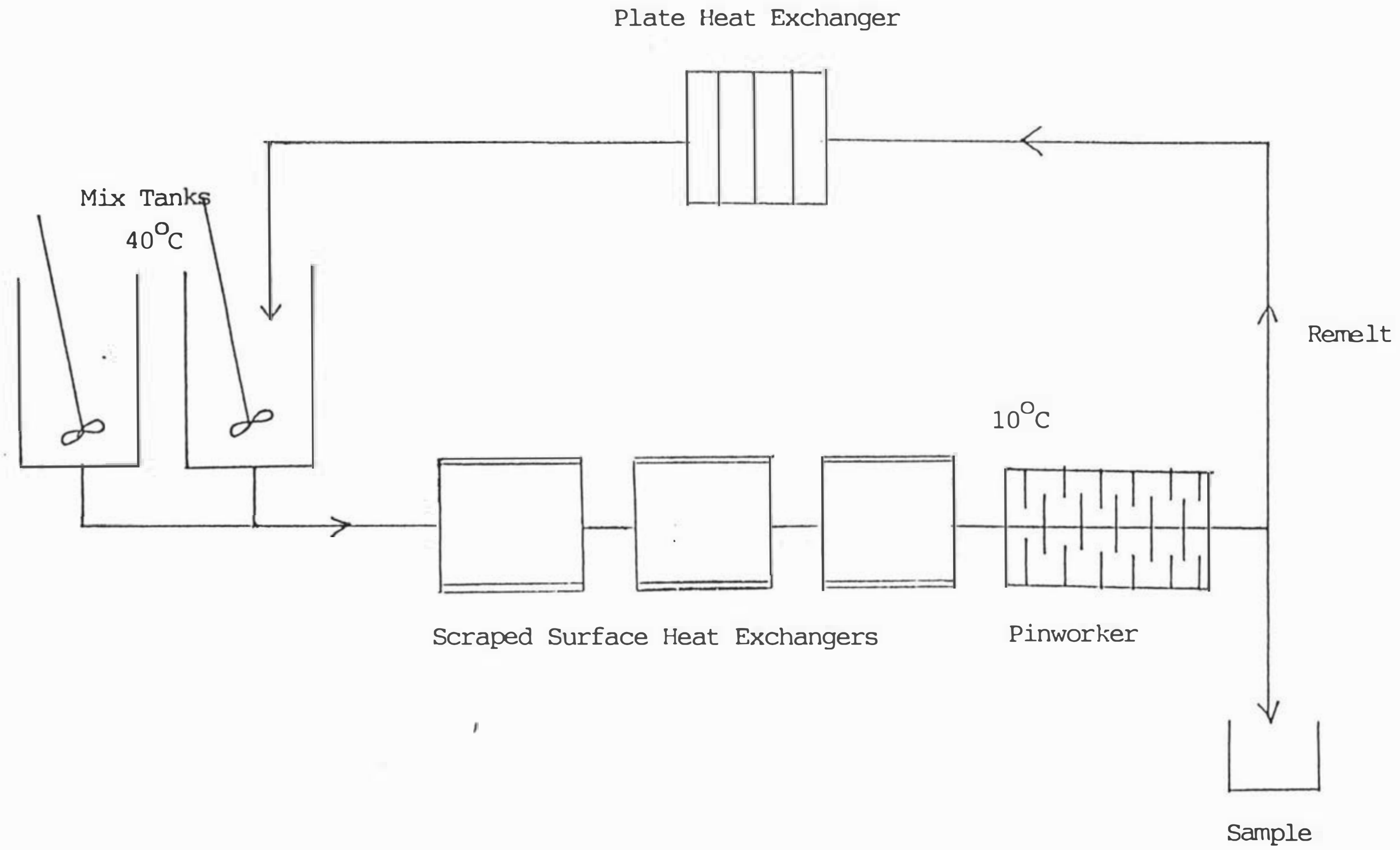


Figure 2.1: Plant configuration used in the manufacture of butter and anhydrous products from the same fat.

Table 2.1. Production conditions used in the manufacture of butter and anhydrous products from the same milkfat.

Mix Temp (^{O}C)	40
Throughput (kg/hr)	150
SSHE# 1 and 2	
Shell Temp (^{O}C)	as required*
Speed (rpm)	700
Shaft Water Temp (^{O}C)	30
SSHE 3	
Product Temp (^{O}C)	10
Shell Temp (^{O}C)	as required*
Speed (rpm)	700
Shaft Water Temp (^{O}C)	30
Pinworker	
Temp (^{O}C)	not contolled
Speed (rpm)	200

Scraped surface heat exchanger.
*Temperatures varied as necessary to cool the product sufficiently.

Table 2.2: Product temperatures recorded during production of butter and anhydrous products from the same milkfat.

	Temperature (^{O}C)		
Run	1	2	3
ex SSHE 1	16.9	17.7	17.0
ex SSHE 2	12.5	13.5	13.0
ex SSHE 3	9.8	10.0	10.0
ex pinworker	12.2	11.7	12.0

into the mix tanks. In between runs the plant was flushed with the new product, with the material used during flushing being discarded as waste.

(1) Plasticized milkfat. Fifty kg of milkfat was melted and held at 40°C until required. The milkfat was pumped through the plant. Twenty 500g pottles of sample were collected.

(2) Butter. Milkfat at 40°C was blended with skimmilk to give a butter with the approximate composition of milkfat 82.5%, solids not fat 1.6% and water 15.9%. The mix was pumped through the plant. Twenty 500g pottles of sample were collected.

(3) Milkfat/oil blend. Milkfat at 40°C was mixed with soya bean oil to make an 80/20 fat/oil blend. The mix was pumped through the plant. Twenty 500g pottles of sample were collected.

The product temperatures recorded during the runs are shown in Table 2.2.

2.4. REWORKING

Reworking on a small scale (up to 10 kg) was carried out using a Toledo Z Blade Reworker (Toledo Engineering PGY Ltd., Lidcombe, N.S.W., Australia) at the New Zealand Dairy Research Institute, Palmerston North. All reworking was done under vacuum, with chilled water passing through the exterior jacket. The butter and anhydrous fat products manufactured fron the same fat source and two commercial butter samples, TUI March '87 and TT March '87, were reworked in this fashion. Temperatures reached during reworking did not exceed 15°C.

2.5. STORAGE

All samples, both commercial and those specially manufactured were stored at $5^{o}C$ for at least a month after manufacture to allow setting to be completed. Samples which were reworked were held for at least one month before reworking, and held for at least a month after reworking.

CHAPTER THREE

ESTABLISHED METHODS

Several analytical methods used in the evaluation of fats are well established. The methods used in the course of this work are described below.

3.1. EXTRACTION OF MILKFAT

Some analyses require pure milkfat. Milkfat was extracted by melting a butter sample at 50°C. The fat layer was centrifuged and the separated fat phase filtered through Whatman filter paper.

3.2. SECTILITY HARDNESS

Samples for hardness measurements were held for thirty days at 4°C to allow full setting prior to analysis. Sectility hardness at 10°C was determined using a modified FIRA/NIRD extrusion apparatus according to the method of Taylor *et al* (1971).

Samples were contained in 48mm diameter stainless steel rings. Longitudinal slots on opposite sides of the rings allowed the cylinder of butter to be cut by a stainless steel wire. The wire was mounted on a bow carried by the longitudinal rod contacting the measuring spring of the instrument. A cutting speed of 40 mm/min was used. Samples plus sample holders were held in a water bath at 10°C for a least five hours before measurement. Duplicate samples were measured.

The instrument is calibrated in terms of load; hence sectility hardness is quoted in units of grams. These units are arbitrary as they depend on the wire dimensions, cutting speed and sample ring dimensions.

3.3. FATTY ACID COMPOSITION

Fatty acid composition was determined by gas chromatography of fatty acid methyl esters prepared by direct trans esterification of a milkfat sample with sodium methoxide/methanol.

A Hewlett-Packard 5840A gas chromatograph with a stainless steel column 2m long, 0.125 inch diameter packed with 10-15% diethylene glycol succinate (Analab, Inc.) on Chromososrb W-HP 80/100 (Varian Aerograph) was used to analyse the fatty acid methyl esters. Nitrogen, flowing at a rate of 15 ml/min, was used as a carrier gas.

A standard anhydrous milkfat was used to calibrate the gas chromatograph. The results obtained should agree with established mean values (Table 3.1) within two standard deviations. Weight correction factors (weight/area of peak) are given in Table 3.2.

Samples were prepared by melting the milkfat at 60°C. When melted, eight drops were transferred to a screw top tube and 2 ml of the esterifying reagent (sodium methoxide/methanol in a mixture of ethyl ether and petroleum ether) was added. Sodium methoxide/methanol was prepared by the method described by Shehata et al, 1970. After 2-4 minutes 5 ml of hexane was added. A further 2 minutes later 5 ml of saturated sodium chloride solution was added. The tube was inverted several times to mix the contents then centrifuged briefly. Four mls of the upper hexane layer were withdrawn and transferred to a vial containing 500 mg of anhydrous sodium sulphate. The vial was shaken and allowed to settle. 1-2 µl of sample was introduced to the gas chromatograph. The solution of esters is stable for a few days if kept refrigerated.

The injector temperature and detector base were maintained at 240°C and 250°C respectively. After injection of the sample

Table 3.1: Composition of standard anhydrous milkfat.

FATTY ACID	MEAN (weight %)	STD. DEV.
4:0	3.58	0.3
6:0	2.07	0.15
8:0	1.22	0.1
10:0	2.48	0.1
12:0	3.24	0.1
14:0	10.0	0.3
16:0	25.0	0.3
18:0	10.4	0.4
18:1	27.5	0.7

Table 3.2: Normalizing factors for fatty acid weight percentages, relative to $C_{16:0}$.

FATTY ACID	NORMALIZING FACTOR
16:0	1.000
4:0	1.37
6:0	1.21
8:0	1.12
10:0	1.07
10:1	1.05
12:0	1.04
14:0	1.01
14:1	1.00
15:0	1.00
16:1	1.00
17:0	1.00
17:1	1.00
18:0	0.98
18:1	0.98
18:2	0.97
18:3	0.97

at an inital column temperature of 100^{o}C, the chromatograph was programmed to increase in temperature at 10^{o}C/min to 130^{o}C and then increase at 5^{o}C/min until a temperature of 210^{o}C was reached. This temperature was held until all methyl esters were eluted. Peak areas were calculated by the 5840A gas chromatograph terminal.

3.4. TRIGLYCERIDE COMPOSITION

Triglyceride composition was determined using a Perkin Elmer Sigma 300 Capillary Chromatograph with on-column injection. The equipment consisted of a hydrogen flame ionization detector and a bonded fused silica column in two parts; a non-phased guard column, two metres long (Alltech) and a normal triglyceride phased column, 2.5 metres in length, internal diameter 0.25mm, stationary phase OV-1 (PE 9-2355). Under normal conditions the carrier gas was nitrogen at 4psi. The flame ionization detector was supplied with air at 30 psi and hydrogen at 20 psi.

Samples were prepared by dissolving six drops of milkfat in 1 ml of hexane. A sample aliquot of 1 µl was used.

Samples were injected into the column at an initial temperature of 60^{o}C. After an initial holding time of one minute the chromatograph oven was programmed to heat at a rate of 30^{o}C/min to 200^{o}C. The oven remained at this temperature for one minute, followed by a second increase in temperature at a rate of 10^{o}C/min to 340^{o}C. The detector was maintained at 350^{o}C.

3.5. SOLID FAT CONTENT BY NUCLEAR MAGNETIC RESONANCE

Nuclear magnetic resonance (NMR) spectroscopy can differentiate between protons in solid and liquid fats and thus determine the solid or liquid fat content of a fat sample.

The method of analysis of solid fat content is described by MacGibbon and McLennan (1987). The method follows that of van Putte and van den Enden (1974) using a Bruker minispec PC120 pulsed nuclear magnetic resonance (NMR) spectrometer (Bruker Analytische Messterchrik GmbH, West Germany) operating at 20 MHz with the magnet temperature maintained at 40°C. The milkfat signal was measured 11µs and 70µs after the pulse and a direct readout of the mean percentage solid fat is provided by the instrument. Four scans of each sample were taken with a repetition rate of 2s. The instrument was calibrated using percentage solid standards provided by Bruker (0%, 30.8%, 71.9%). Because probe temperature was not controlled, the solid fat measurement was performed immediately after removing the sample from a constant temperature block (controlled to ± 0.1°C).

Duplicate NMR tubes were filled to a height of 40mm with milkfat. Samples were heated to 60°C for 30 minutes, then placed in a 0°C block and held overnight at that temperature. The solid fat profile of each sample was determined at 5°C intervals from 0 - 35°C. The samples were equilibrated at each temperature for 45 minutes prior to measurement.

NMR can be performed on samples of anhydrous shortenings without erasing thermal histories. Samples at 5°C are forced into bottomless NMR tubes to the height of 40 mm and placed directly into a 0°C block. Analysis then proceeds as above.

3.6. SOLID FAT CONTENT BY DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry (DSC) is based on the principle that during the heating or cooling of a fat sample the energy transfer to or from a sample indicating thermal transitions in the sample can be recorded as a function of the temperature of the sample.

Thermal analysis of fat samples was carried out using a differential scanning calorimeter (Perkin Elmer DSC2 Differential Scanning Calorimeter connected to a Perkin Elmer 3600 Thermal Analysis Data Station via a Perkin Elmer interface. Perkin Elmer Corporation, Norwalk, Conn., U.S.A.).

Milkfat was melted at 60°C and a 5-10 mg sample was quickly transferred to a sample pan using a glass capillary. The sample pan was then sealed and loaded into the instrument. The sample was cooled from 60°C to -60°C at a rate of 10°C/minute and held at that temperature for five minutes unless otherwise stated. The melting thermogram was then recorded at a heating rate of 5°C/min.

Curves were analysed using a Partial Areas program and solid fat contents were calculated using software provided by Perkin Elmer.

In some cases anhydrous products were loaded cold at 5°C, in which case a small piece of the sample was placed in the sample pan using a spatula. The sample pan was sealed and loaded into the instrument. The sample was then treated as outlined above.

3.7. COMPARISON OF NUCLEAR MAGNETIC RESONANCE AND DIFFERENTIAL SCANNING CALORIMETRY

While melting profiles obtained by nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC) are similar, the solid fat contents estimated by DSC are higher than corresponding NMR values (Norris and Taylor, 1977). The estimation of solid fat from a DSC thermogram involves the assumption that the heat of fusion of triglycerides is constant. In fact the heat of fusion has a positive correlation with melting point resulting in the true proportion of solids being over-estimated at high solid fat contents (low temperatures). Norris and Taylor calculated solid fat contents for milkfat are over-estimated by approximately 10% at 5°C and 7% at 20°C.

Norris and Taylor (1977) and Mortensen (IDF 153) concluded pulsed NMR techniques were superior for determination of the ratio of solid to liquid fat. Norris and Taylor temper this by pointing out DSC melting thermograms also provide additional information in the form of a differential melting curve over the entire melting range, making DSC a useful complement to NMR.

CHAPTER FOUR

CREEP COMPLIANCE METHOD

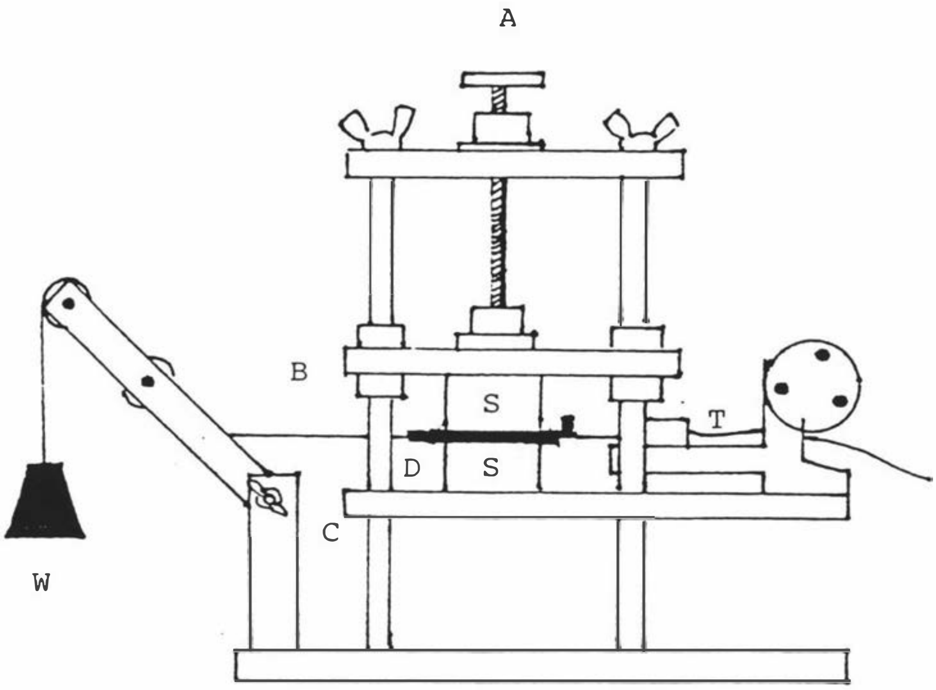
4.1. THE INSTRUMENT

Creep compliance testing can be used to measure fundamental rheological parameters of viscoelastic materials (Chapter 1, Section B.2.1). This technique can be applied to any material which will retain a rectangular shape prior to and during testing. In order to carry out creep compliance testing on butter and related fat systems a parallel plate viscoelastometer, as described by Shama and Sherman (1968), was built (Fig 4.1). Two samples cut from the same butter (S) are loaded between the top plate (B) and the bottom plate (C), with a ridged centre plate (D) separating the two halves of the sample.

The top and bottom plates have milled teeth to prevent samples slipping during testing. The teeth are square pyramids (with a base 4mm^2) truncated at a height of 1mm, spaced 5mm apart. To further prevent samples slipping, both sides of the centre plate have 1mm high ridges 10mm apart running at right angles to the direction of creep compliance movement.

At one end of the centre plate the weight is attached, while at the other end the moving part of a Sangamo DFg 2.5 linear displacement transducer (T) is mounted.

A central screw mechanism (A) raises and lowers the top sample plate (B). Plate (B) moves downward to contact the upper surface of the top sample. Two spacers ensure the samples are fully in contact with the top and bottom sample holding plates and the centre plate and also prevent samples being compressed (Footnote 1). The body of the linear displacement transducer (T) is mounted on a platform which can be moved up and down.



A: Screw mechanism to raise plate B.

B and C: Top and bottom plates respectively.

D: Ridged centre plate.

S: Sample.

T: Transducer.

W: Weight.

Figure 4.1: The parallel plate viscoelastometer.

The lead weight (W) used to apply constant stress is attached by nylon string and hook to the centre plate. The string passes over teflon pulleys mounted on a movable boom.

The instrument is sited so as to be horizontal. Other precautions do not appear to be necessary, for example, small vibrations do not affect creep response.

4.2. TEMPERATURE CONTROL

Temperature control is very important when dealing with fats such as milkfat which contain a wide variety of triglycerides with a correspondingly wide range of melting points.

Examination of melting curves for milkfat shows that small temperature variations cause a lesser change in the solid fat content at $10^{O}C$ than at $15^{O}C$. For example, a difference in temperature of $\pm$ $0.5^{O}C$ at $10^{O}C$ gives rise to a change of approximately 0.6% solid fat as determined by DSC. A similar variation at $15^{O}C$ results in a 2.0% change in solid fat. Figure 4.2 shows a differential scanning calorimetry thermogram illustrating this point. Consequently a temperature of $10^{O}C$ was chosen to conduct creep compliance testing of butter and related systems.

Other tests such as sectility hardness testing were also carried out at $10^{O}C$ so meaningful comparisons of results could be made.

A temperature of $10^{O}C \pm 0.2^{O}C$ was maintained for creep compliance testing by placing the parallel plate

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Footnote 1. The presence of the spacers ensure samples are firmly embedded on the teeth and ridges of all three plates and are not compressed. Compression of samples can also be used to obtain rheological data (eg. Sherman, 1970, Mohsenin, 1986). Excessive compression may therefore alter the observed creep compliance.

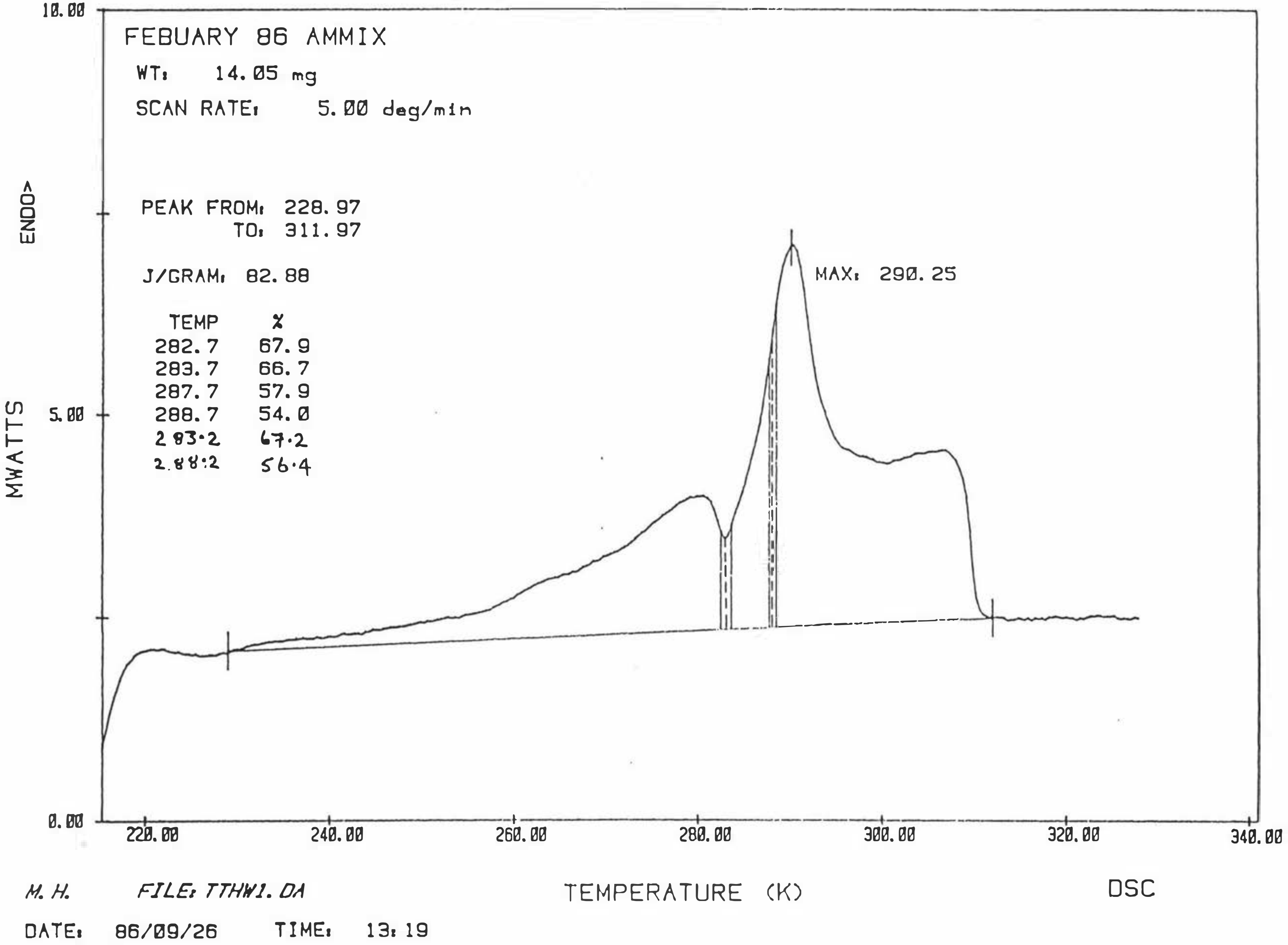


Figure 4.2: Differential scanning calorimetry melting thermogram illustrating the changes in solid fat with temperature at 10 and 15^{O}C

viscoelastometer in an Environ-Shaker 3579-1234&10 (Lab-Line Instruments, Inc. Melrose Park, Illinois) acting as a refrigerated incubator and conducting all experiments in the incubator. Constant temperatures were maintained despite ambient temperatures ranging from 10°C - 30°C during a twentyfour hour period. Figure 4.3 shows a graph of temperature measurements taken over a 40 hour period illustrating the changes in room temperature, sample temperature and the internal temperature of the incubator.

4.3. THE DATA COLLECTION SYSTEM

The very small movements involved in creep compliance testing are measured by a Sangamo DFg 2.5 linear displacement transducer which has a free guided armature incorporating Delfin bearings. The transducer, with a rated stroke of + or - 2.5 mm, was calibrated using a 10 V dc supply and had a reported sensitivity of 776 mV/mm. The mV signal from the transducer is recorded simultaneously by data logger and chart recorder to provide a permanent record of the experiment. Figure 4.4 illustrates diagrammatically the data collection system, while Figure 4.5 shows a typical chart recorder trace.

The data logger was designed and built by Mr. A. Matheson of the Applied Mathematics Section of New Zealand Dairy Research Institute. It is specifically programmed to record data from creep compliance experiments. The data logger records in the 0-400 mV range. Data is recorded with 12 bit precision. The data logger also provides a dc supply to the transducer.

A reading is taken every half second for the first ten minutes of any experiment and then at 20 second intervals. Readings are stored in a random access memory on a microchip with a memory capacity such that 15.5 hours of data can be stored.

On completion of an experiment data is offloaded on to a disk for storage and analysis. A computer program (UART) was

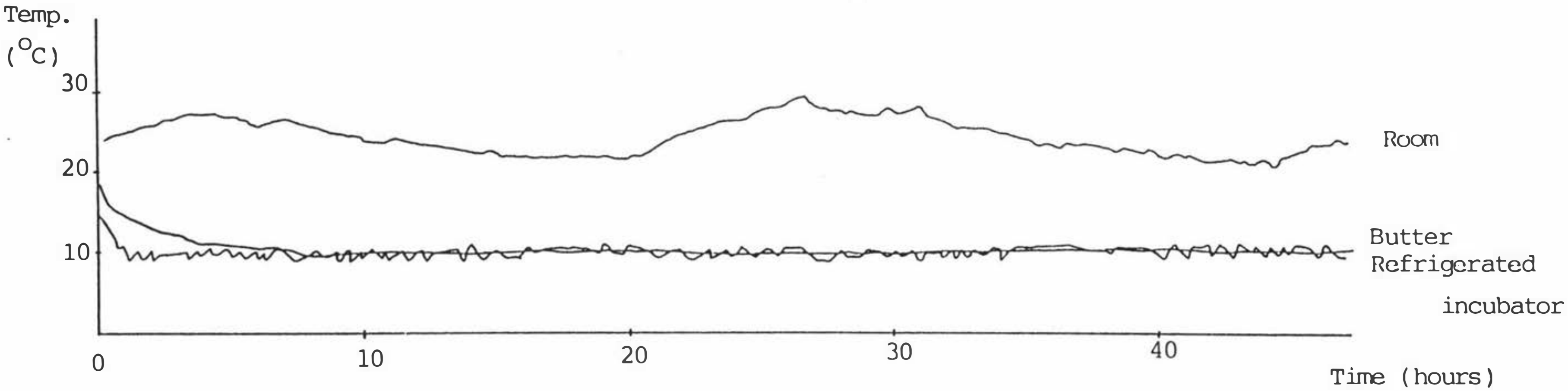


Figure 4.3: Fluctuations in temperature observed over a forty hour period. Butter held at 10°C in the Environ Shaker.

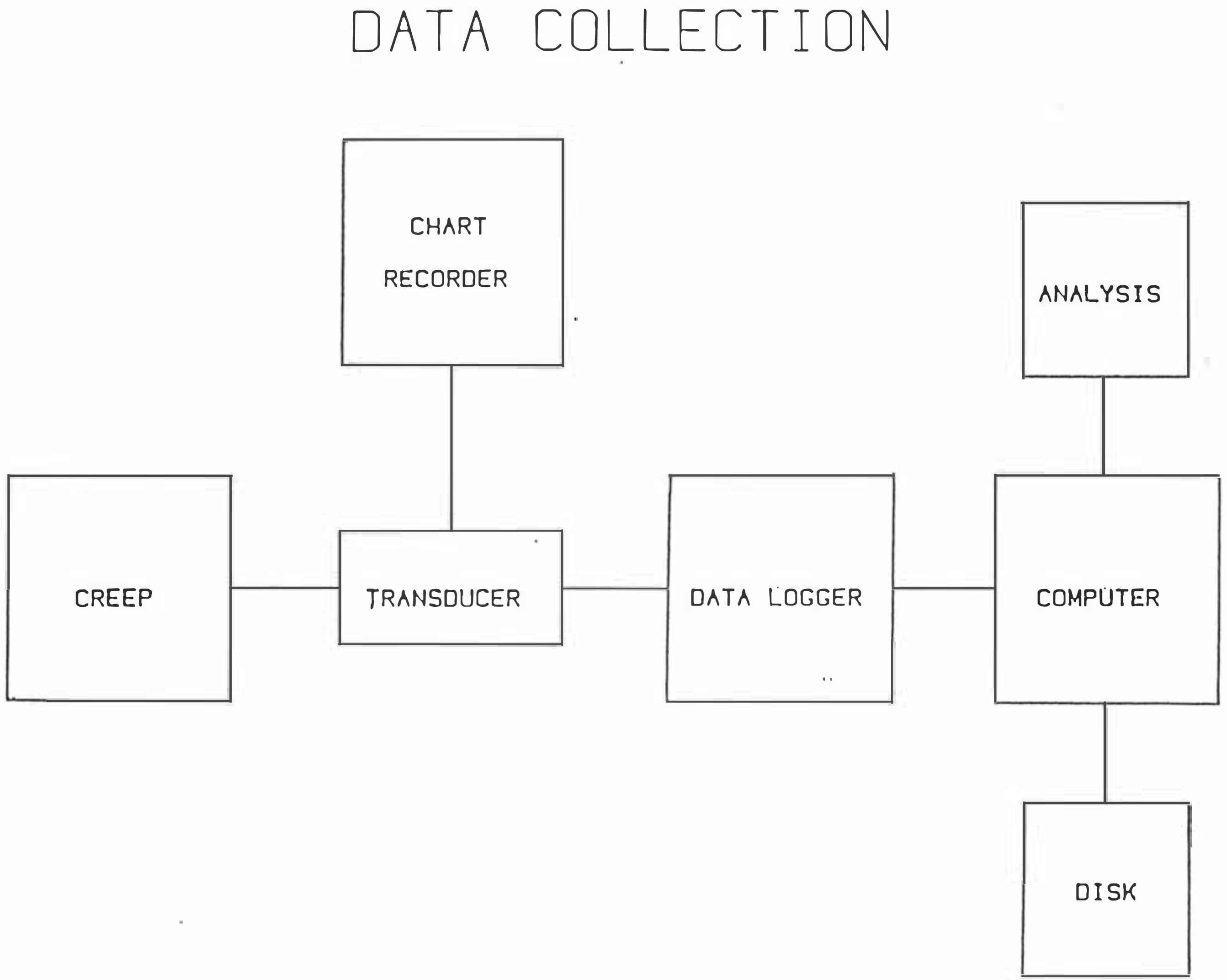


Figure 4.4: The data collection system.

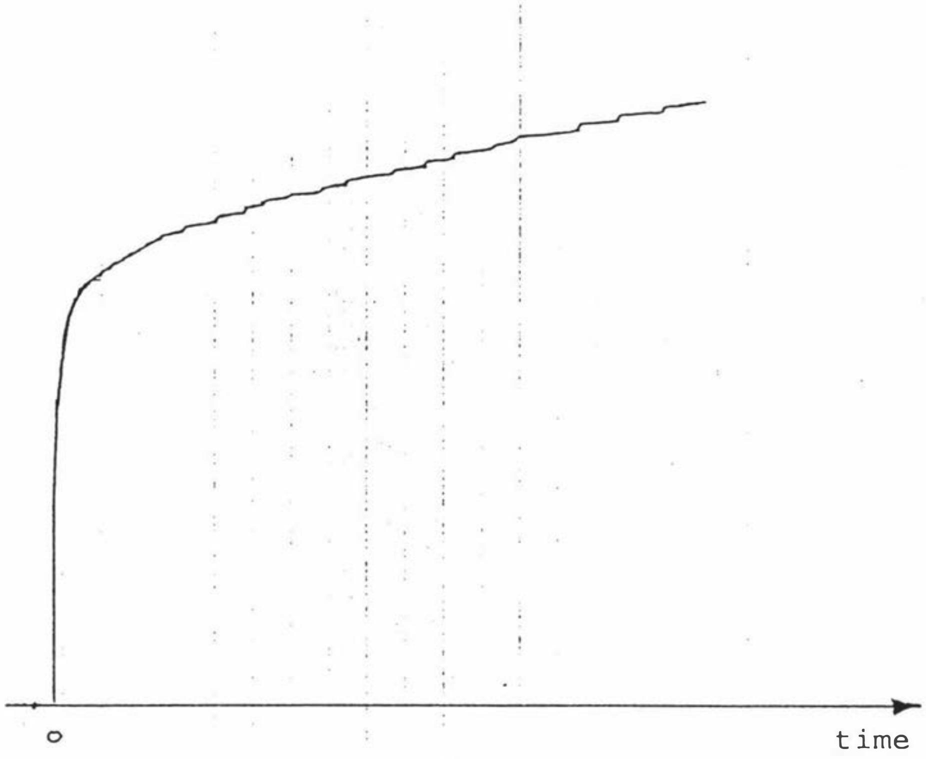


Figure 4.5: Chart recorder trace seen on performing a creep compliance experiment.

provided by Mr. A. Matheson to do this and is included in Appendix 1.

The data undergoes preliminary analysis on an IBM compatible microcomputer. The initial data file of 4000 data points is reduced in size to 212 data points by selecting data at even ln time intervals of 0.055. A second computer program, FILEEDIT, written in Pascal accomplishes this and is included in Appendix 1. The truncated data sets are transferred to a mainframe computer (PRIME 9955) where further analysis using the Marquardt least square algorithm takes place (Marquardt, 1963, Meeter, 1964) (Appendix 1). The non-linear curve fitting program fits data to the classic viscoelastic model outlined in Chapter One, Section A.1.1.2.

4.4. SAMPLE PREPARATION, LOADING AND RUNNING

All fat samples are stored at $5^{o}C$ for at least 30 days to ensure that samples have reached maximum firmness. Prior to creep compliance testing, samples are allowed to equilibrate in the refrigerated incubator at $10^{o}C$ for 24 hours. Samples for testing are removed from the refrigerated incubator and prepared at room temperature. Preparation takes no more than 90 seconds and no appreciable temperature rise is observed during the handling of the samples.

Samples are cut using a cutter made from square steel pipe with an internal measurement of 48 mm x 48 mm. One end of the pipe is sharpened whilst the other end has two handles attached (Fig. 4.6). After pushing the cutter into a sample excess fat is cut away. A wooden block is used to force the sample from the cutter and approximately the first ten mm of sample are cut and discarded, leaving a smooth surface. The sample is then pushed out to the required length (30mm), measured and cut. This results in a sample with dimensions of 48 mm x 48 mm x 30 mm. Fat remaining in the sample cutter is discarded. A second sample is cut in the same way.

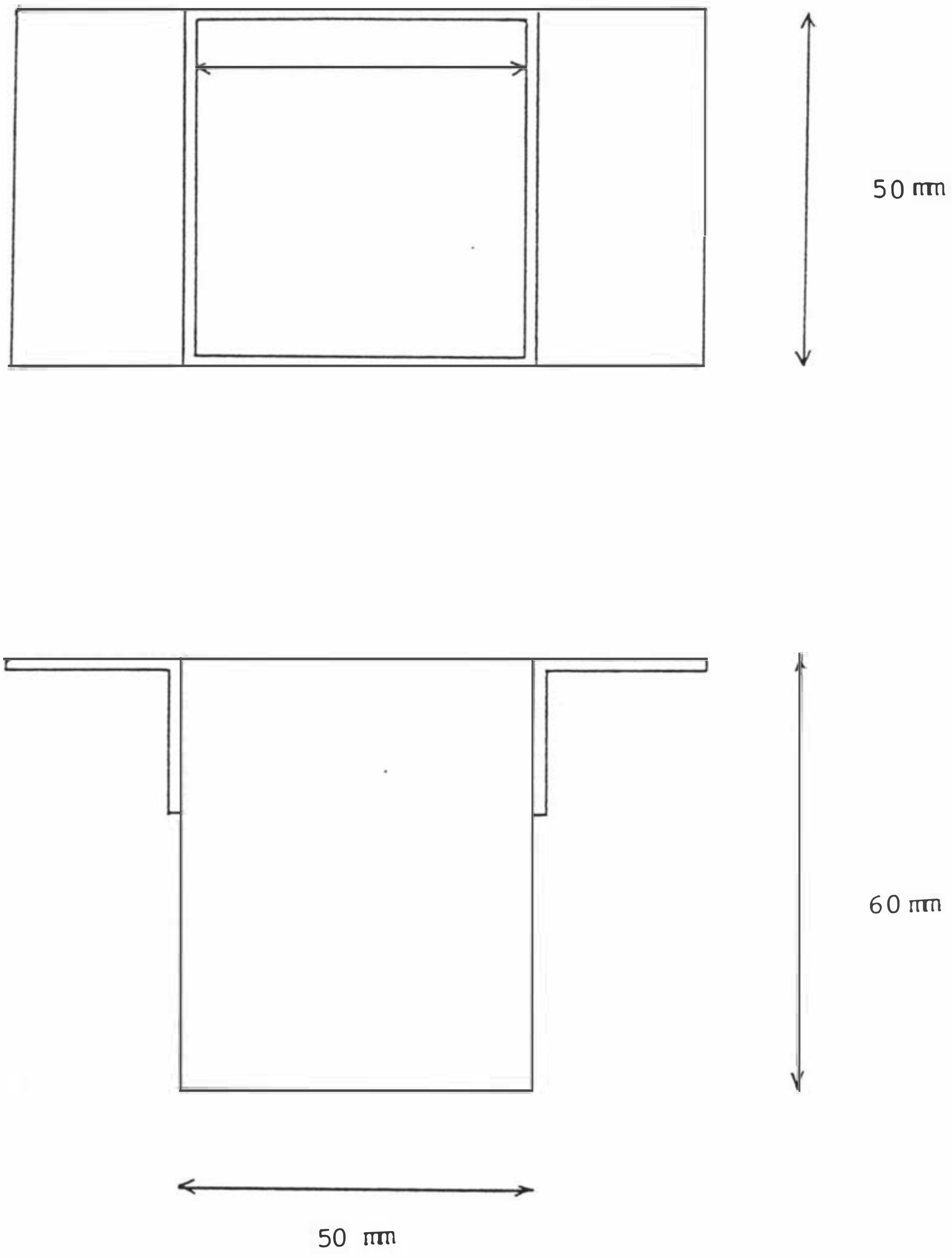


Figure 4.6: Plan and side view of the sample cutter.

Samples for creep compliance are checked to ensure they are homogeneous, free of visible air holes and laminations.

Prepared samples are loaded into the instrument taking care to ensure both the data logger and chart recorder readings are on scale. The top plate is lowered until stopped by the spacers. This ensures that teeth are firmly embedded in the samples. (Footnote 2).

The weight is then attached to the front of the centre plate and data recording systems are started. To release the weight it is held in the palm of the hand which is then rapidly lowered. (Footnote 3) Data is then collected for 15.5 hours.

When the weight is released (stress applied) both samples are subject to shear due to the movement of the centre plate in the direction in which the stress is applied. The rate and distance moved by the centre plate is recorded by data logger and chart recorder. Sample surfaces in contact with the centre plate experience maximum shear displacement, while those in contact with the top and bottom plates experience minimum shear displacement.

Footnote 2. Saint-Venant's principle, that a load applied to a small part of a body will give rise to localized stress and strain (Timoshenko and Goodier, 1970), is applicable here. The stress or strain on a semi-infinite body (or sample of butter) due to loading may be expected to diminish rapidly with distance.

Footnote 3. While it is impossible to apply stress instantaneously it is desirable that stress be applied as quickly as possible. Mechanical systems such as lowering a jack were found to be slower than releasing the weight by hand. Hand release is quick, easy and has proved very satisfactory as long as the weight is not just dropped.

4.5. RECOVERY AND LOAD CYCLING

On removal of stress after creep compliance testing a partial recovery of strain is observed (Fig. 4.7). The application of stress and its recovery can be referred to as a stress/recovery cycle, or a load cycle.

After allowing a sample to recover for some time stress may be applied again. This can be followed by a further recovery. Two or more stress/recovery cycles can be carried out if desired.

The length of time taken by one stress/recovery cycle is theoretically unlimited. However, the data logger can only record 15.5 hours of data, and, if any number of experiments are to be performed the cycles can not be too long. In practice, a cycle of 17 hours creep and 7 hours recovery has been found to be satisfactory and convenient. Unless otherwise stated, all load cycling follows this pattern.

A record of the 1.5 hours of data not recorded by the data logger is kept in the form of the chart recorder trace. The data manipulation and curve fitting performed on data recorded by the data logger involves only the first 15.5 hours of an experiment. Including the additional 1.5 hours of data would have little effect on the results. However, when calculating viscosities from actual creep and recovery curves (see later) the total length of time a sample was allowed to creep becomes important, and this time (17 hours) is used in calculations.

4.6. DATA ANALYSIS

4.6.1. Creep Curves

The creep compliance curve for a substance exhibiting classical viscoelastic behaviour can be said to consist of three regions: a) a region of instantaneous elastic response, b) a region of retarded elastic response and c) a region of pure viscous flow. Viscoelastic behaviour has been modelled by the generalised Kelvin model (Chapter One, Section A.6.1.1.2).

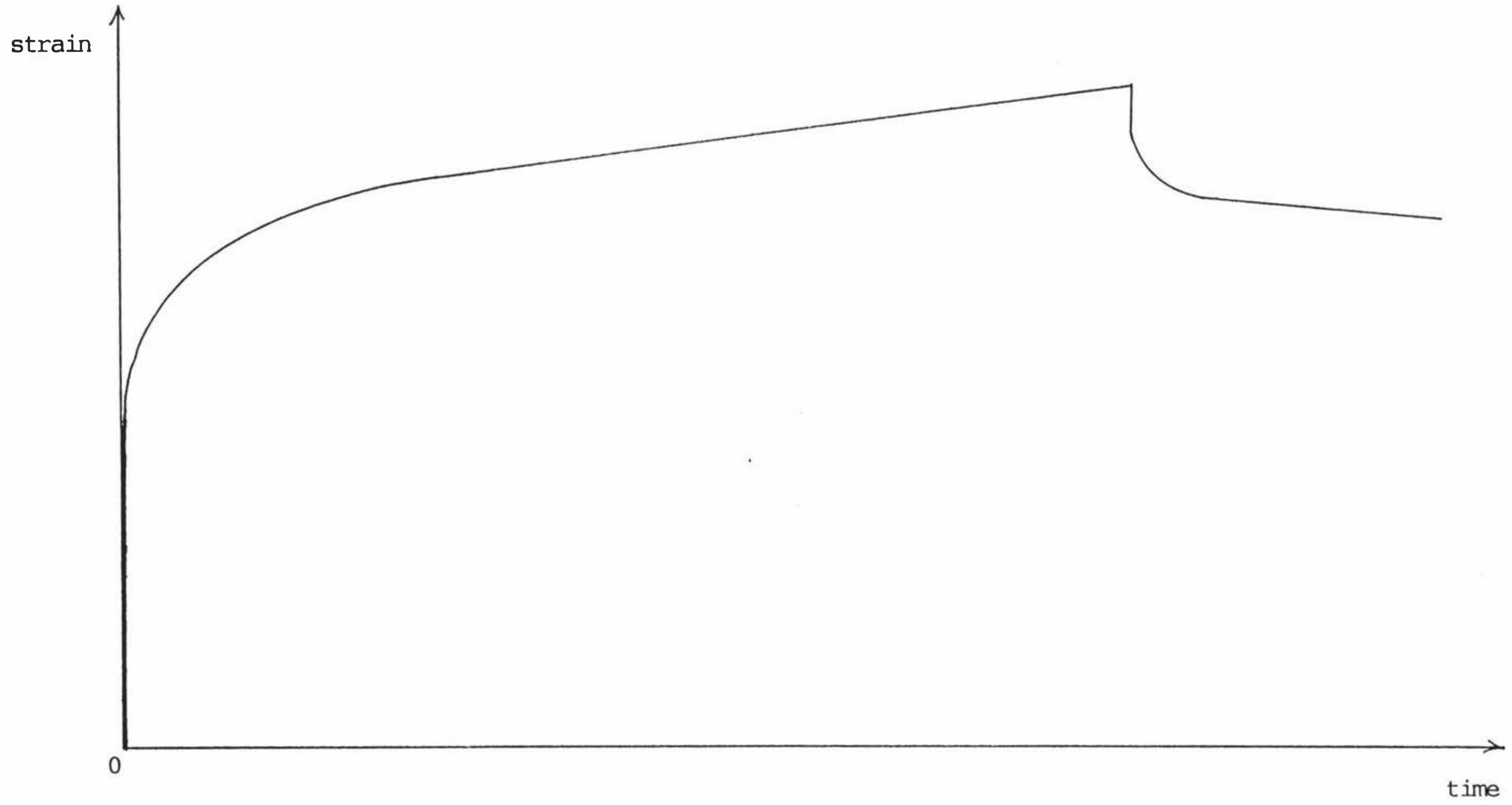


Figure 4.7: A creep and recovery curve.

The equation for creep behaviour based on this model is

$$J(t) = J_o + \Sigma J_i(1-\exp(-t/\tau_i)) + t/\eta_N \qquad (4.1)$$

where J(t) = the overall creep compliance, J_o = the instantaneous elastic response, J_i = the retarded elasticities, τ_i = the retardation times associated with the retarded elasticities, η_N = the viscous flow term and t = time.

This model has been used subsequently to analyse creep compliance data.

4.6.1.1 Graphical Analysis

Graphical analysis of creep compliance data was carried out using the method outined by Sherman (1966). This method is very similar to the techniques used by Datta and Morrow (1983) and Warburton and Barry (1968), and the method of succesive residuals mentioned by Mohsenin (1986).

In graphical analysis the instantaneous compliance can be taken directly from the curve (Fig 4.8), ie. the distance moved on the application of stress.

$$J_o = 1/E_o = \gamma_o/\sigma_o \qquad (4.2)$$

The Newtonian viscous term can be found from the linear portion of the curve (Fig. 4.8). Newtonian flow is proportional to the length of time stress has been applied in this region of the curve. The Newtonian compliance (J_N) = $\gamma_N(t)/\sigma = t/\eta_N$. γ_N is the shear strain in the linear region of the creep curve. In other words the slope of the linear portion of the curve = $1/\eta_N$.

The retarded elasticity (or elasticities) can be calculated once the viscous term and instantaneous response have been

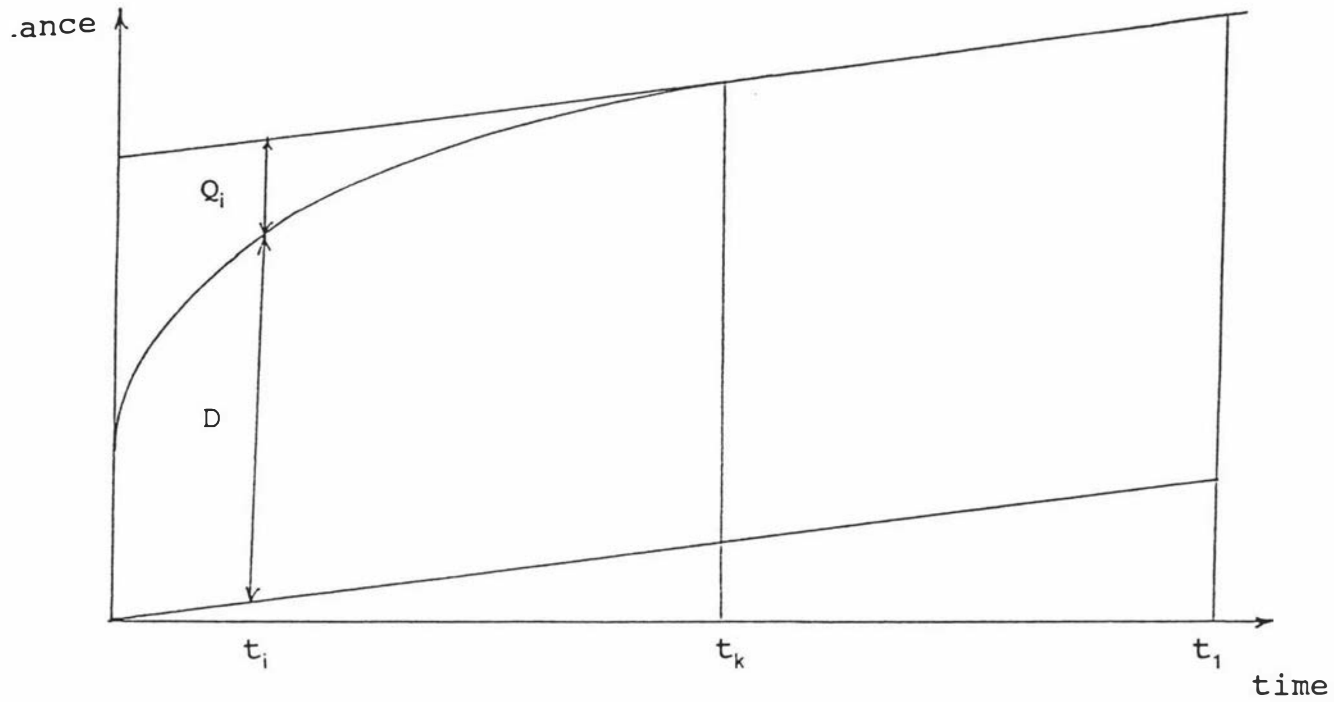


Figure 4.8a: A creep compliance curve showing the extrapolation of the linear portion of the curve back to 0 time, and a second line, starting at the origin, drawn parallel to the first.

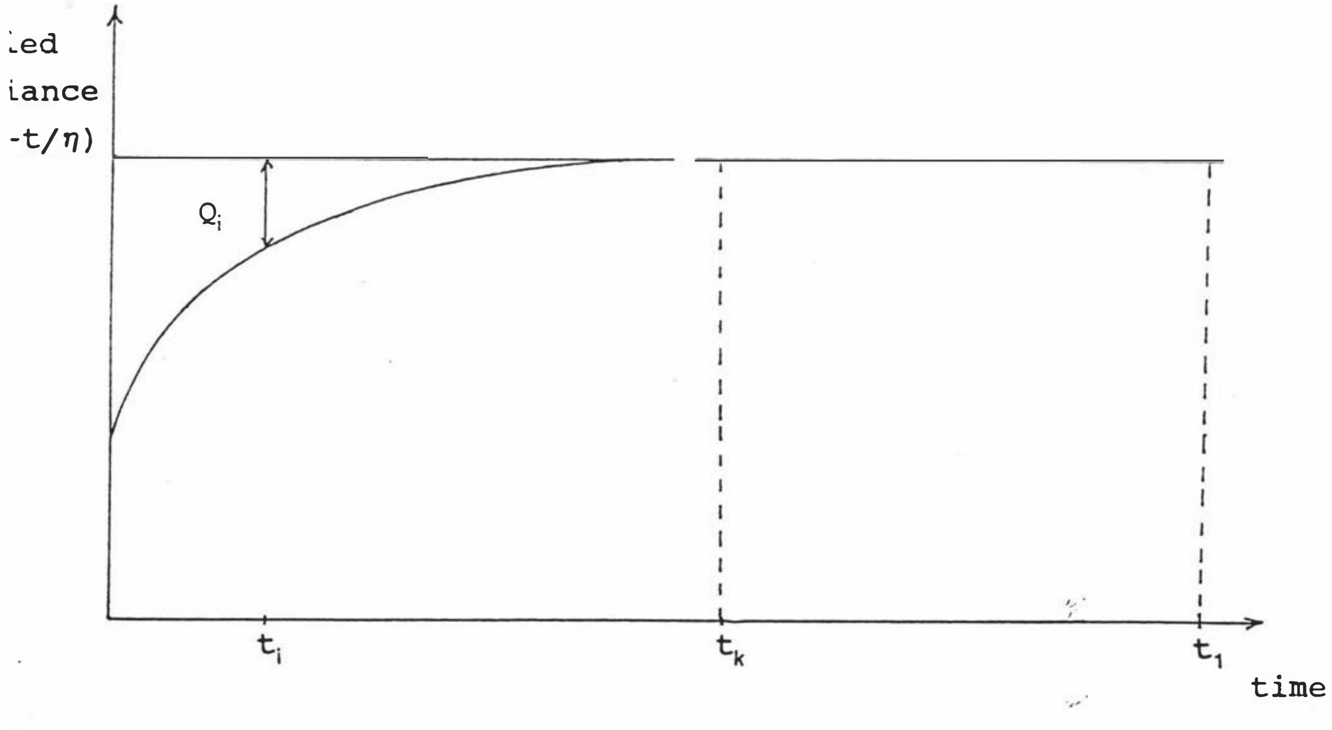


Figure 4.8b: The modified creep curve found after subtracting viscosity and Q ($Q = \Sigma J_R - \gamma_R(t)/\sigma$).

subtracted from the creep curve. The contribution of Newtonian flow is subtracted by extrapolating the linear portion of curve to the y axis. A second line is then drawn from the origin, parallel with the extrapolated line (Fig. 4.8a). Plotting the distances between the second line and the creep curve (eg. D, Fig. 4.8a) ($J(t)-t/\eta=J_0+\Sigma J_i(1-\exp(-t/\tau_i))$ gives a modified compliance, flat after time t_k.

The retarded compliance, J_r, can be written in its expanded form

$$J_r = \Sigma J_i (1 - \exp (-t/\tau_i) = Y_r(t)/\sigma \qquad (4.3)$$

If $$J_r - Y_r(t)/\sigma = Q \qquad (4.4)$$

then $$\Sigma J_i \exp(-t/\tau_i) = Q \qquad (4.5)$$

where Q represents the distance, at any time t, between the modified creep curve and the extrapolated linear portion of the modified compliance curve (Fig. 4.8b). This Q (Fig. 4.8b) is equivalent to the Q in Figure 4.8a.

On plotting ln Q against time a straight line should be obtained at large values of t (Fig. 4.9). The slope of the straight portion of the curve gives the time constant τ_1, while the intercept of the straight line and the ln Q axis gives the creep parameter J_1. As $\tau_{ret} = \eta_r / E_r$, η_1 can be calculated.

If the values of J_1 and τ_1 are inserted into Equation (4.3) and are found to inadequately describe the experimental curve, a second plot of $\ln(Q - J_1 \exp(-t/\tau_1)$ against time is required to determine magnitude of the second retardation time (τ_2) and J_2. The necessity of a second plot can also be ascertained if short time points in the first plot do not lie on the extrapolated straight line (Fig. 4.9). ($Q - J_1 \exp(-t/\tau_1)$ is the difference between the extrapolated line and the plot of ln Q vs. time.)

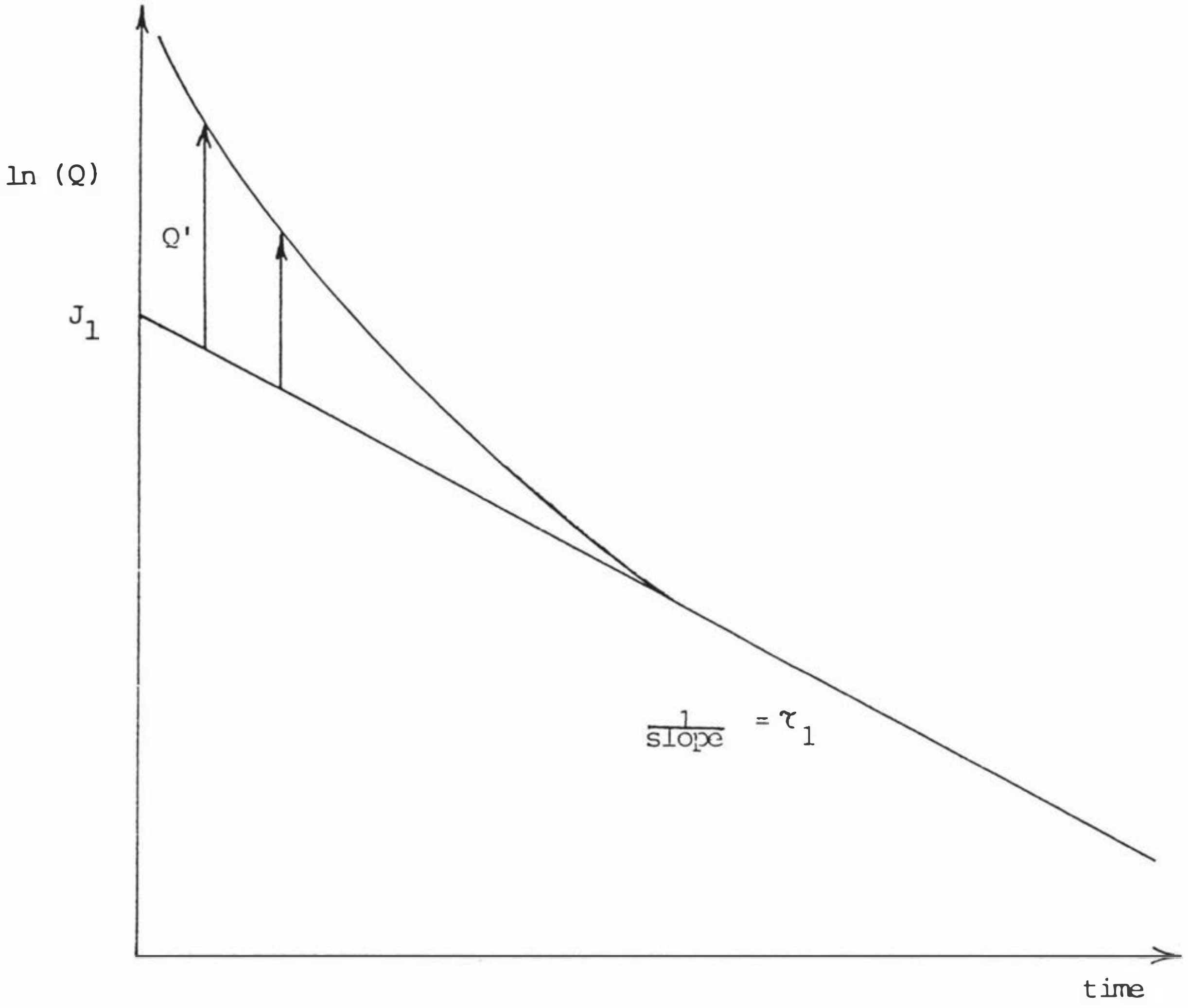


Figure 4.9: ln Q plotted against time showing the straight line portion of the graph extrapolated to 0 to give a value for J_1, the slope of the line giving τ_1. The graph also shows Q', where $Q' = \ln Q-(J_1(1-\exp(-t/\tau_1)$.

Should Equation (4.3) still fail to define the retarded elastic region of the curve, or all plotted points fail to lie on the extrapolated straight line, the procedure can be repeated (ie. by plotting $\ln(Q - J_1 \exp(-t/\tau_1) - J_2 \exp(-t/\tau_2))$ against time) until sufficient retardation times have been calculated for Equation (4.3) to represent adequately the experimentally determined curve (Sherman, 1968 and 1970).

4.6.1.2. Curve Fitting

An alternative method of analysing creep curves involves the use of a non-linear least squares curve fitting program (NONLIN) based on the Marquardt method (Marquardt (1963), Meeter (1964)). The program NONLIN fits the truncated data sets (Section 3) to a user defined model based on Equation 4.1 and obtains the values of J_o, J_i, τ_i, and η_N which give the best fit. The curve fitting program NONLIN and an example of the model used are presented in Appendix 1.

The number of exponential terms fitted by the computer program can be varied from two to five. Table 4.1 presents the creep compliance parameters obtained on fitting 2 - 5 exponentials to one set of experimental data.

As the number of exponential terms increase i), the model is able to fit the curve more closely, ii), the contribution of retarded compliances to the creep curve increases, iii), the contribution of viscosity to the creep curve decreases, and iv), the range of times increases. These effects are illustrated in Table 4.1.

The observed changes are not unexpected. As more exponential terms are imposed on one set of data the spread of times must increase to accommodate the extra terms. It should be noted a five fold increase in retardation time is necessary in order to distinguish between retardation mechanisms (Warburton and Barry, 1968). When five exponentials are fitted the long time

Table 4.1: The effect of varying the number of exponential terms used in fitting data to the prefined model. (Sample TUI August '86, 10^{o}C.)

	No. of exponential terms			
	2	3	4	5
J_o	9.0	7.3	6.7	6.4
J_1	23.6	11.4	6.7	4.2
τ_1	976	31	16	10
J_2	23.4	24.2	16.6	10.1
τ_2	1504	313	121	60
J_3	-	15.9	17.0	18.8
τ_3	-	3793	669	296
J_4	-	-	13.0	11.2
τ_4	-	-	5890	1528
J_5	-	-	-	10.7
τ_5	-	-	-	9220
η_N	32.7	43.9	51.4	61.0
ΣJ^a	42.3	58.8	60.0	61.5

(a) Sum of compliances.

<u>Units</u>

J_i x10^{-8} Pa^{-1}

η_N x10^{10} Pa.s

τ_i s

constants may become so large a region of viscous flow would not have been seen during the time taken for an experiment (15.5 hours). However, a viscous term is calculated by the program, suggesting a five expontial model may be inappropriate.

The insertion of additional exponential terms also increases creep due to compliance at the expense of creep due to viscous flow, resulting in an increased sum of compliances (and an increased viscosity).

4.6.1.3. Discussion of Curve Analysing Methods

Although the graphical analysis method of calculating exponential terms is claimed to be very accurate (Mohsenin, 1986), one disadvantage of this approach is the uncertainty involved in establishing when the curve has become linear and thus ascertaining and subtracting the viscous term. This would affect the first set of parameters found.

A second problem associated with graphical analysis occurs in some cases, with the retardation times ceasing to be distinguishable, as the effect of one retardation mechanism would not have died out completely before the next commenced. (This has been remarked upon previously, a five fold increase in time is neccesary before it becomes possible to distinguish between retardation mechanisms.) These times are marked with * in Table 4.2.

Aside from the problems mentioned above, manual graphical analysis is tedious and, at short times, is prone to large errors.

The problem of deciding when a creep curve has become linear is avoided with the use of the non-linear least squares curve fitting program. The viscosity value found by the program is the value which best fits the data and the model.

Parameters obtained by curve fitting three and four retardation mechanisms and results from graphical analysis for the same samples are presented in Table 4.2.

The J_o value found by both methods is similar. As graphical analysis takes the J_o value directly from the creep curve this indicates the value found by the curve fitting program is close to the instantaneous compliance response observed.

Retardation times calculated by the two methods are not in good agreement, with the curve fitting results at long times suggesting that for graphical analysis the curve was assumed to be linear too soon. Problems with the distinguishability of times has been mentioned previously.

Individual retarded compliances are not similar, however, the overall sum of compliances found by the two methods is in good agreement.

Viscosities found are of the same order, with the curve fitted viscosities being slightly less than those from graphical analysis.

While both methods give similar indications of J_o, overall retarded compliance responses and visc osities, the retardation times found are different. Computerized curve fitting, which does not require a decision on where a curve becomes linear has more advantages, compared with the method of graphical analysis. Consequently computerised curve fitting using the non-linear least squares curve fitting progarm, NONLIN, has been used throughout this work.

While graphical analysis indicates the presence of four retardation mechanisms in practice these a), may not be distinguishable and b), in the case of the fourth retardation mechanism, the values obtained may be influenced by assumptions about the linearity of the curve under

Table 4.2: Parameters fitted to creep compliance data by two methods, exponential peeling and non-linear curve fitting.

			MANIX			MANJX
	Graph.	Curvefit (3)#	Curvefit (4)	Graph.	Curvefit (3)	Curvefit (4)
J_o	8	10 (.3)	9 (.3)	9	9 (.3)	8 (.3)
J_1	7	17 (.7)	13 (.5)	17	18 (.7)	9 (.6)
τ_1	6s	34s (10)	24s (7)	42s*	29s (1)	11s (1)
J_2	19	26 (.7)	22 (.9)	18	31 (.8)	20 (.8)
τ_2	69s	400s (50)	197s (20)	158s*	228s (18)	77s (7)
J_3	19	16 (.8)	14 (.9)	16	21 (.5)	27 (.8)
τ_3	461s	6264s (600)	1277s (120)	529s*	3213s (400)	504s (50)
J_4	19	-	26 (10)	22	-	17 (.5)
τ_4	3345s	-	-**	2885s	-	4445s (200)
η_N	37	27 (2)	-**	33	29 (1)	31 (1)
ΣJ	72	69 (3)	86 (13)	74	79 (2)	81 (3)

Number of retardation mechanisms fitted.

* Retardation mechanisms which would not be clearly distinguishable as the retardation times are not adequately separated.

** Parameters not fitted.

() Standard error.

<u>Units</u>

J_o, J_i, ΣJ $\times 10^{-8}$ Pa^{-1}
η_N $\times 10^{10}$ Pa.s
τ_i s

consideration. After considering the results for a number ofsamples it seemed more appropriate to fit only three retardation mechanisms. Three retardation times have been used consistently throughout this work to analyse initial creep responses. Other workers have used from one to four exponentials to analyse creep curves (Chapter 1, Table 1.1).

In the course of experimentation it was found a three exponential model did not fit curves obtained from the creep portion of the second or any subsequent load cycle. Only one or two retardation mechanisms seem to be present and subsequently, curves obtained from a second (or third etc.) application of stress have had two retardation mechanisms fitted.

4.6.2. Recovery Curves

A recovery curve is observed after the removal of stress (Fig. 4.10). The instantaneous elastic recovery (J_{oR}), the sum of the elastic compliances (ΣJ_{iR}) and an apparent viscous term (η_{NR}) indicative of permanent deformation can be taken directly from the curve.

The instantaneous elastic recovery is found as for J_o as outlined above (Section 6.1.1). The sum of the elastic compliances recovered is the total distance recovered (Fig. 4.10). The apparent viscous term is calculated from the unrecovered portion of the creep curve. Viscosity is equal to the stress multiplied by the time at which the stress was removed divided by the unrecovered strain. The unrecovered strain is also shown in Figure 4.10.

4.6.3. Presentation of Results

Analysis of creep data by the curve fitting program NONLIN presents results as shown in Figure 4.11.

Retardation times are presented as compliance divided by time. These values can be converted to seconds by multiplying by the appropriate compliance term, ie. $\tau_i = J_i$ x calculated term.

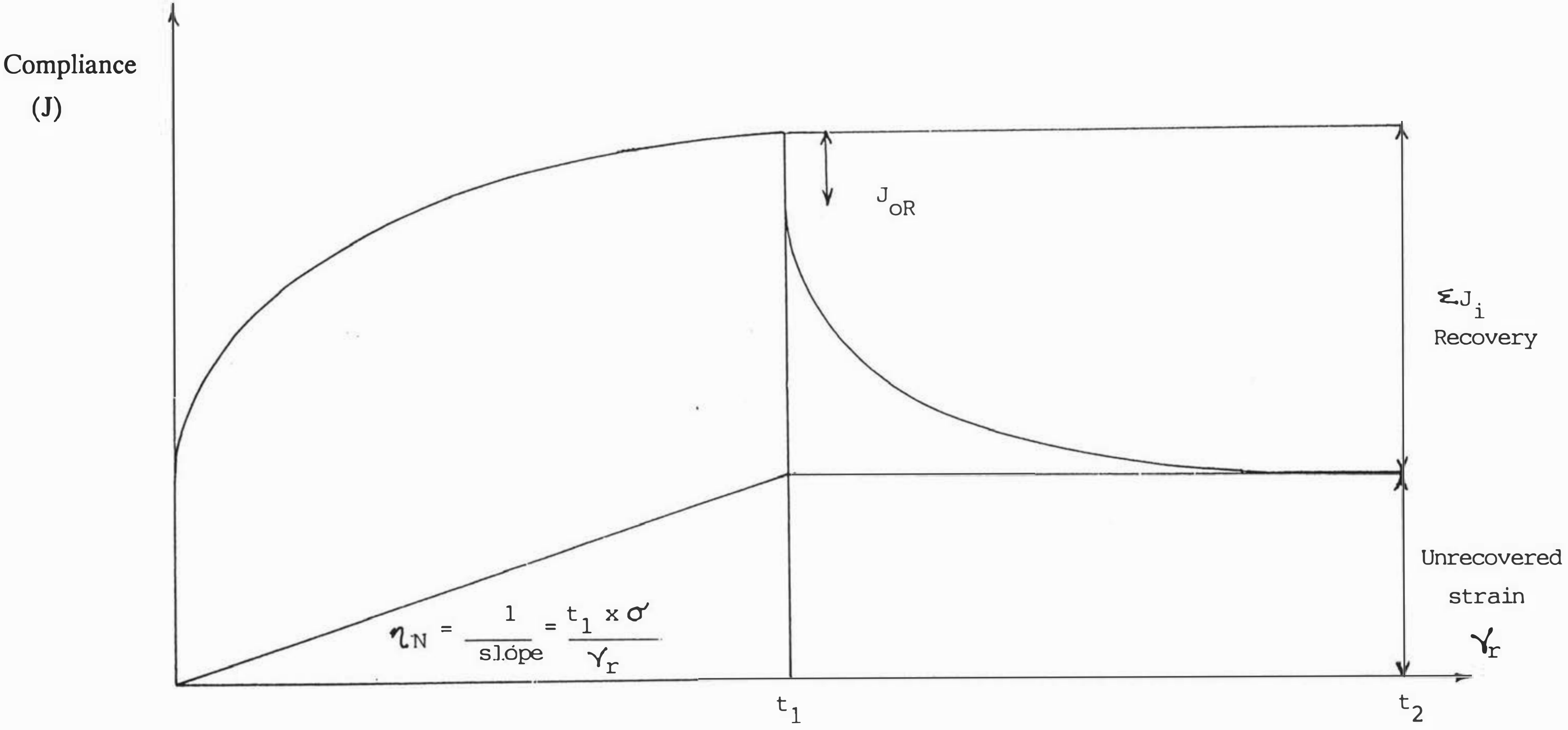
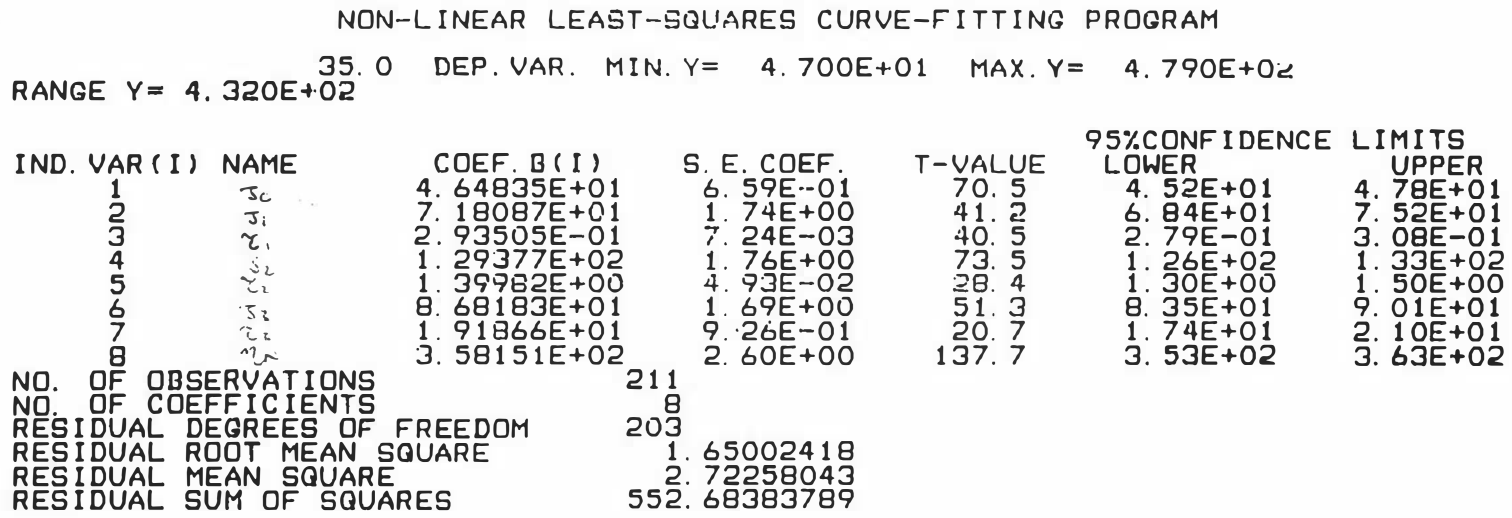


Figure 4.10: Creep and recovery curves showing instantaneous compliance, J_{oR}, the sum of compliances recovered, J_{iR} and the unrecovered strain, γ_r.



```
                   NON-LINEAR LEAST-SQUARES CURVE-FITTING PROGRAM

                  35. 0   DEP. VAR.  MIN. Y=   4. 700E+01   MAX. Y=   4. 790E+02
RANGE Y= 4. 320E+02

                                                              95%CONFIDENCE LIMITS
IND. VAR(I) NAME        COEF. B(I)     S. E. COEF.    T-VALUE   LOWER          UPPER
     1       Jc       4. 64835E+01     6. 59E-01     70. 5     4. 52E+01     4. 78E+01
     2       Ji       7. 18087E+01     1. 74E+00     41. 2     6. 84E+01     7. 52E+01
     3       τ1       2. 93505E-01     7. 24E-03     40. 5     2. 79E-01     3. 08E-01
     4       J2       1. 29377E+02     1. 76E+00     73. 5     1. 26E+02     1. 33E+02
     5       τ2       1. 39982E+00     4. 93E-02     28. 4     1. 30E+00     1. 50E+00
     6       J3       8. 68183E+01     1. 69E+00     51. 3     8. 35E+01     9. 01E+01
     7       τ3       1. 91866E+01     9. 26E-01     20. 7     1. 74E+01     2. 10E+01
     8       mr       3. 58151E+02     2. 60E+00    137. 7     3. 53E+02     3. 63E+02
NO.  OF OBSERVATIONS                211
NO.  OF COEFFICIENTS                  8
RESIDUAL DEGREES OF FREEDOM         203
RESIDUAL ROOT MEAN SQUARE             1. 65002418
RESIDUAL MEAN SQUARE                  2. 72258043
RESIDUAL SUM OF SQUARES             552. 68383789
```

Figure 4.11: Result presentation by the curve fitting program NONLIN.

The viscous term η_N, an indication of the viscous response, and the sum of the compliance values, ΣJ, an indication of the elastic response, have been found to be most useful in the discussion of creep compliance behaviour. The instantaneous compliance term, J_o, also gives a good indication of creep response.

In general only J_o, ΣJ and η_N values will be given in the text, with full results included in the appropriate appendix. However, where it is warranted, all parameters will be reported.

4.6.4. Retardation Spectra

A retardation spectrum ($L(\tau)$) is a continuous spectrum of retardation times, usually found by plotting $L(\tau)$ against log time. Retardation spectra offer an alternative way to view raw data from creep compliance experiments. Retardation spectra are introduced in Chapter One, Section A.6.1.1.3 and give an insight into the number of retardation times present and their contribution to the observed creep response.

$L(\tau)$, or continuous retardation spectra can be calculated from data obtained from creep compliance experiments using the second order approximation of the inverse Laplace transform,

$$L(\tau) = (d/d\ln t)\,[J(t)-dJ(t)/d\ln t]_{t=2\tau} \qquad (4.6)$$

An ideal viscoelastic material, whose creep behaviour can be described by the classic equation (Equation (4.1) above), and which has distinguishable retardation times would have a smooth continuous retardation spectrum with a well defined peak at each retardation time. An 'ideal' creep curve was calculated from NONLIN parameters for the sample MAN May 87 (Table 4.2). Figure 4.12 shows the continuous retardation spectrum ($L(\tau)$) calculated using Equation (4.6) for the ideal creep curve. The spectrum exhibits three retardation mechanisms.

A computer program, RETARD (Appendix 1), was written in Pascal to calculate retardation spectra. First and second order derivatives of the creep function were calculated using equations outlined by Fox and Maynes (1968) ie.

$$df/dx=1/12h[f(xo-2h)-8f(xo-h)+8f(xo+h)-f(xo+2h)] \qquad (4.7)$$

and

$$d^2f/dx^2=1/12h^2[-f(xo-2h)+16f(xo-h)-30f(xo)+16f(xo+h)-f(xo+2h)] \qquad (4.8)$$

The retardation spectrum obtained for raw data (sample MAN May 87) on plotting $L(\tau)$ against ln time gave a very jagged spectrum (Fig. 4.13), in sharp contrast with the ideal spectrum shown in Figure 4.12.

In an effort to obtain a smoother retardation spectrum data was smoothed using a convoluting, smoothing function mentioned by Savitzky and Golay (1964). Subsequently this data was differentiated as outlined above. This procedure was included in the computer program RETARD.

Figure 4.14 illustrates the spectrum obtained for raw data after smoothing and differentiating while Figure 4.15 shows an ideal spectrum after similar treatment. The spectrum obtained for raw data is still very rough, containing no apparent maxima. The spectrum shows very little improvement on the spectrum found for unsmoothed data. Smoothing does not seem to have affected the ideal spectrum.

The data was differentiated using an alternative method suggested by Savitzky and Golay (1964). Differentiation was carried out using a simplified least squares method. The number of points used in the differentiation, and the degree of polynomial are selected by the user. The differentiation

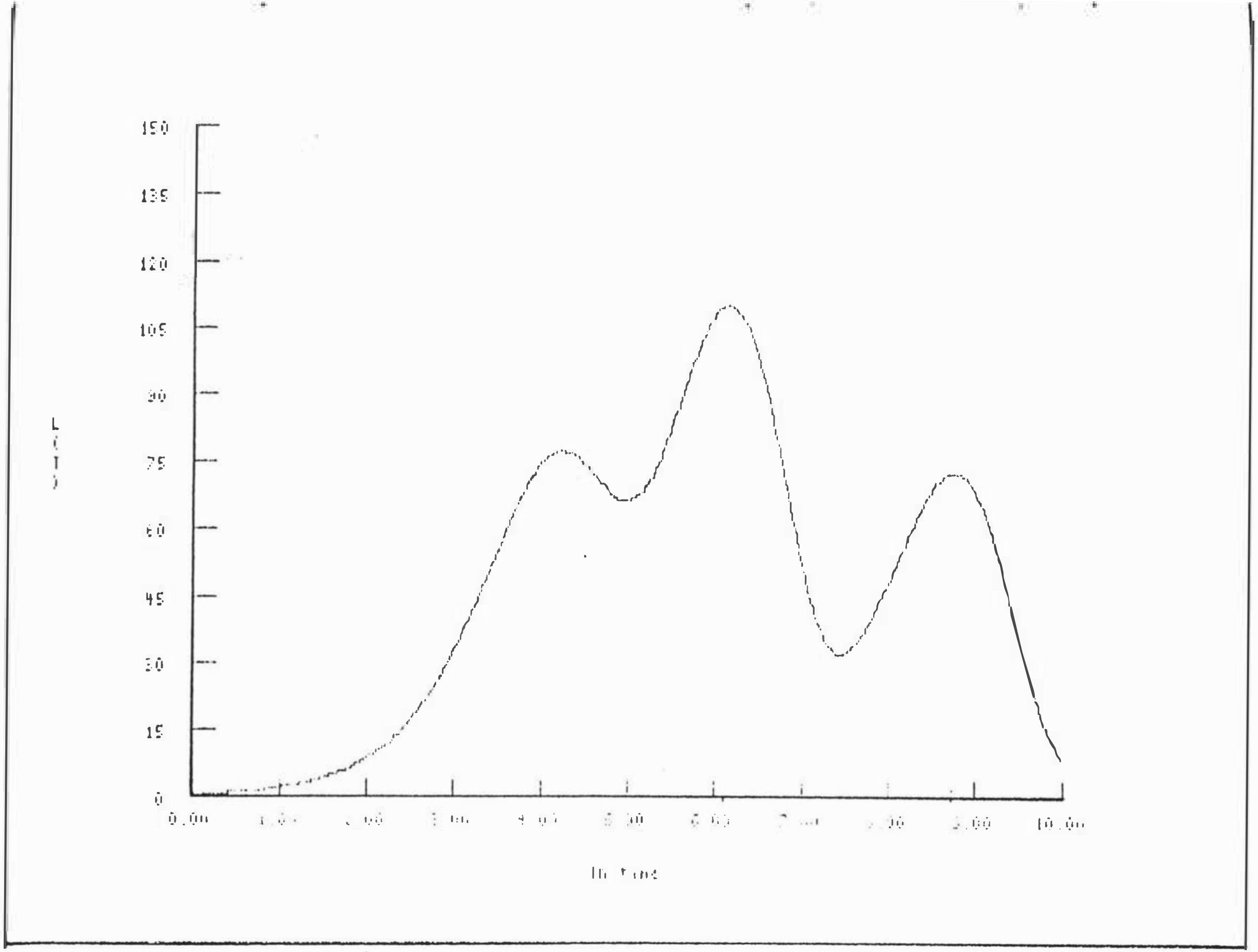


Figure 4.12: An ideal continuous retardation spectrum calculated for the sample MAN May 1987 from the following parameters: J_o $9x10^{-8}$, J_1 $18.2x10^{-8}$, J_2 $33.1x10^{-8}$, J_3 $21x10^{-8}$ (Pa^{-1}), τ_1 29s, τ 228s, τ 3123s, η $29x10^{10}$ Pa.s.

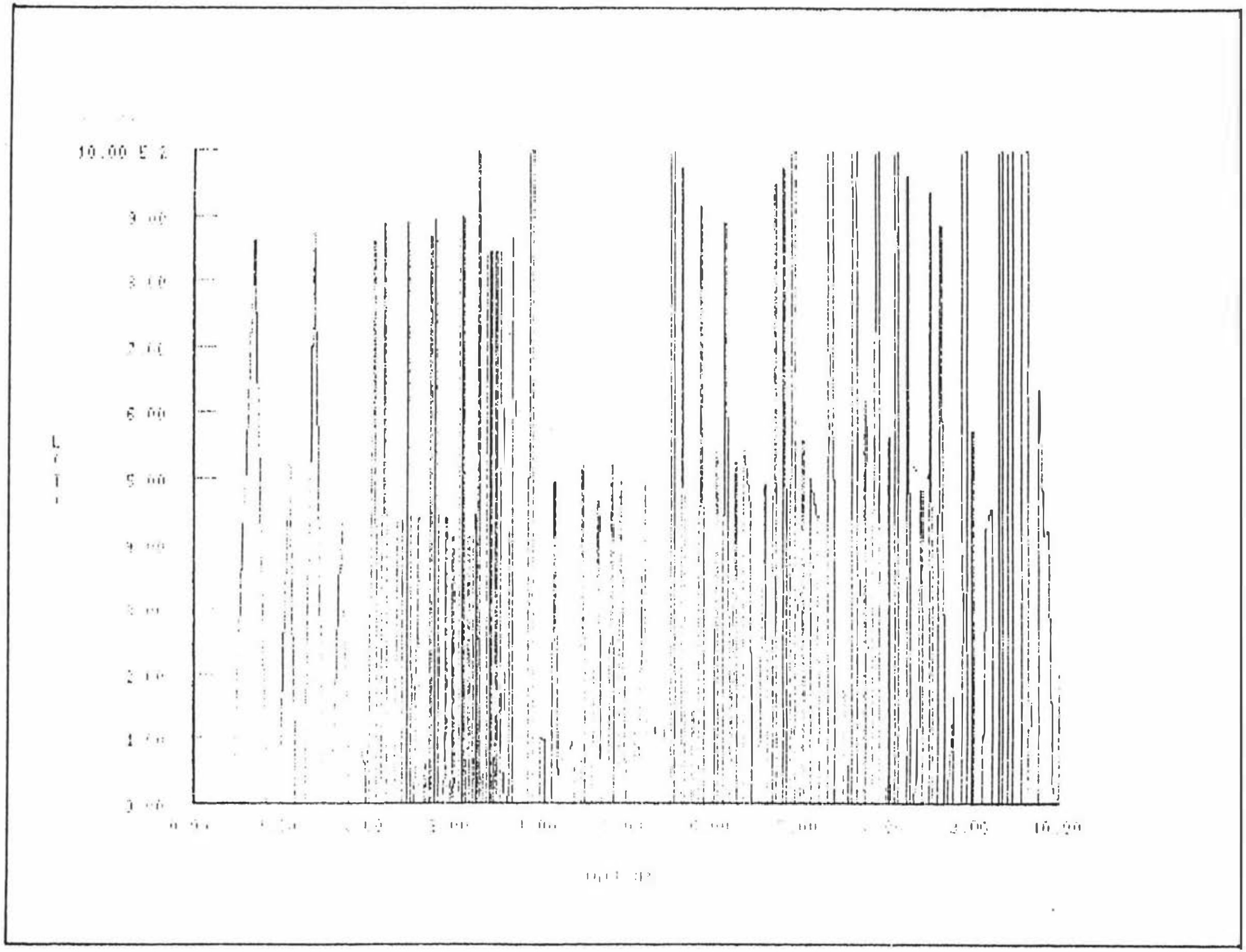


Figure 4.13: Retardation spectrum found for the sample MAN May 1987 using raw data only.

procedure was included in a computer program, SandD (Appendix 1).

The spectra obtained for raw data and the ideal data are shown in Figures 4.16 and 4.17. Once again the spectrum obtained for raw data is unlike that found in the ideal case. However, the spectrum obtained for the raw data is closer to that of a (smooth) curve, with identifiable maxima.

Increasing the number of points used in differentiation had little effect on the spectra. Figure 4.17 shows the spectrum found for the ideal data after a seven point cubic differentiation. Figure 4.18 shows the spectrum found after a thirteen point differentiation was carried out on the same data. Differentiation by the method of Savitzky and Golay seems to move spectra to the left as can be seen if Figures 4.17 and 4.18 are compared to Figure 4.12 (where the retardation spectrum was obtained using Equation (4.7) and (4.8) above).

Increasing the degree of polynomial also had little effect. This can be seen on comparing Figure 4.17, a seven point cubic differentiation with Figure 4.19, a seven point quartic calculated using the same (ideal) data.

A fourth alternative involved plotting data which has been both smoothed and differentiated by the methods of Savitzky and Golay. (The smoothing function is included in SandD.) Retardation spectra calculated in this manner show a vast improvement on those found previously. Figure 4.20 shows a spectrum found for raw data, and Figure 4.21, the spectrum found for ideal data. The retardation spectra found for a second sample, MAN April 87, is shown in Figure 4.22, with the ideal spectrum calculated from parameters obtained from curve fitting in Figure 4.23.

From curves such as those shown in Figures 4.20 and 4.22 a reasonable indication of the actual retardation spectra can be

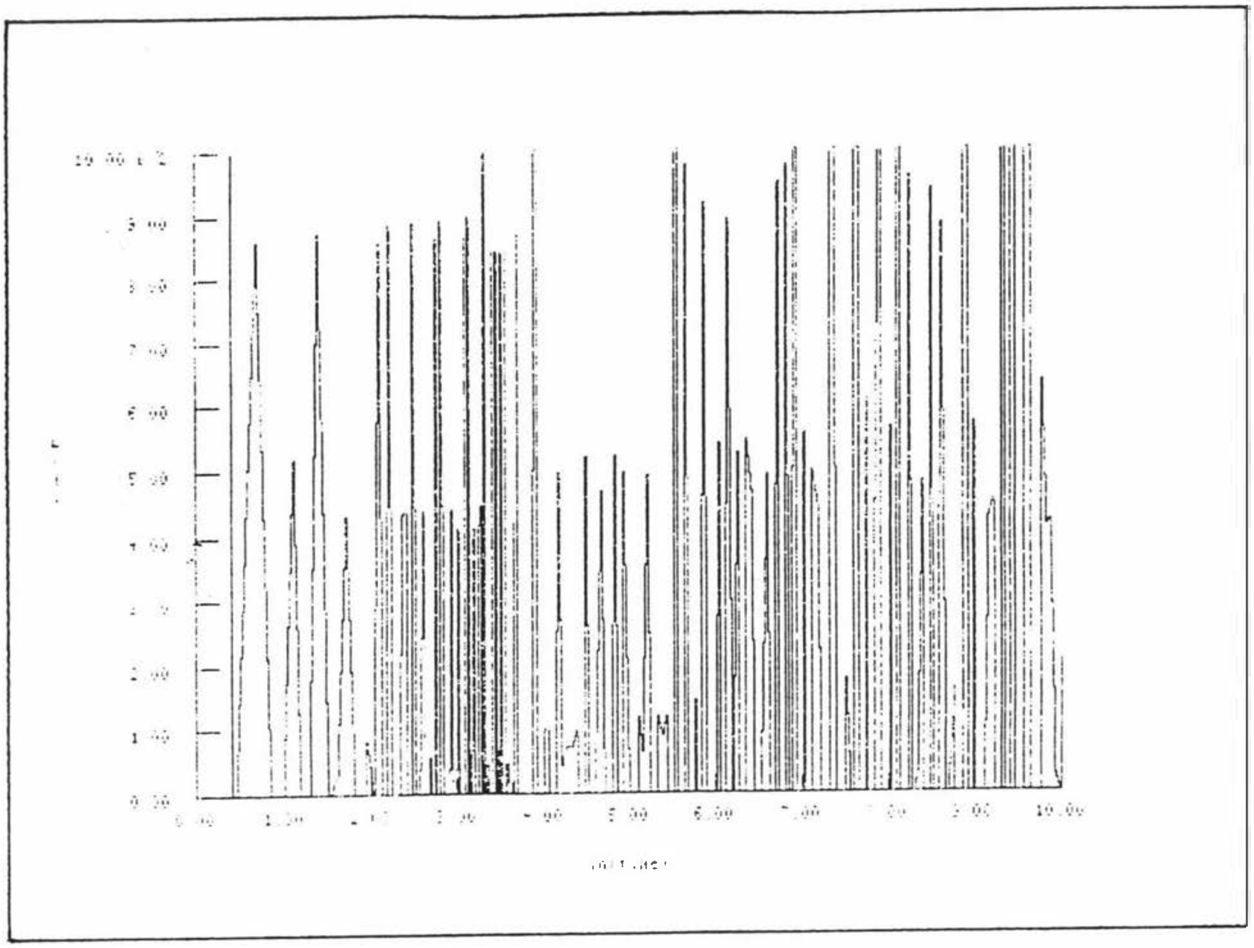


Figure 4.14: Continuous retardation spectrum found for MAN May 1987 after smoothing raw data.

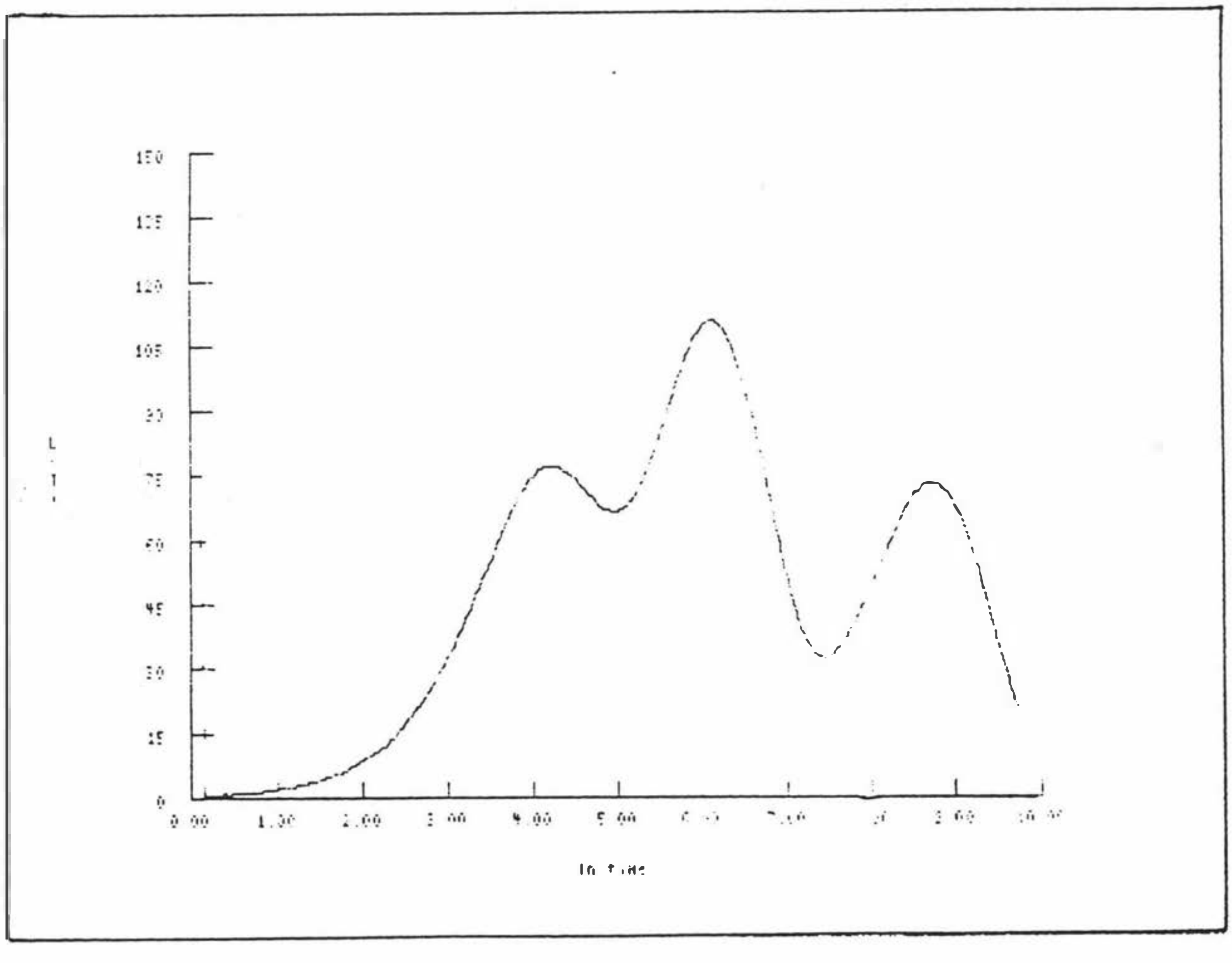


Figure 4.15: The ideal continuous retardation spectrum found for MAN May 1987

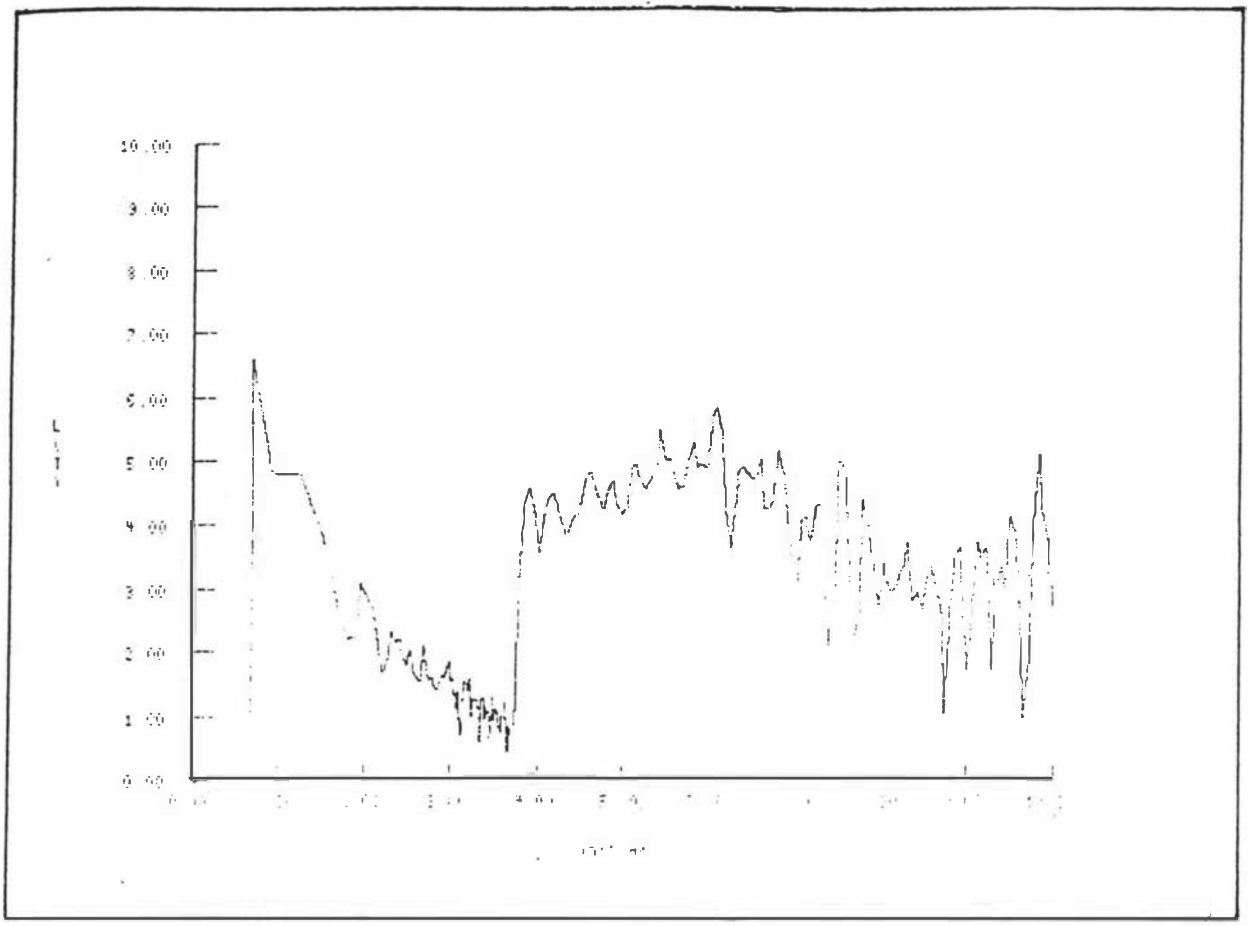


Figure 4.16: The continuous retardation spectrum found for MAN May 1987 after differentiating the raw data (Savitzky and Golay, 1964).

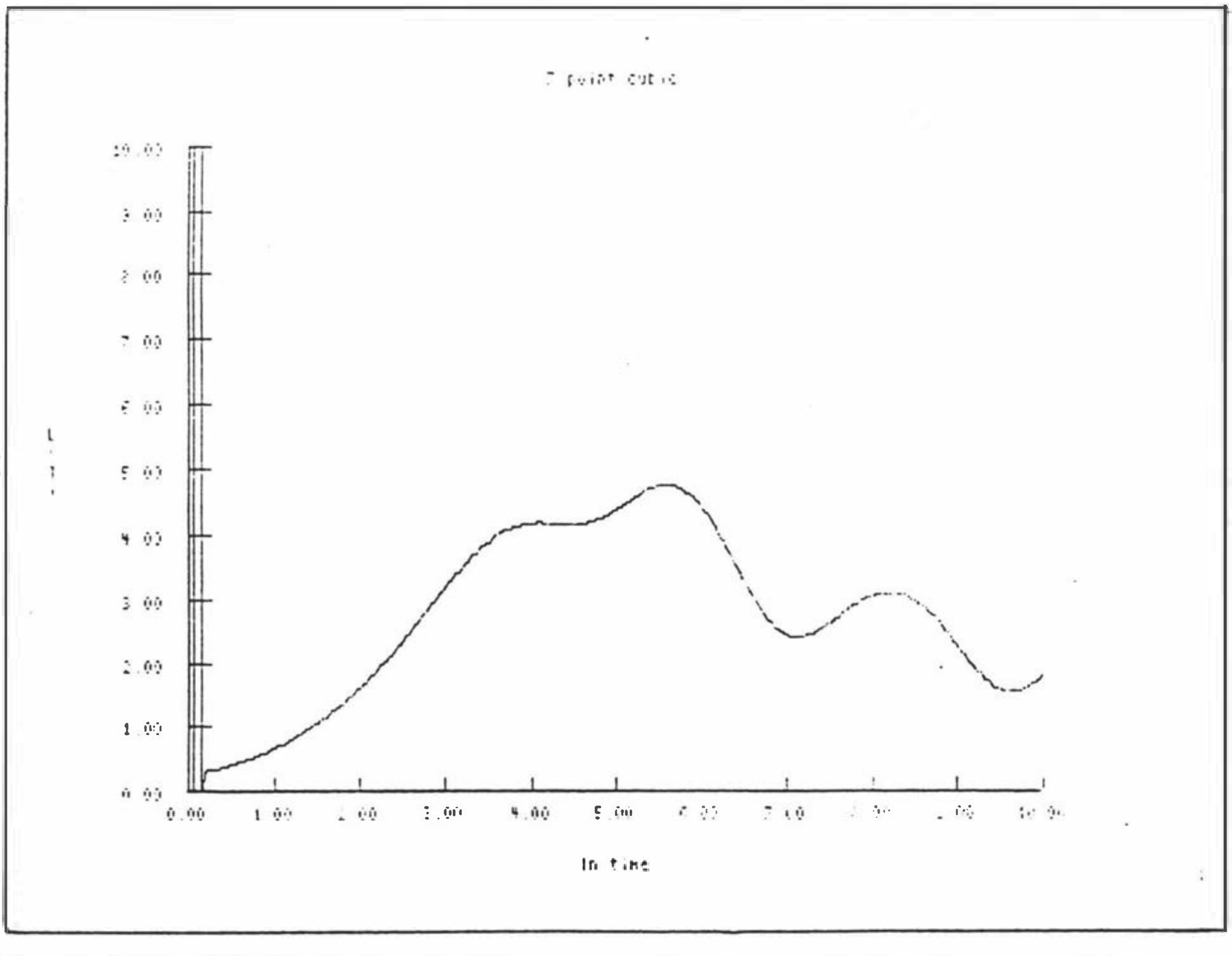


Figure 4.17: The ideal continuous retardation spectrum found for MAN May 1987

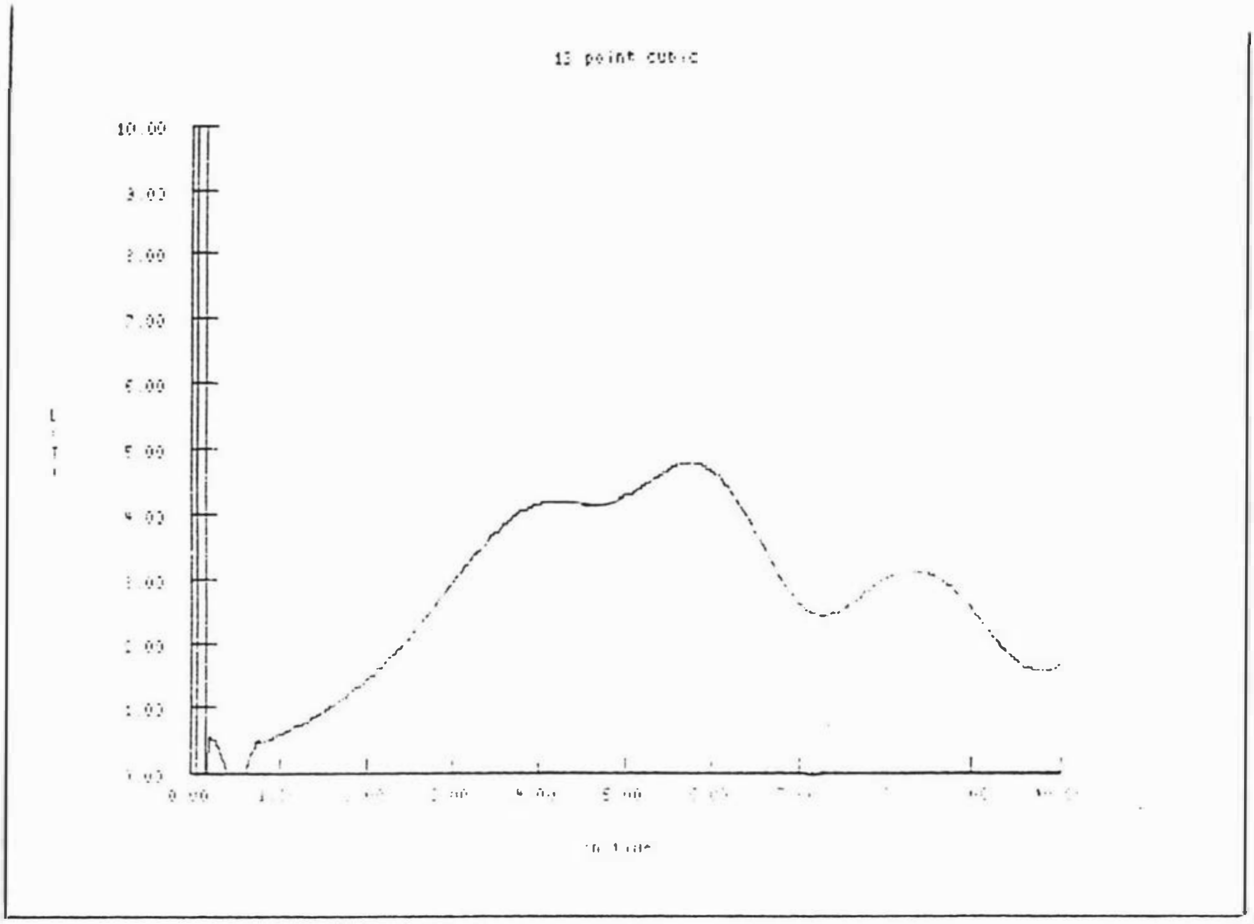


Figure 4.18: The ideal continuous retardation spectrum found for MAN MAy 1987 after a 13 point cubic differentiation.

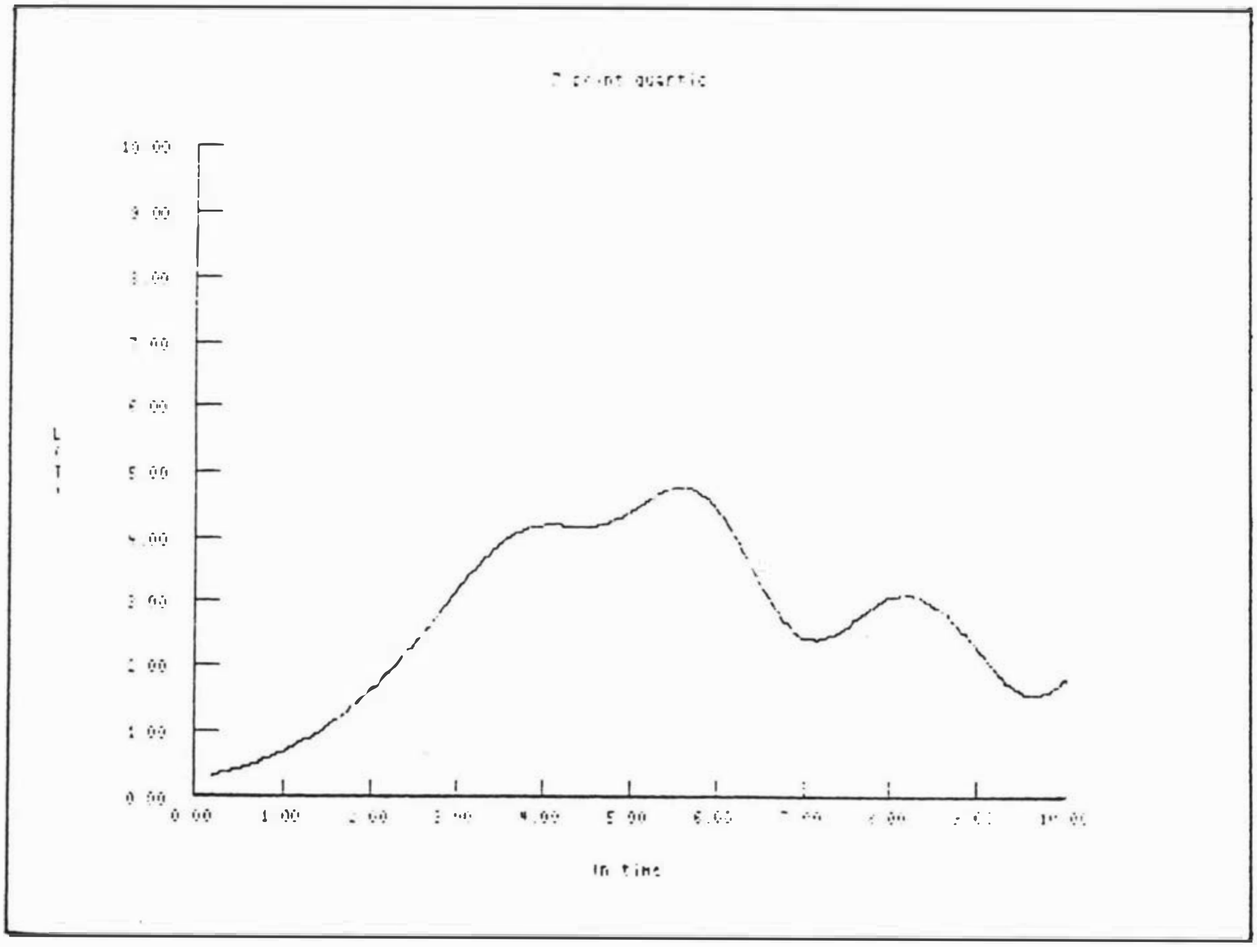


Figure 4.19: The ideal continuous retardation spectrum found for MAN May 1987 after a 7 point quartic differentiation.

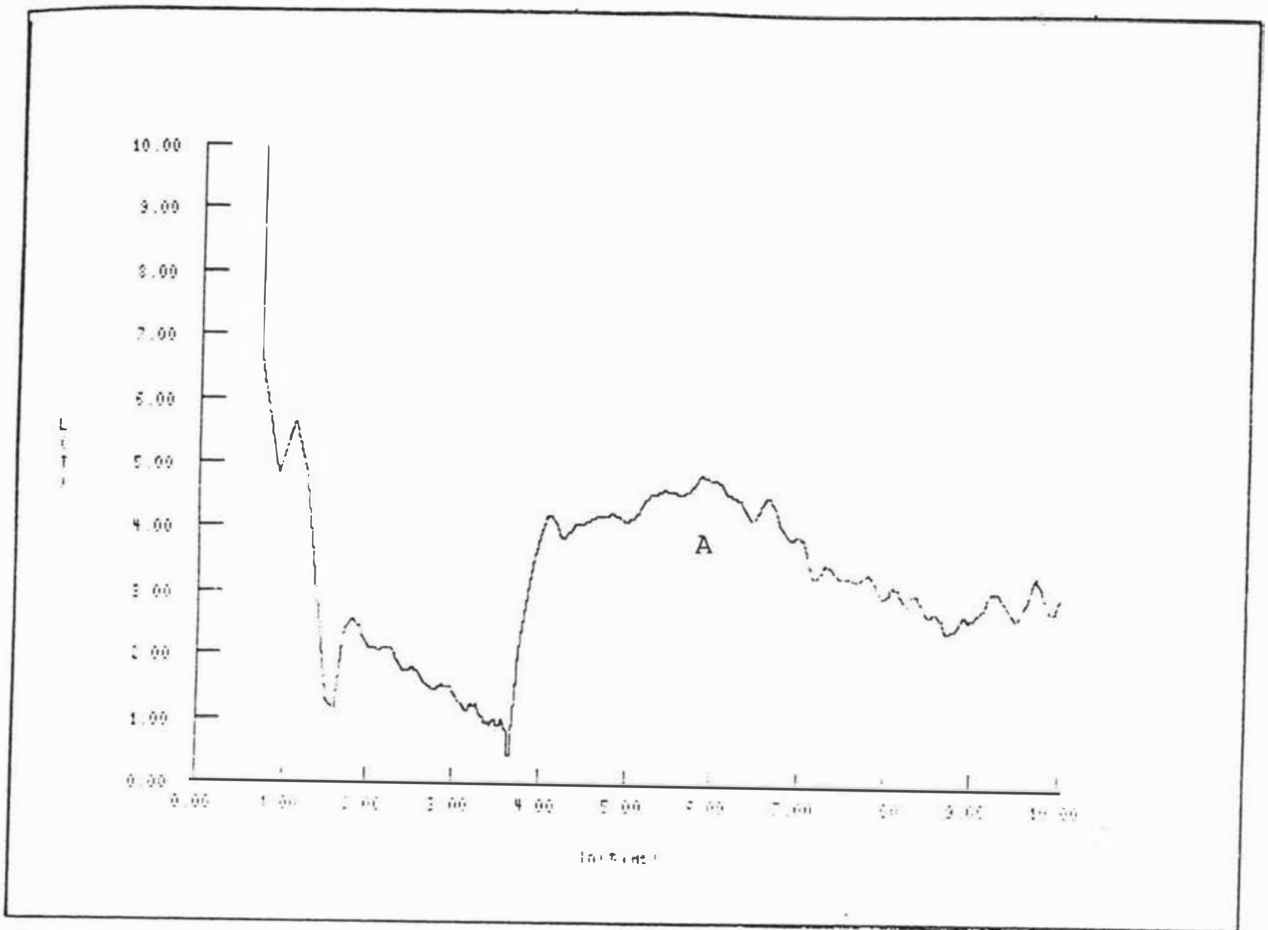


Figure 4.20: The continuous retardation spectrum found for MAN May 1987 after smoothing and differentiating according to the method of Savitzky and Golay (1964)

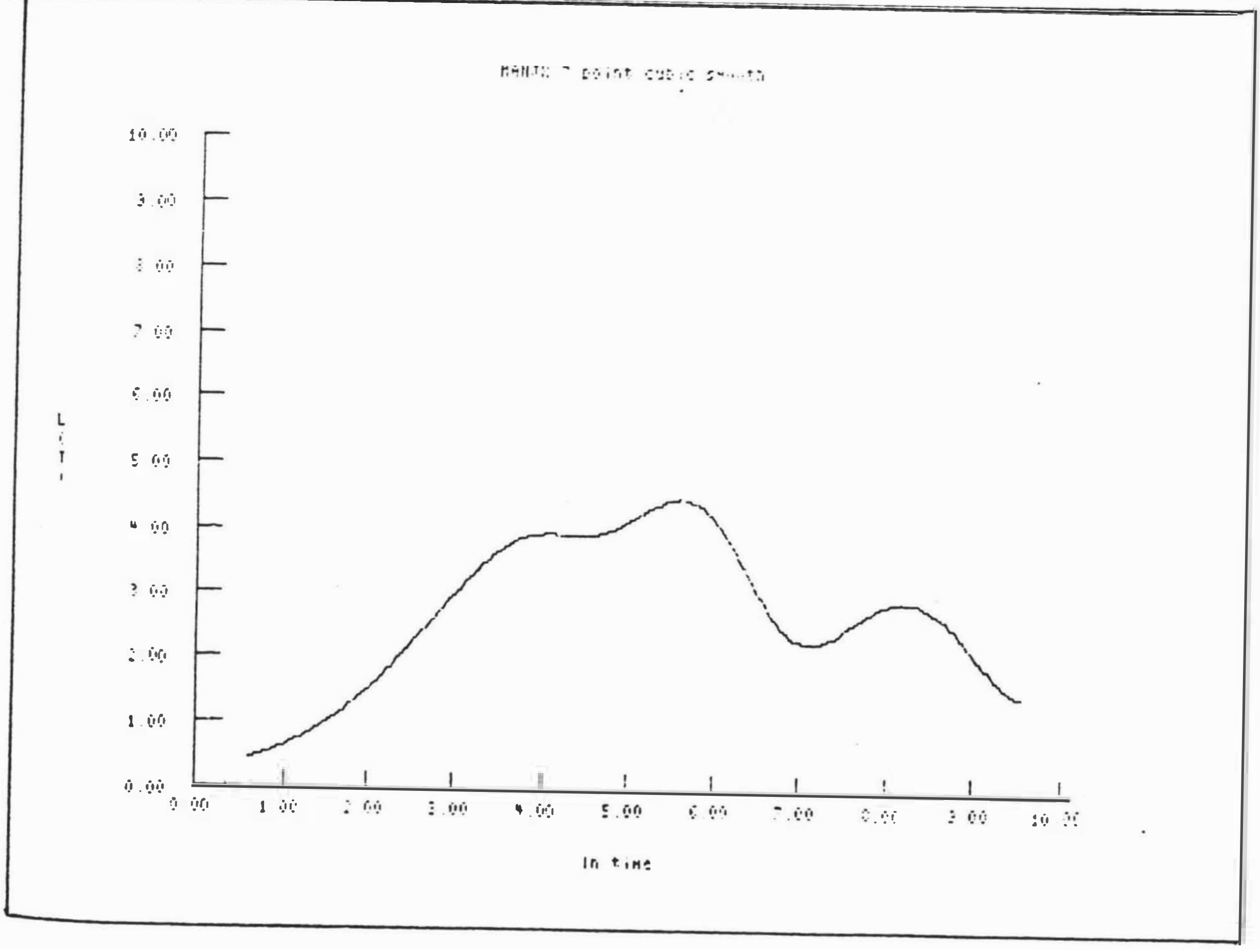


Figure 4.21: The ideal continuous retardation spectrum found for MAN May 1987 after smoothing and differentiating according to the method of Savitzky & Golay.

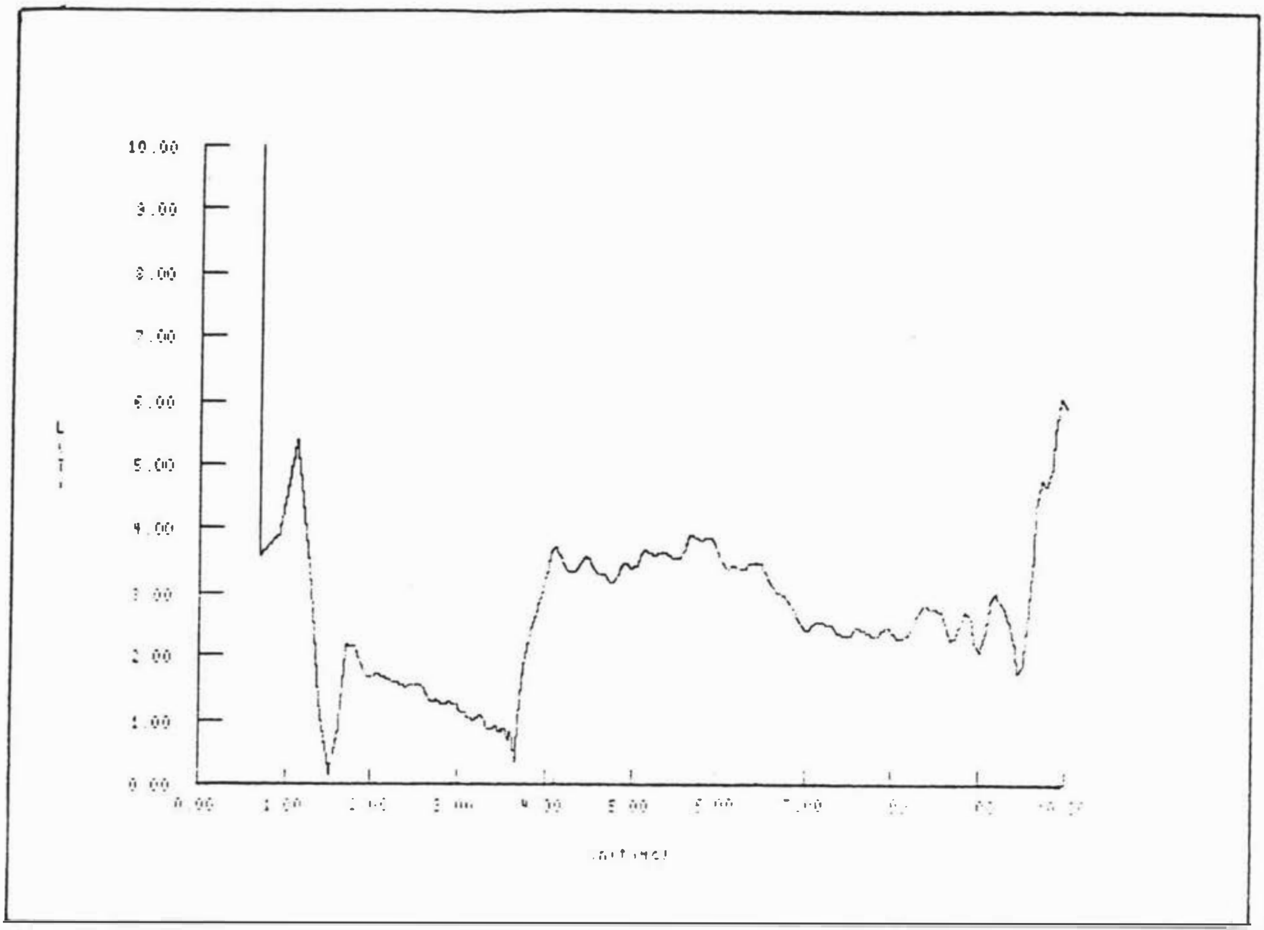


Figure 4.22: The continuous retardation spectrum found for the sample MAN April 1987, smoothing and differentiating according to Savitzky and Golay.

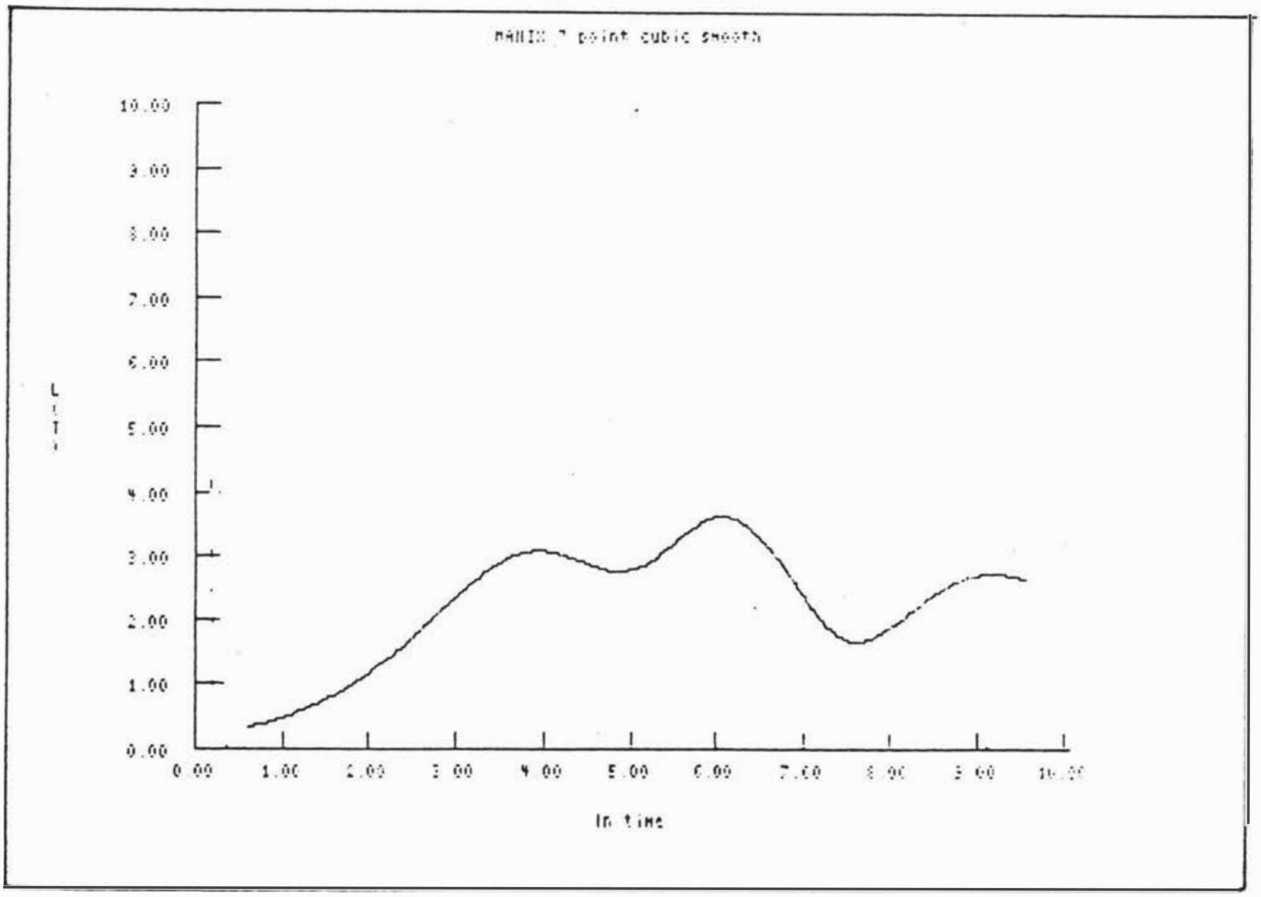


Figure 4.23: The ideal continuous retardation found for MAN April 1987 on smoothing and differentiating according to the methods of Savitzky and Golay. Parameters: J_o 9.7x10^{-8}, J_1 17.3x10^{-8}, J_2 25.6x10^{-8}, J_3 15.9x10^{-8} (Pa^{-1}), τ_1 34s, τ_2 374s, τ_3 6264s, η_o 27x10^{10} Pa.s.

obtained. The complex nature of the spectra makes them difficult to interpret, however, the retardation spectra found for raw data after smoothing and differentiating offers some evidence for the existence of three or four main groups of retardation mechanisms between the times of 0 and 10000 seconds.

The region between ln time 0 and 3.5 is thought to be due to the instantaneous compliance response. This is followed by a sudden, marked increase at ln time 3.5 (22 s), after which a number of individual retardation times contribute to the resultant curve. It has been found in some cases peaks are better defined than in others. The rise at long times seems to be a function of the differentiation method of Savitzky and Golay, rather than an indication of a real maximum. This can be seen on comparing Figures 4.12 and 4.22, for example.

The series of peaks seen in the spectra seem to represent groups of times. Attempts can be made to obtain retardation times from the spectra. Assuming the marked increase at ln time 3.5 to be the first retardation time (22 s), and taking into account a spacing of five times the previous time is necessary before the next time can be seen, a second time can be postulated between 100 - 200 seconds. The contribution of retardation mechanisms operating between 20 and 200 seconds accounts for the major region marked A in Figure 4.20. Third (and fourth) peaks may exist, giving further retardation times.

The appropriateness of the viscoelastic model can be checked by comparing line spectra with continuous spectra (Chapter 1, Section A.6.1.1.3). A comparison of the continuous spectra found (Figs. 4.20 and 4.22) with the ideal or line spectra calculated using the parameters fitted by the program NONLIN (Section 6.1.2) (Figs. 4.21 and 4.23) for the two above samples (MAN May 87 and MAN April 87), shows the two different types of spectra do not look too dissimilar.

Table 4.3: A comparison of retardation times calculated by a least squares curve fitting program (NONLIN) and taken from continuous retardation spectra, Figures 4.20 and 4.22.

	MAN April 87		MAN May 87	
	Ret'n	NONLIN	Ret'n	NONLIN
$\tau 1$ (s)	30	34	27	29
$\tau 2$ (s)	161,332	374	182	228
$\tau 3$ (s)	3317	6264	3123	4051

Retardation times from curve fitting used to generate the ideal spectra, and those obtained from the retardation spectra (Figs. 4.20 and 4.22) calculated from experimental creep curves, are compared in Table 4.3. Corresponding times are of the same order. Differences in the times illustrates a shift to the left has occurred during the calculation of the retardation spectra for the raw data. This has been noted above.

In general, the retardation spectra obtained for experimental data after smoothing and differentiation by the methods of Savitzky and Golay seem to be similar to those obtained using parameters fitted by the program NONLIN which have also been smoothed and differentiated. Given the parameters used to calculate the ideal spectra are obtained using a model based on Equation (4.1), with all the implied limitations of a model, their similarity suggests the viscoelastic model is appropriate to model creep compliance behaviour. The similarity also suggests that fitting a model with three retardation times is not too inappropriate.

4.7. PRELIMINARY EXPERIMENTS

4.7.1 Linearity

With non-linear viscoelastic materials there is a curvilinear relationship between stress and strain. The creep compliance time response is influenced by applied stress so that for each stress a different creep compliance / time curve is obtained (Sherman, 1986).

Most viscoelastic materials exhibit linear stress/strain behaviour at very low stresses. If the stress selected does not exceed the value beyond which non-linearity develops it is possible to analyse the creep compliance data obtained.

In order to establish whether linear viscoelastic behaviour was exhibited by butter at low stresses, and the range of limiting stresses, a series of experiments were performed. Two butters, a Fritz autumn sample at 15°C (an average butter) and a reworked Ammix sample at 10°C (a very soft butter) were exposed to a range of stresses varying from 784 - 3920 Pa for five minutes. Samples were tested in duplicate. The creep compliance responses were observed. Results are presented in Table 4.4.

Stress vs. strain plots indicate a linear creep compliance response for the Fritz butter up to a stress of 3920 Pa at 15°C ($r = 0.984$, $y = 0.0004x + 0.13$) with the Ammix butter also exhibiting a linear response up to a stress of 3136Pa at 10°C ($r = 1.0$, $y = 0.002x - 0.245$). The response of butter to a creep compliance test of five minutes duration is essentially elastic in nature. The response would include the instantaneous compliance, J_o, and the first retarded compliance, J_1, which has a retardation time of approximately 30 seconds. Consequently, Table 4.4 shows a linear response for the elastic part of the curve. The contribution of the viscous term to overall response would be negligible in the first five minutes.

The contribution of viscosity to the total compliance should be independent of the stress used. In order to determine the response of the viscous term to varying stresses a single Ammix sample (TT Oct. 1987) was exposed to stresses of 784, 1568, 3136 and 3920 Pa for 15.5 hours. The results, which are presented in Table 4.5 show that viscosity appears to be independent of the applied stress, remaining approximately the same as stress increases. It can also be seen that the sum of the compliances increases linearly as stress increases ($r = 0.988$, $y = 0.078x + 0.25$). The instantaneous compliance term responds in a similar manner. It seems a linear elastic response is observed over long time creep experiments as well as experiments lasting only five minutes.

Table 4.4: Strain responses observed on the application of stress.

Stress	Strain	
Pa	Fritz 15°C $\times 10^{-3}$	Ammix 10°C $\times 10^{-3}$
784	0.52	1.32
1568	0.72	2.97
2352	1.32	4.62
3136	1.53	6.10
3920	1.80	-

Table 4.5: Creep compliance parameters found for one sample on the application of different stresses.

	Stress			
	784 Pa	1568 Pa	3136 Pa	3920 Pa
J_o $(\times 10^{-9})$ Pa^{-1}	14 (1)	19.2 (.3)	43.8 (.1)	64.4 (.2)
ΣJ $(\times 10^{-9})$ Pa^{-1}	79 (4)	186 (3)	305 (3)	441 (1)
η_N $(\times 10^{10})$ Pa.s	33 (4)	36 (3)	42 (.7)	33 (.5)

() 95% confidence intervals.

In choosing a constant stress with which to perform creep compliance experiments two points must be considered; first, the viscoelastic response should be linear for the stress chosen and second, the response seen must be of sufficient magnitude for analysis. While a linear response is seen in butters of average hardness at 15^{o}C for a stress of 3920 Pa, it is possible very soft samples may not exhibit a linear response at this stress. At a stress of 3136 Pa a very soft sample at 10^{o}C responded in a linear fashion. 3136 Pa is also large enough to get a response from the hardest samples. Therefore all creep compliance work has been carried out using a stress of 3136 Pa (400g) at 10^{o}C.

4.7.2. Orientation

On considering a pat of butter the fold face can be designated the top face. A set of three-dimensional axes can then be imposed on a butter pat such that the top and bottom faces lie in the xy plane, side faces in the xz plane and end faces in the yz plane (Fig. 4.24).

A sample cut from the top face of a pat of butter (ie. sampled in the z direction) can be sheared in either the x or y direction. Similarly, sampling in the y direction allows shear in the x or z directions while shear is possible in y or z directions if sampling is done in the x direction.

In order to evaluate any possible effect of the direction of shear two Fritz patted butters (TUI April '86, TUI April 87) and two Ammix patted butters (TT Jan. 86, TT April '86) were sheared in all three directions. The TUI April '87 samples were allowed to recover for seven hours after shear. Creep compliance responses were recorded and analysed in all cases using the non-linear least squares curve fitting program (Section 6.1.2 above). Compliance and viscosity values are presented in Table 4.6, while recovery data for TUI April '87 is presented in Table 4.7. All results presented are averages of duplicates.

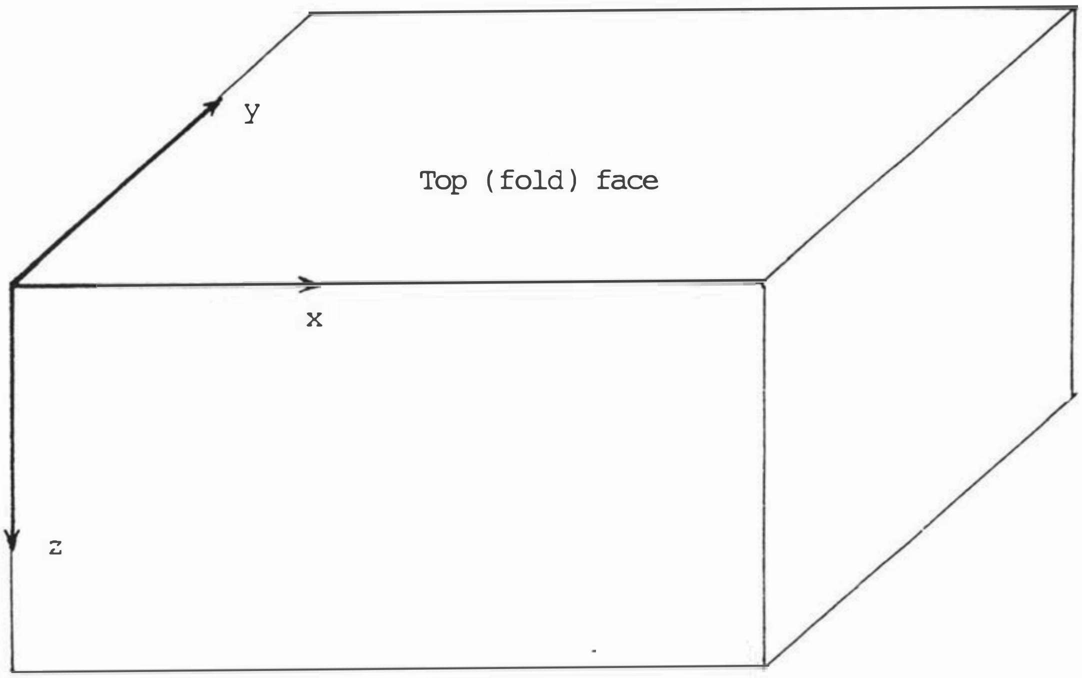


Figure 4.24: Three dimensional axes imposed on a pat of butter.

Table 4.6: Creep compliance parameters obtained from patted butters sheared in the three possible directions.

	FRITZ						AMMIX					
	TUI April '86			TUI April '87			TT Jan. '86			TT April '86		
	x	y	z	x	y	z	x	y	z	x	y	z
	2.5	4.8	6.6	6.2	7.8	10	6.3	5.8	6.7	7.8	7	7.5
	(.7)	(.7)	(.5)	(.4)	(.5)	(2)	(.6)	(.3)	(.5)	(.5)	(1)	(.3)
	4.5	8.2	10	13	15.1	14	10	9.6	9.6	10.0	11	10
	(.7)	(.7)	(1)	(1)	(.2)	(3)	(1)	(.3)	(.1)	(.7)	(2)	(2)
	10.0	15.9	17.8	20	28	25	19.9	15.7	20.8	17.5	18.9	25.5
	(.7)	(.8)	(.4)	(1)	(1)	(4)	(.2)	(.4)	(.2)	(.7)	(.7)	(.1)
	9	9	11.6	8.4	12	20	18	14	14	12.1	9.6	14
	(2)	(2)	(.3)	(.5)	(3)	(2)	(3)	(1)	(2)	(.4)	(.5)	(3)
	73	49	46	44	37	18	33	26	24	49	51	46
	(10)	(6)	(10)	(7)	(1)	(2)	(7)	(5)	(1)	(1)	(7)	(8)
a	26	38	46	47	63	68	54	44	51	47	47	50
	(4)	(3)	(2)	(3)	(4)	(11)	(50)	(2)	(3)	(3)	(4)	(60
ıc	-	45	77	-	33	44	-	-	-	-	-	-
		(10)	(15)		(4)	(10)						

) Sum of compliances.

) Standard error.

its:

, J_i, ΣJ x 10^{-8} Pa^{-1}

x 10^{10} Pa.s

The creep compliance results for the Ammix butters indicate the direction in which shear occurs does not affect the creep compliance response greatly.

In contrast, a difference in the magnitude of creep compliance response was observed for patted Fritz butters, shear in the x direction gave the smallest response, followed by shear in the y direction, with shear in the z direction giving the greatest response. The sum of the compliances increase and the viscous terms decrease as shear direction changes from x to y to z, indicating an increasing creep compliance response as the samples seem to become easier to shear.

On examining the recovery data for TUI April '87 (Table 4.7) it can be seen that the percentage recovery, ie. the sum of the recovery compliances divided by the sum of creep compliances, decreases as the direction of shear changes from x to y to z.

To further investigate the extent of the effect of sample orientation (ie. direction of shear) on the creep compliance responses of patted Fritz butters two more samples, TUI Oct. '85 and TUI Jan. '86 were sheared in two directions, x and y in the case of TUI Oct. '85, x and z in the case of TUI Jan. '86 (Table 4.8).

A comparison of these results with data presented in Table 4.6 shows that the change in the sum of compliance for TUI Oct. '86 is not as great as that for TUI April '86 or TUI April '87 as one changes from shear in the x to the y direction. Furthermore, there is essentially no change in the sum of compliances for TUI Jan. '86 as the direction of shear changes from x to z. Viscosity decreases for TUI Oct '85 as the shear direction changes from x to y and x to z, while for TUI Jan. '86 change in direction of shear has little effect on viscosity.

Table 4.7: Recovery data for the butter TUI April '87.

Shear direction	ΣJ_{Creep} $(\times 10^{-8} \text{Pa}^{-1})$	ΣJ_{Rec} $(\times 10^{-8} \text{Pa}^{-1})$	% rec,
X	49	9.9	22
Y	59	8.6	15
Z	70	7.1	10

Table 4.8: Creep compliance parameters obtained from patted Fritz butters sheared in two directions.

	TUI Oct. '85		TUI Jan. '86	
	x	y	x	z
J_o	4.6 (.3)	5.7 (.3)	5.6 (.3)	4.9 (.3)
J_1	6.1 (.7)	7.3 (.7)	11.5 (.8)	11.2 (.8)
J_2	16 (1)	17.6 (.8)	18.0 (.8)	16.3 (.6)
J_3	12 (1)	12 (1)	20 (6)	21.7 (.8)
η_N	28 (3)	35.1 (.7)	-	46 (1)
ΣJ^a	38 (3)	43 (3)	55 (8)	54 (3)
% inc ΣJ	-	12	-	-

(a) Sum of compliances.
( ) Standard error.

<u>Units:</u>

J_o, J_i, ΣJ x 10^{-8} Pa_{-1}
η_N x 10^{10} Pa.s

Additionally, two samples of Fritz butter (MAN April '87 and MAN May '87) were collected as the butter left the butter making machine (ie. before patting). The samples were sheared in the direction of flow from the butter making machine and at right angles to the flow.

Creep compliance results for these unpatted Fritz butters are presented in Table 4.9. Samples which were sheared in the direction of flow gave similar results to samples sheared at a right angles to the flow.

Some patted butters made by the Fritz process appeared to be particularly sensitive to the direction in which stress was applied, while other patted Fritz samples were less sensitive. In contrast, patted butters made by the Ammix process are not affected to any great extent by the direction of shear. Bulk butters made by the Fritz process are also unaffected by changes in shear direction.

A possible explanation for the difference in behaviour observed for shear in the three directions, x, y, and z, exists. Both pumping through pipes and the process of patting exposes butter to shear stresses. It is possible some order is imposed on fat crystals during pumping and patting, thus leading to a larger creep compliance response in some directions. Additionally, the shear forces involved may cause 'bonds' or weak van-der-Waals forces to break which are not later reformed (ie. a form of reworking).

The decrease in percentage recovery after shear in the x to y to z direction for TUI April '87 supports the idea some form of structural alignment or damage has occurred which makes recovery more difficult.

Both the Fritz and Ammix samples were packed using a pump fed SIG FD140 patter. In simple terms, a patting machine a), moulds a fixed quantity of butter, by volume, into a pre-

Table 4.9: Creep compliance parametrs obtained from unpatted Fritz butters sheared in two directions.

	MAN April '87		MAN May '87	
	with flow	90^o to flow	with flow	90^o to flow
J_0	9.9 (.2)	8.7 (.4)	8.2 (.9)	8.1 (.7)
J_1	17.7 (.4)	19 (2)	16 (2)	16 (1)
J_2	26.1 (.4)	22 (2)	28 (3)	28 (5)
J_3	16.2 (.5)	15 (1)	21.7 (.3)	23 (1)
η_N	28 (1)	35.1 (.6)	31 (3)	36 (7)
ΣJ^a	70 (2)	64 (5)	73 (6)	75 (8)

(a) Sum of compliances.
( ) Standard error.

<u>Units:</u>
J_o, J_i $\Sigma J \times 10^{-8}$ Pa^{-1}
$\eta_N \times 10^{10}$ Pa.s

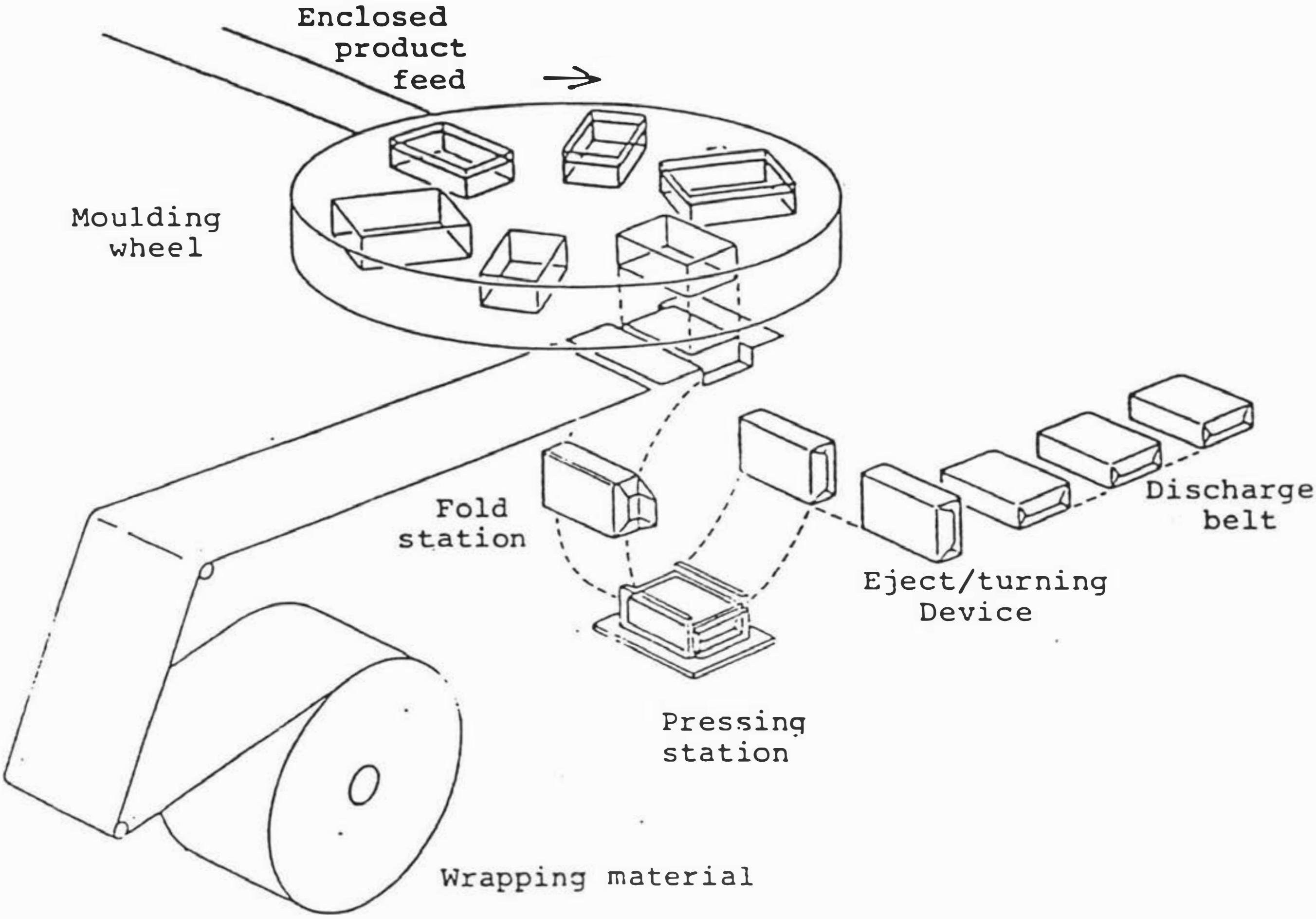


Figure 4.25: Operating principles of the Sig FD140 patter.

determined shape, and b), folds the wrapper around the block of butter. SIG machines operate by filling a mould with a piston backstop with butter. The mould rotates and the piston ejects the formed block from the mould. The block is cut from the piston, placed onto the wrapping material with subsequent wrapping, folding and pressing completing the pat. These operations are shown diagrammatically in Fig 4.25.

The direction of butter flow through pipes, as butter is pumped into the patter, is manifested in the z axis of the finished pat. Butter is then exposed to further stresses during the process of patting and wrapping. The major stress during patting seems to be caused by the removal of the block of butter from the piston. As this happens the butter is sheared in what will be the y direction in the finished pat.

The above explanation implies increasing shear will lead to an increase in creep compliance response. If it is assumed that pumping produces more shear than the patting process, then the trends in creep compliance parameters can be explained.

Sensitivity to shear in the processes of pumping and patting is mainly exhibited in Fritz butters. In the manufacture of Fritz type butter the milkfat is completely crystallized before churning. Any rearrangement of the fat crystals which occurs after churning and working would be permanent. In contrast, in the manufacture of butter by the Ammix process, crystallization is not completed until after processing. Presumably any rearrangement or imposed order resulting from pumping or patting would be obscured by subsequent crystallization.

The question of direction of shear presents a problem in terms of creep compliance testing. Obviously for consistent results it is important that samples are always cut and orientated in the parallel plate viscoelastometer in the same way to ensure shear is always in the same direction. Sampling so as to shear in the x direction will ensure the butters' rheological parameters are as unchanged as possible, ie. that the effect of pumping and packing are not obscuring the basic creep compliance response. For consistent, reproducible results all patted butters are prepared by cutting samples from the top face of the pat, with shear occurring in the x direction.

The above results suggest creep compliance testing is very sensitive and capable of picking up the effect of stresses applied to butter during pumping and patting operations. Measurements on similar patted samples showed sectility hardness results were not detectably affected by direction of shear.

4.7.3. Reapeatability

For rheological measurements to be meaningful they must be repeatable. Ideally, creep compliance testing performed on the same butter should give the same results each time.

The curve fitting program NONLIN performs some statistical analyses. Standard error coefficient, t-value and 95% confidence levels are calculated for all parameters (eg. Fig. 4.11). For sets of results observed for samples to be judged significantly alike, confidence levels should overlap. This was seen for many samples, especially in the case of J_o and J_1 values. However, in some cases good overlap was not seen.

Possible Reasons for Departure from Repeatability

i) Sample Inhomogeneity.

Creep compliance has been seen to be very sensitive to slight differences in samples (see above, Section 7.2). Materials such as butter and related fat products are often inhomgenous. This can range from the presence of air to the crystalline network differing in structure in places. Changes occurring with time and temperature, for example, during setting, may contribute to these differences. Sample inhomogeneity presents a significant problem in creep compliance testing. While every effort is made to ensure samples are homogenous, some will fall short of the mark. This will cause a decrease in repeatability.

Another problem is the samples for one test only can be cut form a 500g pat of butter, As pats are packed into cartons which contain 40 pats there is the possibility the stress and temperature history of each pat in a carton may differ from it's neighbour. This means that although two pats may be filled with the same butter their responses during creep testing may be different. Samples manufactured specifically for creep compliance testing (Chapter 2) gave the most repeatable results while commercial samples collected from butter factories often gave less repeatable results.

ii) Curve Fitting.

While compliance testing can be affected by variables relating to samples, a second significant factor contributing to the difficulty in obtaining repeatable results involves the curve fitting process itself. Two curves which may look superficially alike, ie., show a similar overall creep, may be fitted with differing parameters. In some cases where the curves are similar, parameters may vary by 10 - 20% or more.

Figure 4.26 shows two curves found for the sample TT January '86. While overall creep was approximately the same for both samples, the two curves are very different in shape. This is reflected in the parameters listed in Table 4.10. Instantaneous compliance, viscosity and the retardation times are different for each sample, however, the sum of complainces are the same.

While the above example illustrates the expected, ie., different curves defined by different parameters, Figure 4.27 shows two creep curves found for the butter TT April '86. The figure shows the curves differ slightly in shape and have

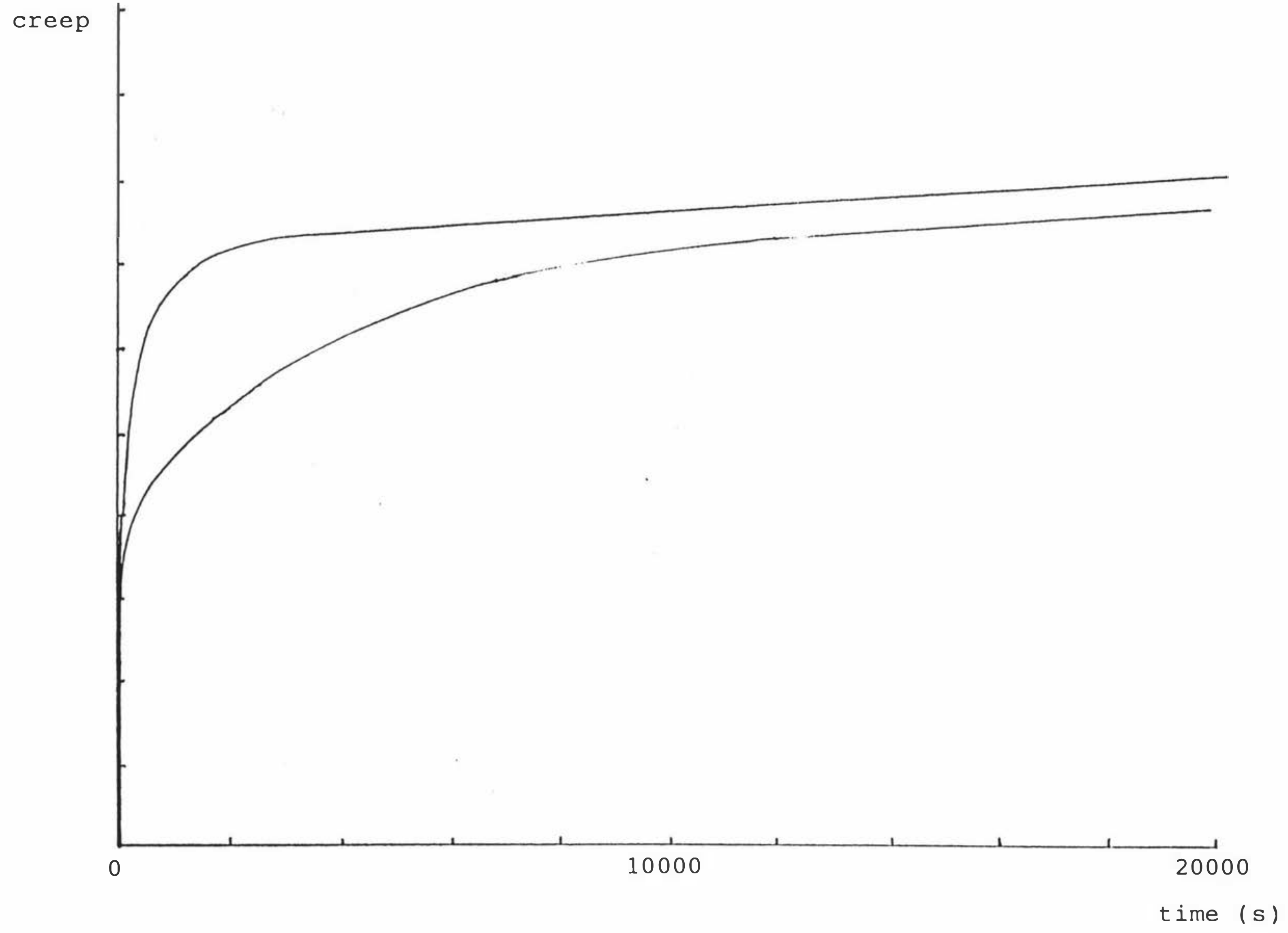


Figure 4.26: Creep compliance curves found for the sample TT January 1986.

Table 4.10: Creep compliance parameters fitted to creep curves observed for the butter TT January, 1986.

	1	2
J_o	11 (.2)	5 (.1)
J_1	6 (1)	5 (1)
τ_1	19 (.3)	17 (.6)
J_2	16 (1)	16 (1)
τ_2	139 (1)	187 (2)
J_3	15 (2)	22 (1)
τ_3	694 (14)	3780 (10)
η_N	35 (1)	50 (5)
ΣJ^a	48 (4)	48 (4)

(a) Sum of compliances.
( ) Standard Error.

Units:

J_o, J_i, ΣJ x 10^{-8} Pa^{-1}.
η_N x 10^{10} Pa.s.
τ_i x s.

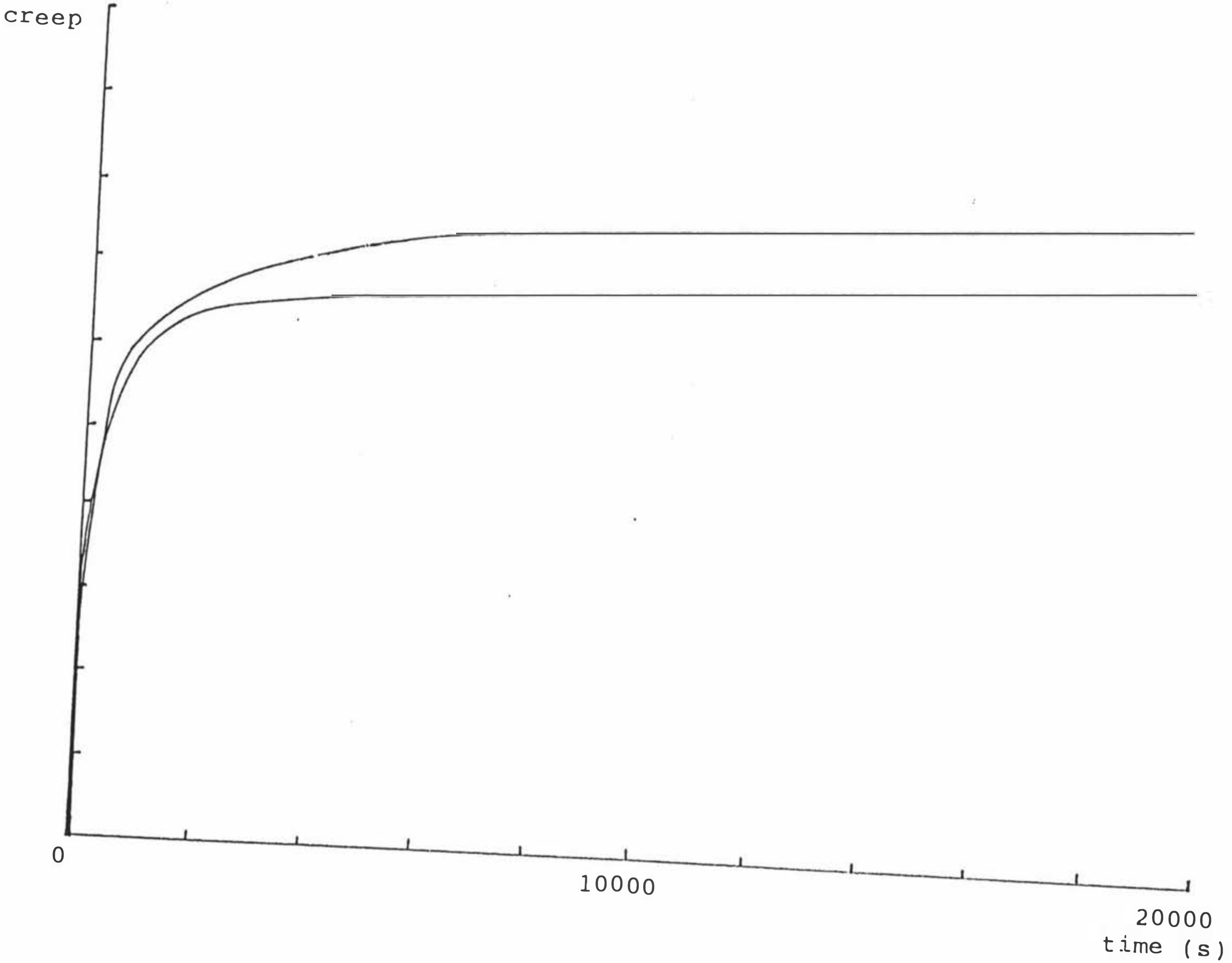


Figure 4.27: Creep compliance curves found for the sample TT April 1986.

approximately the same total creep (± 10%). The parameters fitted are listed in Table 4.11. From these parameters it can be seen the sum of compliances are similar (44 and 51 x 10^{-8} Pa^{-1}) but that these figures differ by about 15%. The viscosity values found, 39 and 63 x 10^{10} Pa.s respectively differ by approximately 60% and yet the curves are still similar.

iii) Other Factors.
Other facets of creep compliance testing may also decrease repeatability. For example, the impossibility of obtaining an instantaneous start. While a standard operating procedure is used at the start of a creep experiment it is not possible to start each experiment in exactly the same way. In addition the possibility of samples slipping during a test would decrease repeatability. However, no evidence of samples slipping (in the form of plateaux in the chart recorder trace) is seen during experiments.

Another minor source of error is found in sample preparation and introduction of the sample into the instrument. The preparation of samples for creep compliance testing involves the measuring and cutting of butter. Small errors will therefore be present in the size of the prepared sample. Little damage, however, occurs as samples are loaded into the parallel plate viscoelastometer. A standard procedure minimizes problems in this area.

A further consideration when dealing with materials such as fats is temperature control. Any temperature fluctuations would result in changed creep behaviour and would diminish repeatability. Temperature during creep compliance experiments was maintained at 10 ± 0.2°C (Section 2). Temperature fluctuations of ± 0.2°C had no discernable effect on creep behaviour.

The most suitable samples for creep compliance testing were of average hardness. The creep behaviour of very soft samples

Table 4.11: Creep compliance parameters fitted to creep curves observed for the butter TT April, 1986.

	1	2
J_o	6 (.3)	8 (.1)
J_1	9 (.5)	12 (.3)
τ_1	13 (.3)	22 (.1)
J_2	18 (.7)	18 (.3)
$\tau 2$	120 (.4)	202 (.1)
J_3	10 (.8)	12 (.3)
τ_3	792 (12)	2730 (4)
η_N	39 (1)	63 (2)
ΣJ^a	44 (2)	51 (1)

(a) Sum of compliances.
( ) Standard Error.

Units:
J_o, J_i, ΣJ x 10^{-8} Pa^{-1}.
η_N x 10^{10} Pa.s.
τ_i x s.

(eg. sectility hardness of 600g) tended to be less reproducible. The soft nature of the samples made sample preparation more difficult. The parameters fitted to the creep responses of harder samples tended to be less accurate due to the small numbers involved. This also applies to the (small) second creep responses observed.

Due to the difficulties involved in obtaining repeatable reults a general technique of testing in triplicate was adopted. Odd results being discarded, for example, those with very low t-values. If problems were still found to exist further runs were carried out.

CHAPTER FIVE

LARGE DEFORMATION TESTING

5.1. INTRODUCTION

It is widely recognised that most methods used to evaluate the rheological properties of butter and other fat systems give empirical, instrument dependent results. These methods generally use large forces which permanently deform the material being tested. While results often correlate well with sensory characteristics and indicate whether samples differ in their response to the test conditions, they have little fundamental value.

In an attempt to find a test method which involved large structural deformations and gave fundamental rheological information on butter Kawanari *et al* (1982) evaluated three test procedures. The procedures, shear, uniaxial compression and penetrometry all produced shear yield stress values which agreed closely. The first two procedures used low rates of deformation producing quasistatic properties. Instrumental results were also compared to sensory data and were found to predict spreadability and firmness.

The quasistatic shear test outlined by Kawanari *et al* exerted nearly pure shear stress on samples. The stress needed to cause failure, ie. the shear fracture stress, and the apparent shear modulus were found to be highly correlated. As the apparent shear modulus represented product stress/strain moduli and the shear failure stress represented strength, it was felt the two moduli were good indicators of butter strength, ie. the more rigid a fat crystal system, the greater the stress needed to fracture a butter.

Shear failure stress was also found to correlate very well with spreadability as determined by a trained panel. Firmness, also determined by a panel, was highly correlated with both shear failure stress and the apparent shear modulus. Kawanari *et al* conclude from the strong correlations that butter fracture strength is the primary factor influencing spreadability at 10^{o}C.

5.2. EXPERIMENTAL METHOD

5.2.1. Shear Testing

An apparatus, based on that described by Kawanari *et al* for quasistatic shear testing, was designed for use with the Stevens Compression Response Analyser (C R Analyser) (C. Stevens and Son Ltd.,St. Albans, Great Britain.) The apparatus is in two parts; the bottom part being held stationary while the top half is attached to the probe of the C R Analyser and capable of movement in a vertical plane (Fig. 5.1). Initially, the two portions of the apparatus are lined up together and the sample holder containing the sample is slipped in. The sample is clamped securely in each half of the apparatus. On starting the instrument, the top portion of the apparatus moves downward, exerting almost pure shear. The peak force, change in force with time and the distance moved by the top portion of the apparatus during shear can all be measured. Travel speed ranges from 5 - 100 mm/min.

Butter samples for large deformation shear testing were stored at 5^{o}C. Prior to sample preparation, samples were held overnight in a waterbath at 10^{o}C. The use of a temperature of 10^{o}C, as opposed to 5^{o}C for sample preparation, was to reduce possible damage to samples during preparation.

Samples were prepared by pushing two lengths of square pipe (each 25mm x 14mm x 14mm), one on top of the other, into butter. Excess butter is cut away. A gap between the two halves of the sample holder is necessary to avoid the sample being simply cut by the sample holder. The gap must be small to ensure stresses differing from pure shear by less than 3% are obtained (Kawanari *et al* (1982)).

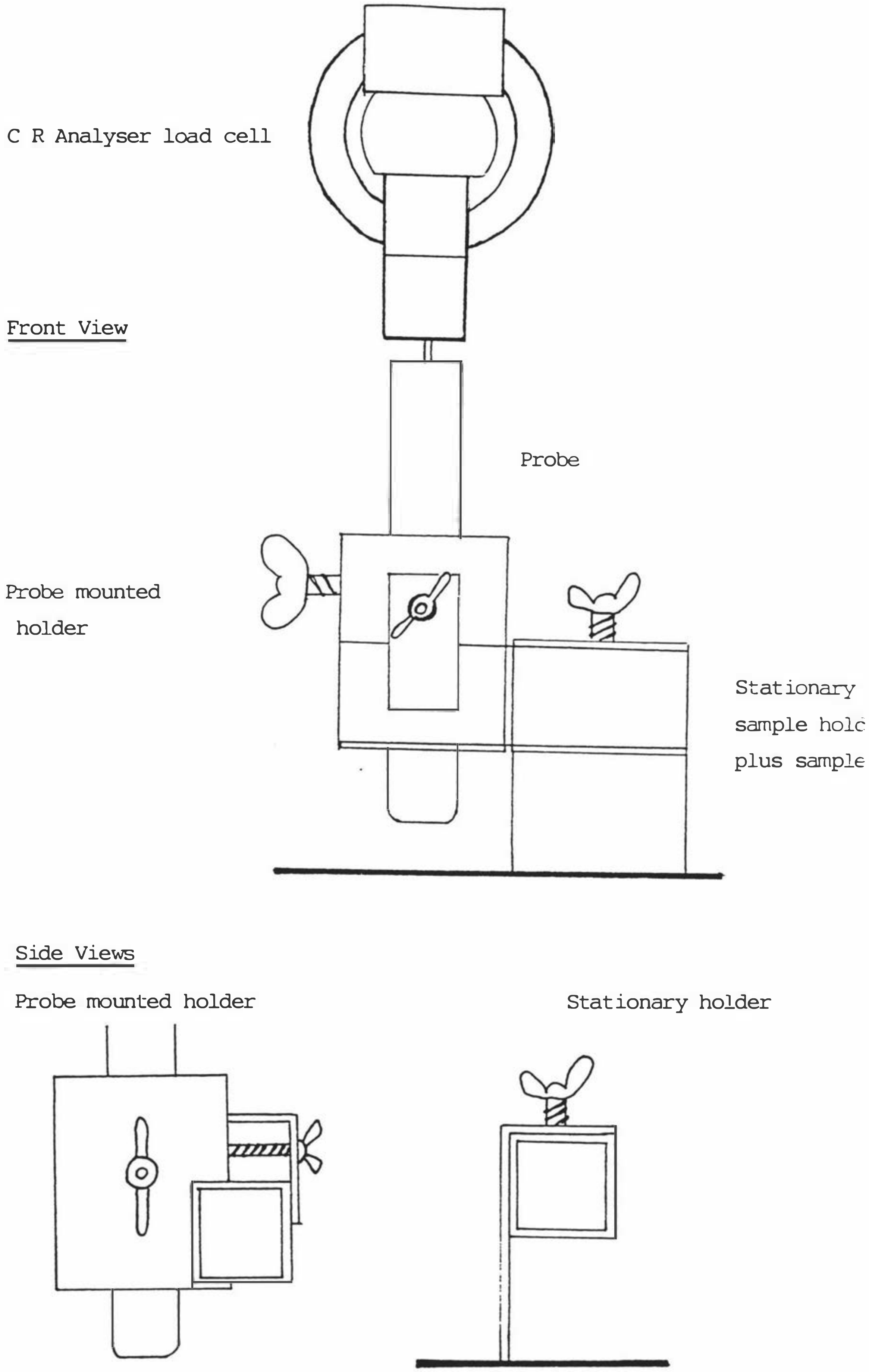


Figure 5.1: Front and side views of the appartus attached to the C R Analyser used for shear testing.

Once samples have been prepared they were tempered for a minimum of five hours in a waterbath at the desired temperature (5, 10 or 15^{o}C). When tempering was complete, the sample holders, containing the sample, were loaded into the apparatus and the test was done immediately. Testing has been carried out at 5^{o}C and at room temperature. As tests were very quick, ie. less than ten seconds in duration, the sample temperature did not change perceptibly.

5.2.2 Reproducibility

The method was found to be sensitive, however, reproducibility was poor, with an error at best, of approximately 10%. The poor reproducibility is probably due to the small sample size. As any damage to the sample, or sample inhomogeneity would affect results, readings were done in triplicate and any readings indicating a damaged sample were discarded. One disadvantage of the C R Analyser is that speeds below 5mm/min are not very accurate (C. Stevens and Son).

5.2.3. Shear Failure Stress

Shear failure stress was found by converting the force used to cause failure in grams to N/m^{2}, ie. force divided by cross sectional area of the sample.

5.2.4. Apparent Shear Moduli

Apparent shear moduli can be calculated from the slope of the shear stress vs. shear strain graph. Shear stress was calculated by dividing the shear force by the sample cross-sectional area, and shear strain by dividing distance moved by the top portion of the apparatus by the gap between the two pieces of the sample holder. Data for this purpose was collected using a Perkin Elmer data station (Perkin Elmer Corporation), capable of taking 3 readings a second. Eight samples were sheared for each butter.

5.2.5. Sectility Hardness

Traditional sectility hardness testing using the modified FIRA - NIRD extruder was performed at 40 mm/min. The method is described in Chapter Three.

Sectility hardness can also be performed using the C R Analyser by attaching a cutting wire accessory. Samples were prepared as for traditional sectility hardness (Chapter 3) and placed on the sample platform. As the probe moved downward the cutting wire was forced into the butter and the force required was measured. Tests were done in duplicate.

5.3. EXPERIMENTAL AND RESULTS

Sectility hardness (traditional) at 10 °C and percentage solid fat as determined by NMR at 5, 10 and 15 °C were found for all samples used in large deformation testing. Results are presented in Table 5.1.

5.3.1. Shear Testing

Four commercial autumn butter samples, two manufactured by the Fritz process (TUI Feb. 87, MAN May 87) and two manufactured by the Ammix process (TT Feb. 87, TT Mar. 87), were subjected to different tests. The butters were sheared at speeds of 1, 2, 5, 10, 20, 30, 40 and 50 mm/min at three different temperatures, 5, 10 and 15 °C.

5.3.1.1. Shear speed.

The results of shearing the four chosen butter samples at different speeds are shown in plots of probe speed vs. cutting force. (Figs. 5.2 (TUI Feb. 87), 5.3 (MAN May 87), 5.4 (TT Feb. 87) and 5.5 (TT Mar. 87)).

Increasing the probe speed (or shear rate) during large deformation testing resulted in increasing force being needed to shear butter samples. This effect is more marked at 5 and 10°C. At 15°C, the increase in force needed is smaller.

Table 5.1: Percentage solid fat determined by NMR and traditional sectility hardness values at 10°C for butters used in large deformation testing.

Sample	% Solid fat NMR			Hardness 10°C
	5°C	10°C	15°C	(g)
TT Feb. 87	64.5	58.4	42.6	1700
TT Mar. 87	61.1	54.3	37.2	1450
TUI Feb. 87	67.0	61.1	45.8	2000
MAN May 87	60.6	54.0	38.0	1325
TT Jan. 87	63.7	57.5	42.5	1800
TUI Mar. 87	63.9	57.8	42.0	1800

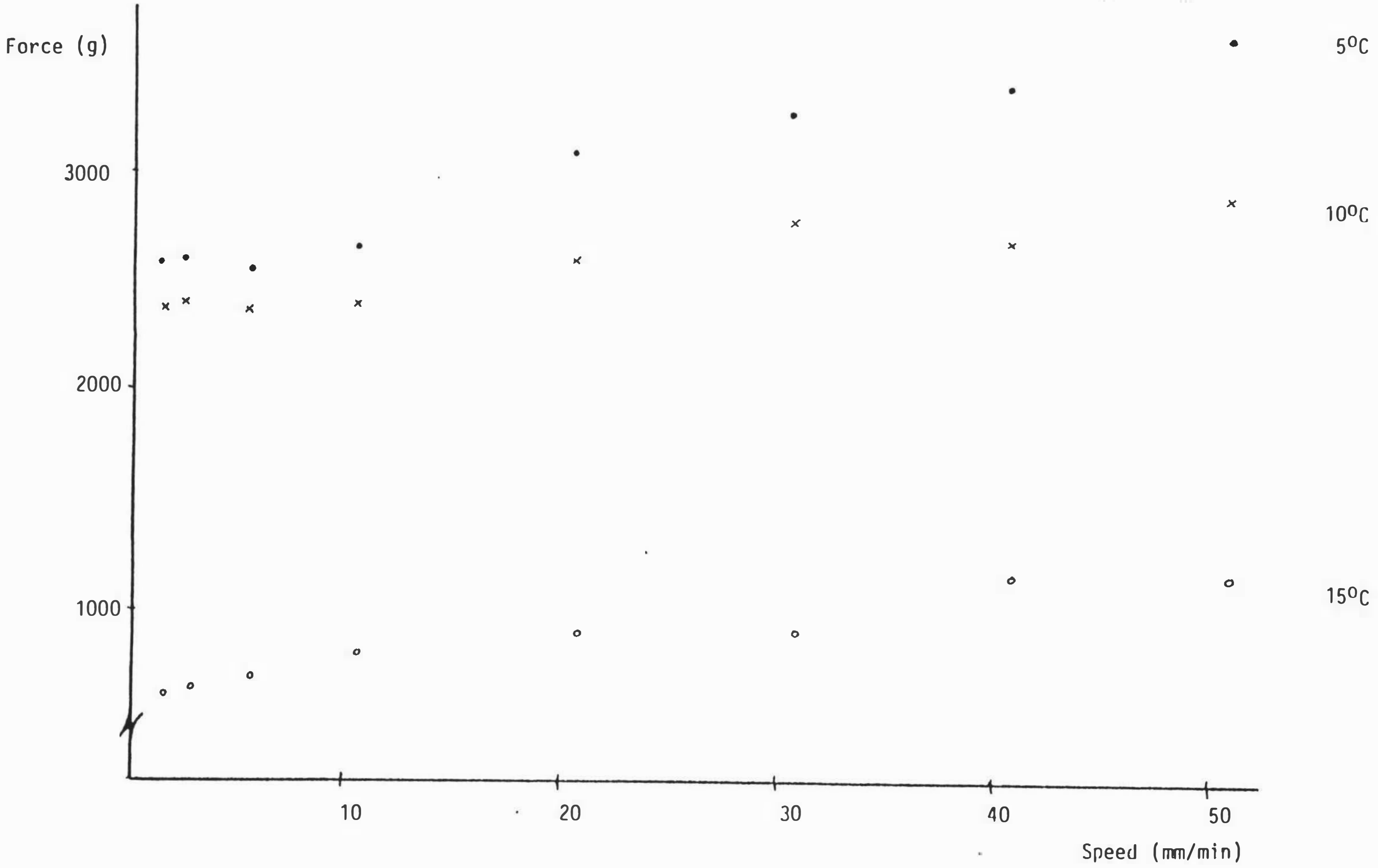


Figure 5.2: Force vs. shear speed for the sample TUI February 1987.

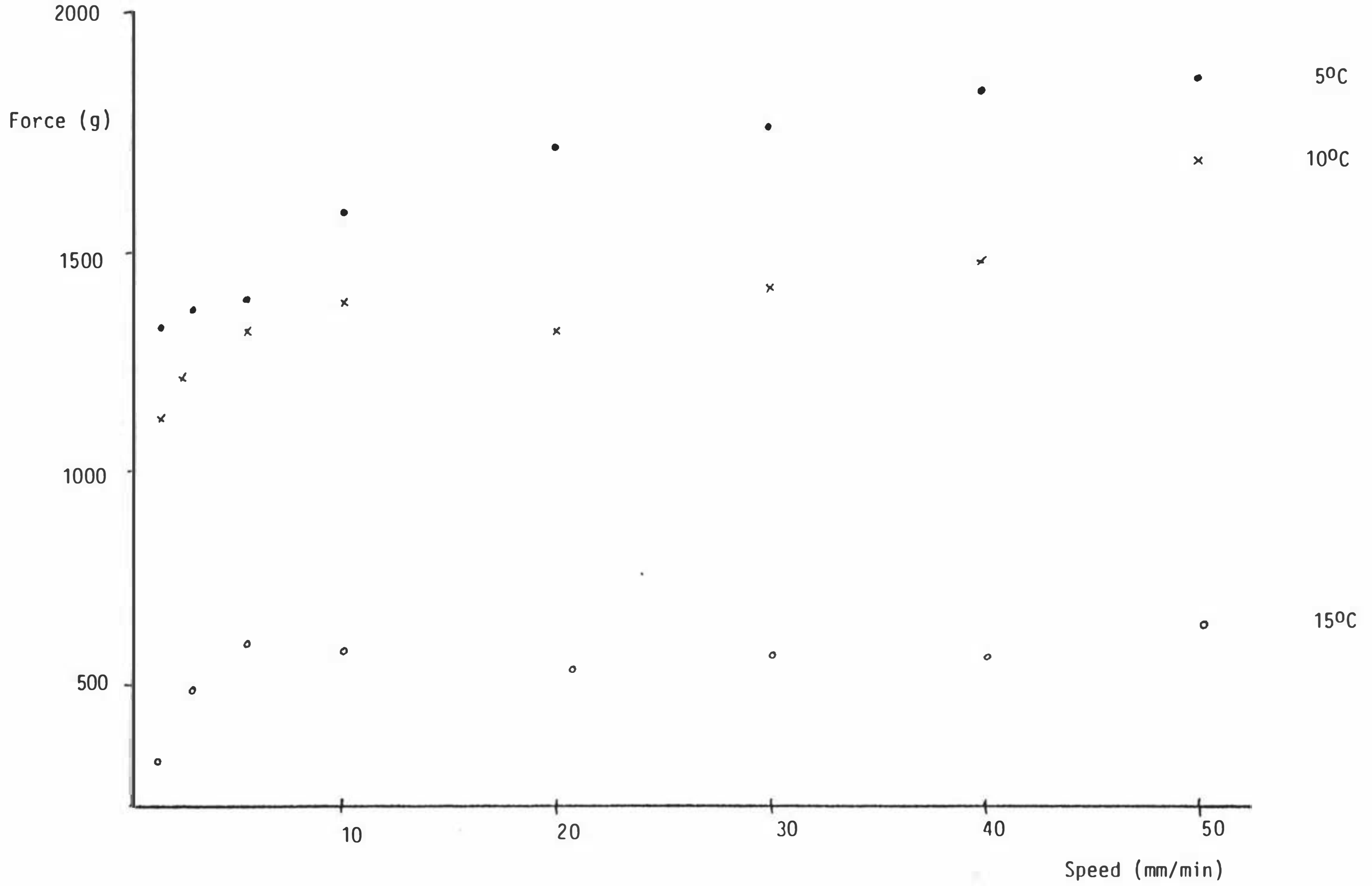


Figure 5.3: Force vs. shear speed for the sample MAN May 1987.

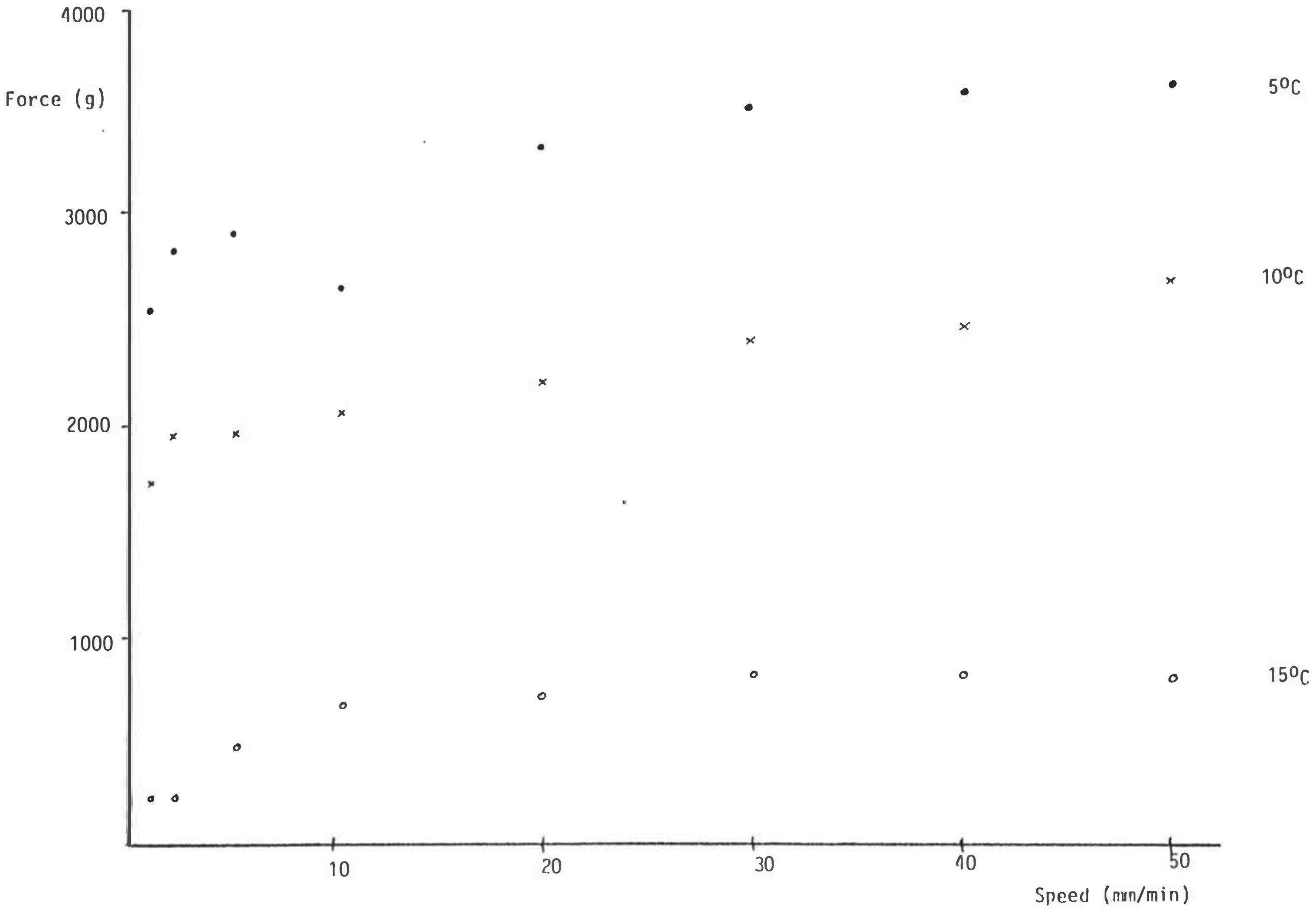


Figure 5.4: Force vs. shear speed for the sample TT February 1987.

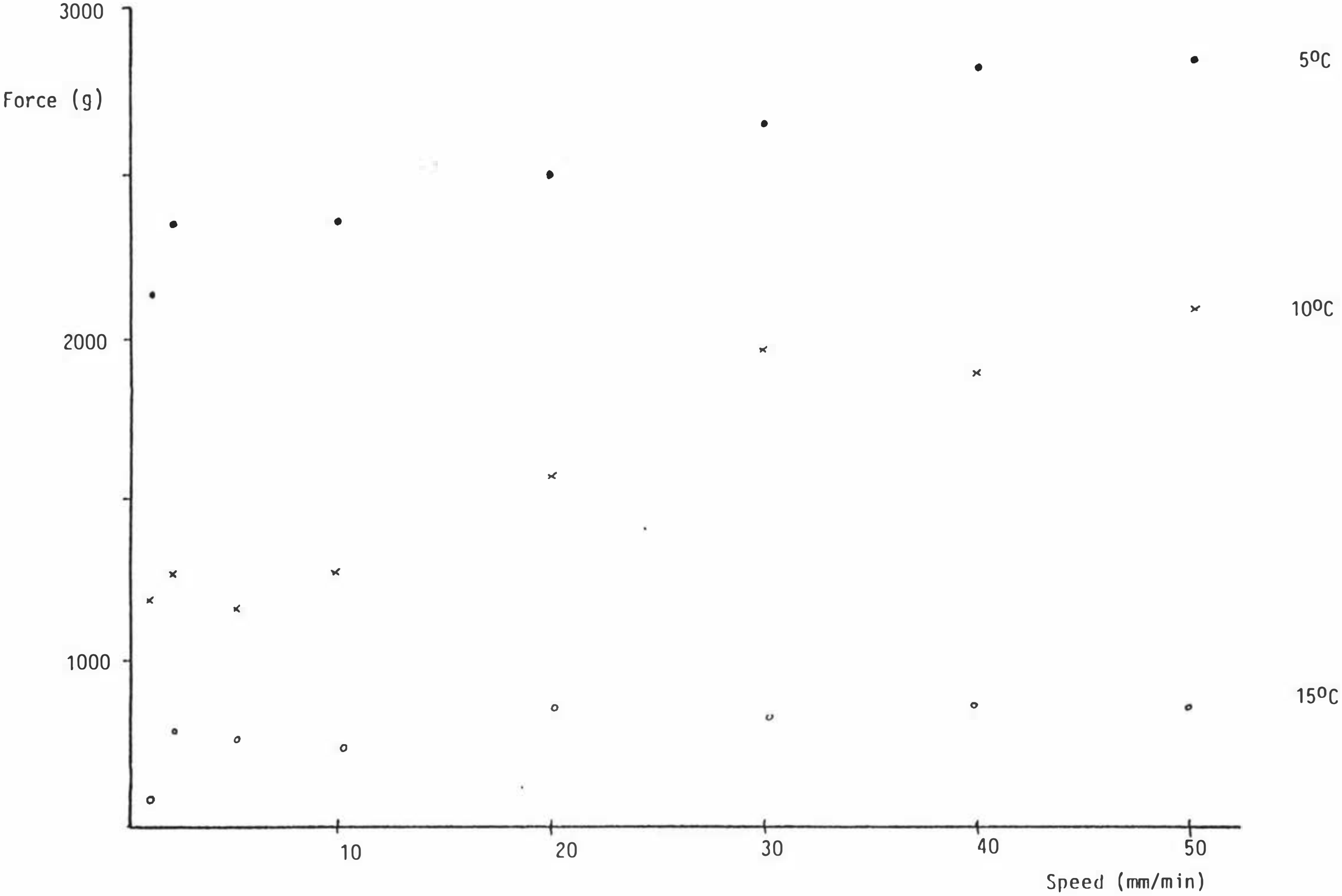


Figure 5.5: Force vs. shear speed for the sample TT March 1987.

5.3.1.2. Shear Failure Stress.

Figure 5.6 shows the shear failure stresses calculated from the large deformation shear testing, at 10 mm/min, for the three test temperatures.

5.3.2. Apparent Shear Modulus

Apparent shear moduli where found for two Fritz and two Ammix butters. The samples, TUI Mar. 87, TUI Feb. 87, TT Feb. 87 and TT Jan 87, were sheared at a temperature of 10°C and a speed of 5 mm/min.

An example of results as recorded by the Perkin Elmer data station, are presented in Table 5.2. Typical graphs of shear stress vs. shear strain are shown in Figure 5.7.

The apparent shear moduli found on averaging 8 tests each for the samples tested are: TT Feb. 87 - 4.7×10^4, TUI Feb. 87 - 12.0×10^4, TUI Mar. 87 - 10.2×10^4 and TT Jan. 87 - 5.0×10^4 Pa. The apparent shear modulus correlates well with traditional sectility hardness ($r = 0.81$). Hardness seems to account for approximately 66% of the apparent shear modulus ($R^2 = 66.3\%$). On comparing the apparent shear moduli of the two samples with the same hardness and solid fat content, TUI Mar. 87 and TT Jan. 87, it seems easier to shear the Ammix sample, compared to the Fritz sample.

5.3.3. Comparison of Shear Testing with Traditional Sectility Hardness Testing.

A comparison between shear testing and traditional sectility hardness was carried out. Two samples known to have the same sectility hardness and solid fat content at 10°C were chosen, one manufactured by the Fritz process (TUI Mar. 87), the other by the Ammix process (TT Jan. 87). Samples were sheared at 7 and 8 mm/min.

Results are presented in Table 5.3. Shear testing carried out at 7mm/min required approximately the same force to shear

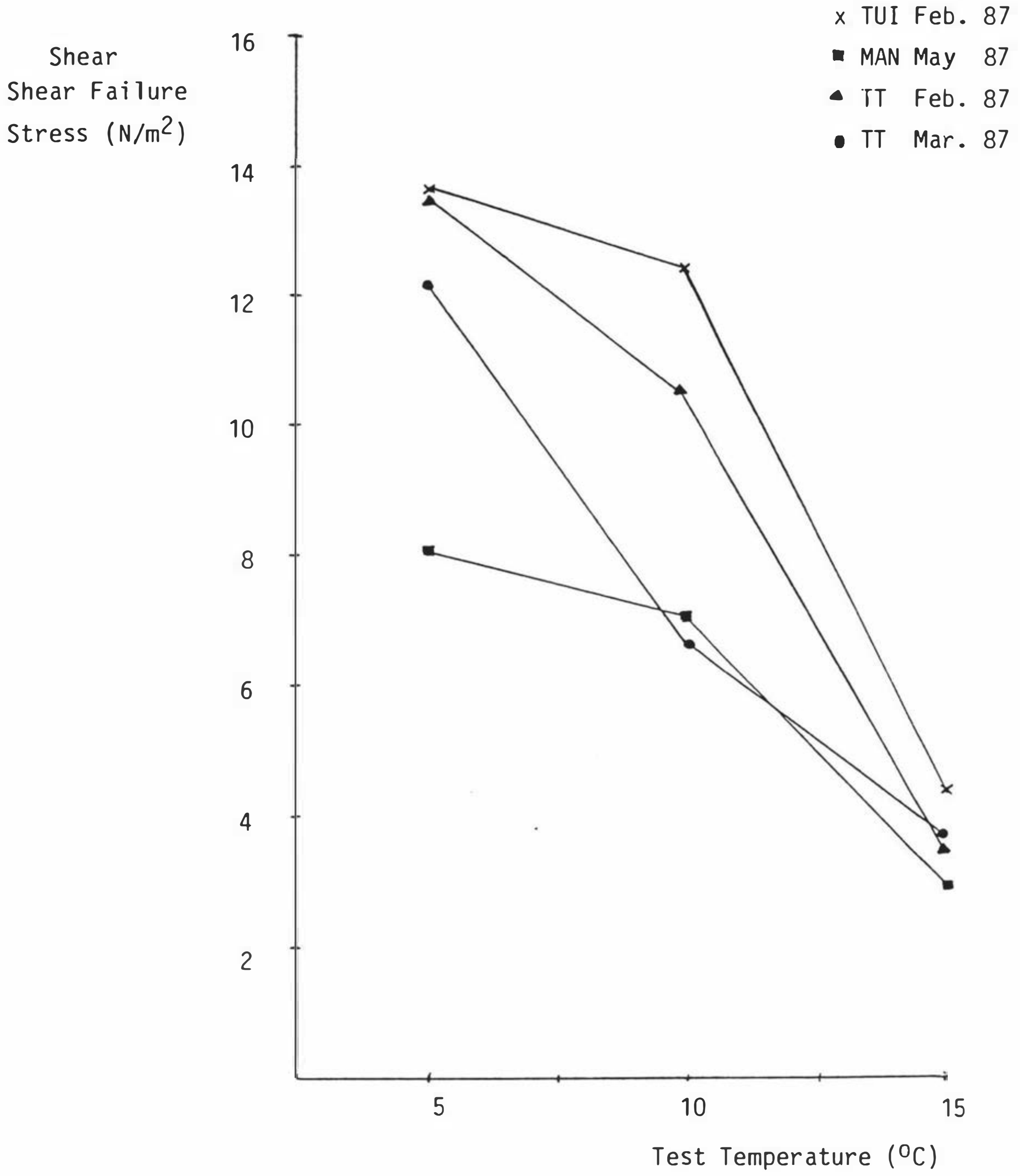


Figure 5.6: Shear failure stress plotted against temperature.

Table 5.2: An example of data recorded by the Perkin Elmer data station during large deformation testing.

```
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DATE:  87/11/27                              TIME:  13:16

     STRING                           LOAD      PENETRATION
------------------------------------------------------------------
L  00194  D  000.0                     194                0
L  00266  D  000.0                     266                0
L  00208  D  000.1                     208                .1
L  00210  D  000.1                     210                .1
L  00222  D  000.1                     222                .1
L  00254  D  000.2                     254                .2
L  00266  D  000.2                     266                .2
L  00306  D  000.3                     306                .3
L  00350  D  000.3                     350                .3
L  00564  D  000.3                     564                .3
L  00638  D  000.4                     638                .4
L  00762  D  000.4                     762                .4
L  00778  D  000.4                     778                .4
L  00862  D  000.5                     862                .5
L  00894  D  000.5                     894                .5
L  00966  D  000.6                     966                .6
L  00984  D  000.6                     984                .6
L  01036  D  000.6                     1036               .6
L  01066  D  000.7                     1066               .7
L  01110  D  000.7                     1110               .7
L  01122  D  000.8                     1122               .8
L  01162  D  000.8                     1162               .8
L  01174  D  000.8                     1174               .8
L  01194  D  000.9                     1194               .9
L  01184  D  000.9                     1184               .9
L  01204  D  001.0                     1204               1
L  01222  D  001.0                     1222               1
L  01268  D  001.0                     1268               1
L  01262  D  001.1                     1262               1.1
L  01276  D  001.1                     1276               1.1
L  01280  D  001.1                     1280               1.1
L  01300  D  001.2                     1300               1.2
L  01288  D  001.2                     1288               1.2
L  01302  D  001.3                     1302               1.3
L  01302  D  001.3                     1302               1.3
L  01298  D  001.4                     1298               1.4
L  01310  D  001.4                     1310               1.4
L  01286  D  001.5                     1286               1.5
L  01298  D  001.5                     1298               1.5
L  01268  D  001.5                     1268               1.5
L  01268  D  001.6                     1268               1.6

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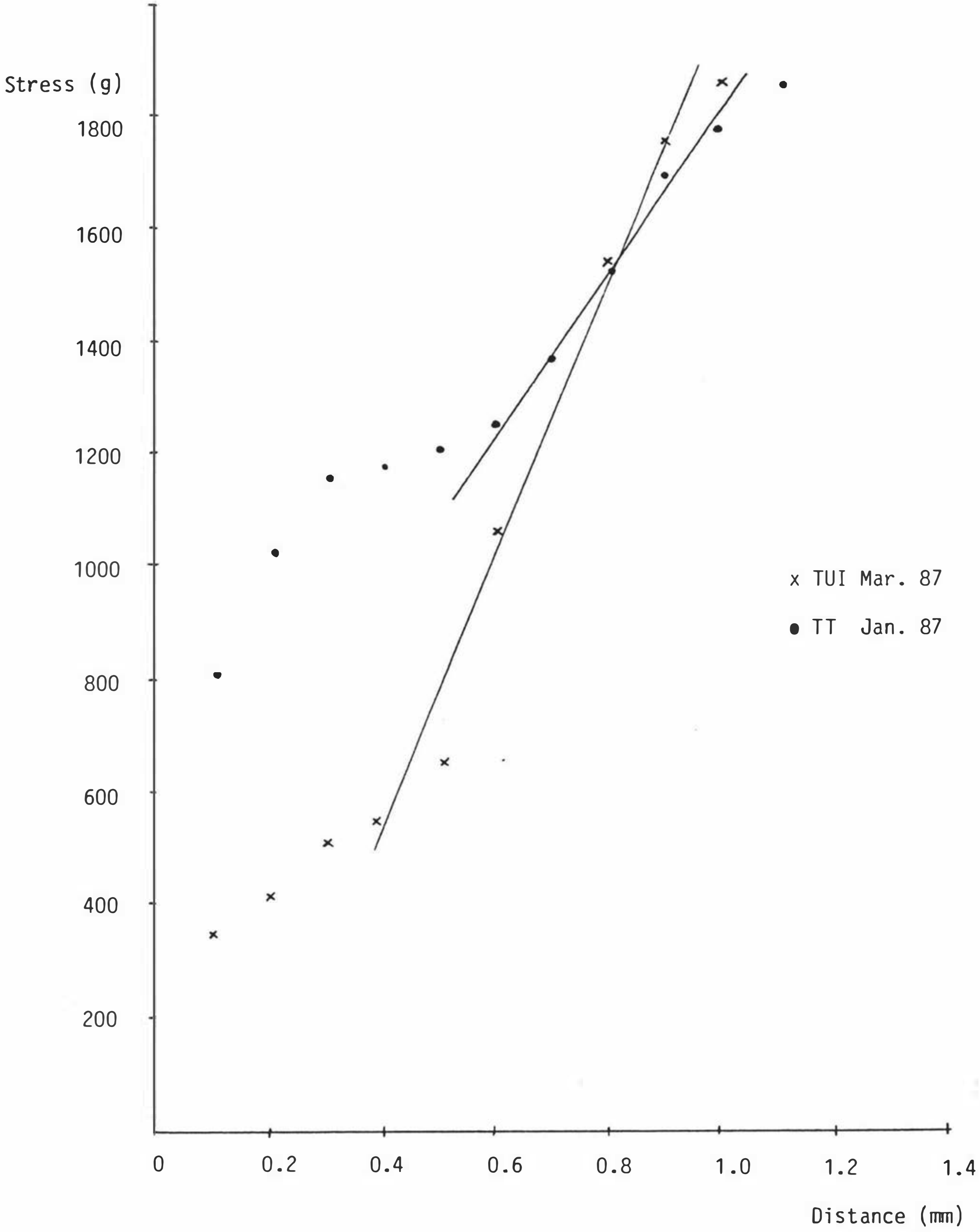


Figure 5.7: Stress vs. distance moved by the probe (slope = apparent shear modulus).

samples as the cutting force required in traditional sectility hardness testing.

5.3.4. Sectility Hardness (C R Analyser)

Sectility hardness testing was performed on two samples, one Fritz (MAN May 87) and one Ammix butter (TT Mar. 87). Samples were tested at speeds of 10, 20, 30, 40 and 50 mm/min at a temperature of 10°C.

5.3.4.1. Shear Speed

Results are presented in Table 5.4. Plots of probe speed vs. force required (Figures 5.8 and 5.9), indicate a linear relationship between shear speed and deformation force.

5.3.4.2. Comparison of Shear Testing with Sectility Hardness (C R Analyser)

Shear testing and sectility hardness testing (C R Analyser) was performed on two samples (MAN May 87 and TT Mar. 87) at different speeds. The results obtained for the sample MAN May 87 at 10°C are presented in Figure 5.8. It shows approximately the same force is required for shear and cutting at speeds of 20 - 50 mm/min. A comparison of the results obtained for sample TT Mar. 87 (Fig. 5.9) shows the forces required for shear and cutting do not coincide until speeds of 5 - 10 mm/min.

5.4. DISCUSSION

5.4.1. Shear Testing

5.4.1.1. Shear Speed

For both shear testing and sectility hardness (C R Analyser) an increased force is needed to 'shear' a sample as speed increases. This is not unexpected. If butter was acting in a Newtonian manner shear stress would increase as shear rate increased. However, as Figures 5.2, 5.3, 5.4 and 5.5 indicate a Newtonian (linear response) is not seen. The shape of the curves indicates butter is acting as a shear thinning material.

Table 5.3: Comparison of sectility hardness testing (traditional) with shear testing.

Sample	Sectility	Shear	
	40 mm/min (g)	8mm/min (g)	7mm/min (g)
TUI Mar. 87	1800	2130	1850
TT Jan. 87	1800	1980	1790

Table 5.4: Sectility hardness results (C R Analyser).

Speed (mm/min)	TT Mar. 87	MAN May 87
5	1112	1200
10	1170	1261
20	1346	1375
30	1318	1496
40	1369	1510
50	1380	1600

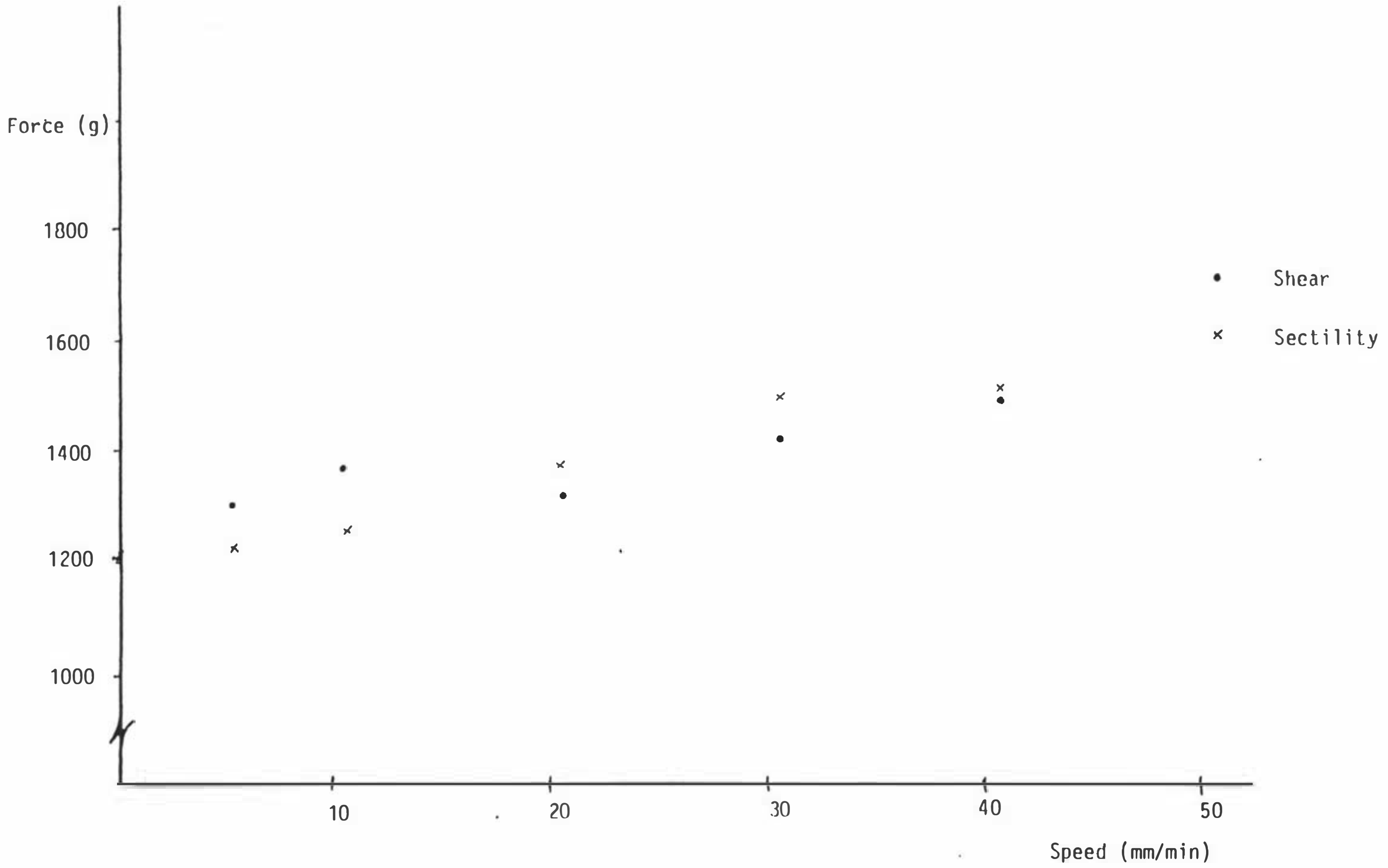


Figure 5.8: Force vs. shear speed for both shear testing and sectility hardness testing, sample MAN May 1987.

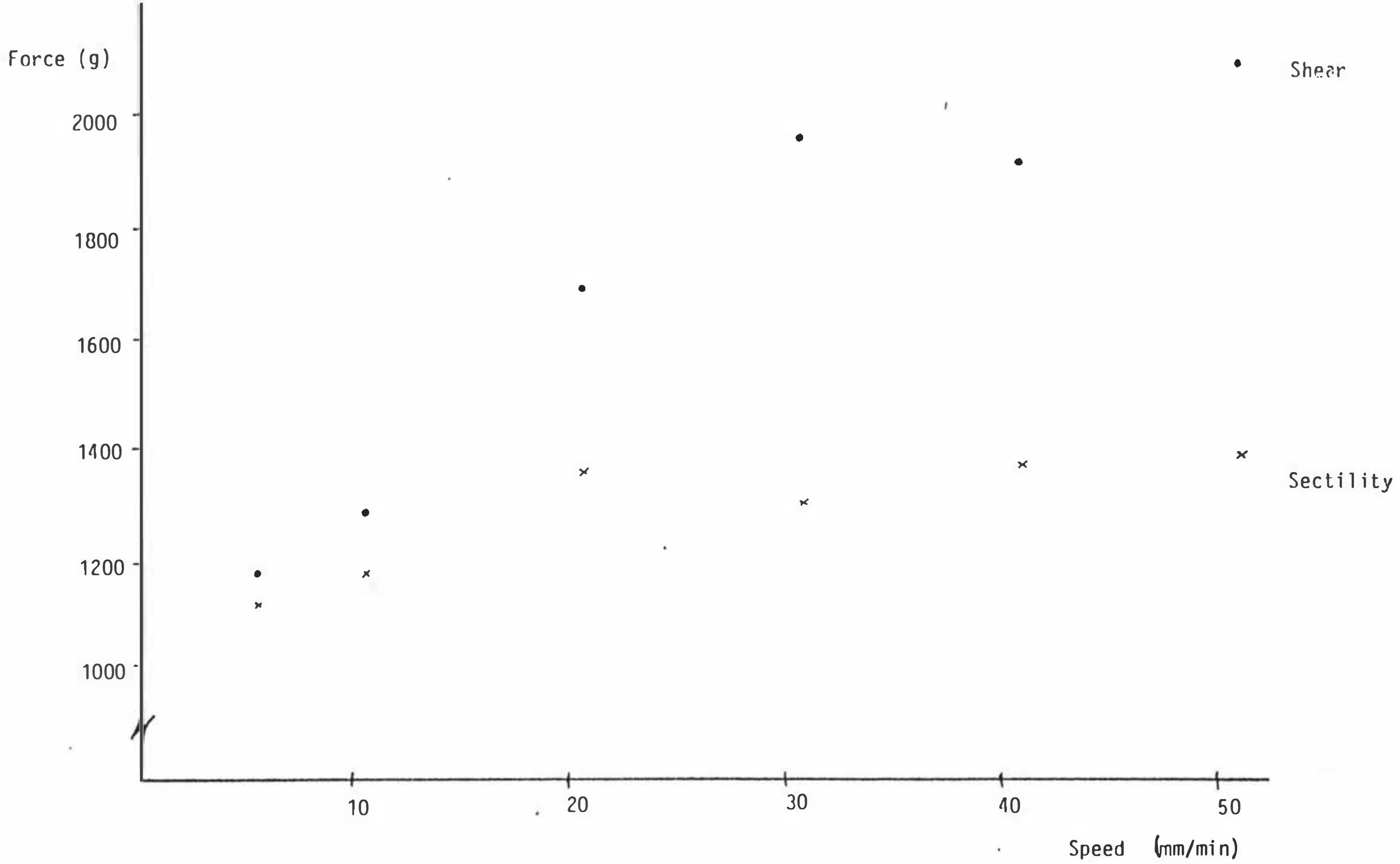


Figure 5.9: Force vs. shear speed for both shear testing and sectility hardness testing, sample TT March 1987.

This general relationship found between deformation speed and stress (force needed for deformation) has been observed in sectility hardness testing by a number of workers including Dolby (1941), Knoop (1972), Dixon and Williams (1977) and Mortensen and Danmark (1982).

The behaviour of butter during sectility hardness testing has been variously regarded as characteristic of a Bingham plastic (Knoop (1972)) and of a power law fluid (Dolby (1941)). Dixon and Williams (1977) found the Bingham plastic model did not describe the relationship between cutting force and cutting speed as well as an exponential, semi-log or power law relationship, all of which correlated extremely well with the observed behaviour. Dolby and Dixon and Williams point out the relationship between force and speed may seem linear over the range of speeds tested, but in fact be curved. Sectility testing using the C R Analyser over a wide range of speeds (up to 100 mm/min) reveals a relationship between force and speed that is, in fact, curved (MacGibbon, 1987).

Knoop carried out his experiments at speeds of 0.2 - 10 mm/s, while the maximum speed used by Dolby was approximately 0.65 mm/s. Dixon and Williams used speeds in the same range as Knoop, from 0.45 - 9 mm/s to reach their conclusions. Based on the reports of the above workers it seems butter is behaving more like a Bingham plastic at higher speeds, and responding in a more elastic fashion. In contrast, at low speeds, butter seems to behave more as a power law fluid, with viscous flow becoming more important.

Parallels exist between the changing response of butter to increasing speed, temperature and hardness during sectility hardness testing and shear testing. On attempting to fit Bingham plastic, semi-log and power law relationships to the curves obtained by shear testing presented here it was found the Bingham plastic model best described the results recorded at 5 and 10°C. However, at 15°C a semi-log or power-law relationship was often found to be more appropriate (Table 5.5). In addition, in going from hard to medium to soft butters (as determined by sectility hardness), the best description of butter behaviour appears to progress from Bingham plastic (to semi-log) to power-law relationship.

It is interesting that Dolby (1941), who found a power-law relationship most appropriate for sectility hardness testing, used relatively soft samples at 12.5°C. Similarly, Dixon and Williams (1977) used a range of butter and butter/oil blends, none of which appears to have had a sectility hardness of greater than about 600g at 13°C. They too concluded a power-law or semi-log relationship described the behaviour of butter better than the Bingham plastic model. Presumably as temperature and liquid fat content increase, butter is more inclined to flow on application of shear stresses. Conversely, at low temperatures solid fat content would be higher and the response would be elastic rather than viscous, requiring a larger shear stress to cause deformation.

It seems a power law relationship is most appropriate to describe the behaviour of softer butters under stress at low speeds and at higher temperatures, while the Bingham plastic model best characterizes behaviour of harder butters at high speeds and lower temperatures.

5.4.1.2. Shear Failure Stress

The shear failure stresses of Ammix butters appeared to decrease more rapidly than Fritz butters as temperature increased from 5 to 10°C. However, at 15°C all samples had approximately the same shear failure stress (Fig. 5.6). The decrease in shear failure stress as temperature increases depends largely on the decrease in percentage solid fat which occurs as temperatures rise.

Kawanari *et al* (1982) found butter made by the Cherry-Burrell process to be harder at all temperatures, to have greater

Table 5.5: The fit of various models to shear speed vs. force data found at 5, 10 and 15^{o}C for four samples expressed as correlation coefficients.

		TUI Feb. 87	MAN May 87	TT Feb. 87	TT Mar. 87
5^{o}C	Bingham[a]	0.98	0.91	0.93	0.97
	semilog[b]	0.89	0.95	0.90	0.93
	powerlaw[c]	0.90	0.95	0.90	0.94
10^{o}C	Bingham	0.95	0.92	0.98	0.97
	semilog	0.84	0.88	0.94	0.88
	powerlaw	0.85	0.91	0.96	0.89
15^{o}C	Bingham	0.98	0.54	0.88	0.76
	semilog	0.93	0.74	0.94	0.87
	powerlaw	0.95	0.74	0.98	0.85

(a) Bingham: $s = a + b/V$

(b) Semi-log: $s = a + b\log V$

(c) Power law: $s = aV^{b}$

(s = stress (cutting force), V = shear speed, a and b = constants.)

shear failure stresses and found shear failure stress to decrease more rapidly as test temperature increased. A difference between Fritz and Ammix butter might therefore be expected. However, the Ammix process differs from the Cherry-Burrell process in that the Ammix butter is cooled more slowly and worked more during manufacture resulting in a product close in texture and hardness to corresponding Fritz butters.

5.4.2. Apparent Shear Moduli

The apparent shear modulus found for the Ammix butter (TT Jan. 87) is lower than that found for the Fritz butter (TUI Mar. 87). This is in contrast with shear failure stress and traditional sectility hardness results. The apparent shear modulus of the other Ammix butter tested is also lower then shear failure stress or sectility hardness would predict.

Shear failure stress is a measure of butter strength. Two butters may require the same amount of force to cause shear failure, for example, the samples TUI Mar. 87 and TT Jan. 87 (force = 1900-2000g). However, on calculating the apparent shear modulus of these two butters, the Ammix sample shears more easily, ie., Ammix butters are either deforming more quickly, or more deformation is needed before failure occurs, in comparison with Fritz butter. The question which must be asked is why, or how does Ammix butter deform more than Fritz, or, why is less deformation needed before shear failure in Fritz butter?

Factors which may influence the physical properties of butter have been mentioned in the Introduction (Chapter 1, Section C). These include the proportion of solid to liquid fat the extent of the crystalline network and the number of intact fat globules present. It is thought these factors would influence hardness, shear failure stress and apparent shear modulus to the same degree, however the apparent shear modulus for Ammix butter is substantially lower than would be predicted.

Kawanari *et al* (1982) found Cherry-Burrell butter to have a higher apparent shear modulus than Fritz butter. An explanation of this observation can be offered, based on the above factors. The absence of fat globules in Cherry-Burrell butter would result in all solid fat present being able to participate in crystalline networks. This would lead to a more rigid butter. Rapid cooling and little working would also contribute to strength and rigidity of the butter, resulting in a butter which is more difficult to shear.

Unlike Cherry-Burrell butter, no easy explanation for the behaviour of Ammix butter presents itself at this stage. One possibility relates to the observation more deformation may be needed before failure occurs. If Ammix butter is more plastic than Fritz butter this effect may be seen.

5.4.3. Sectility Hardness

5.4.3.1. Comparison between Shear Testing and Traditional Sectility Hardness

Shear testing experiments performed at different shear rates indicated that the force required for shear at a probe speed of 7-8 mm/min was approximately the same as the force required for the sectility wire to cut a sample. (Traditional sectility hardness is performed at a speed of 40 mm/min.)

5.4.3.2. Comparison between Shear Testing and Sectility Hardness Testing (C R Analyser)

Using the C R Analyser comparisons between the force required to shear a sample with the force required to cut a sample at different speeds were made. At speeds of 5- 10 mm/min the forces needed for shear and cutting were close (Figs. 5.8 and 5.9), however, at higher speeds the forces needed tended to diverge especially for the sample TT Mar. 87.

The relationship between shear testing and traditional sectility hardness, and (more tenuously) shear testing and sectility hardness testing using the C R Analyser implies sectility hardness carried out using traditional methods and the C R Analyser should give similar results. In connection with this MacGibbon and Van der Does (1987) found traditional sectility hardness carried out at a speed of 40 mm/min correlated highly with C R Analyser sectility results.

5.5. CONCLUSION

Shear testing did not differentiate between Fritz and Ammix butter in the course of ordinary testing. However, calculation of apparent shear moduli indicate the structure of the two types of butter differs. Ammix butters either deform more quickly or more deformation is needed before failure occurs. A possible explanation for this apparent difference may be the greater plasticity of Ammix butter. In contrast, Kawanari et al (1982) found a large difference between Fritz butters and Cherry-Burrell butter. Ammix butter is made to be as close to Fritz butter in texture as possible, which may explain why no major difference between Fritz and Ammix butter was seen.

5.6. TRADITIONAL SECTILITY HARDNESS TESTING VS. LARGE DEFORMATION TESTING

Traditional sectility hardness and shear testing seem to measure the same property of butter, hardness or firmness. Sectility hardness testing, with an error of ± 25g, has been found to be more reproducible than large deformation testing. In addition, preparation of samples for sectility hardness tesing is easier and samples are much larger. Consequently, results are less affected by any damage to samples or inhomogeneities.

For a quick, routine 'hardness' measurement sectility testing would be the favoured method. Shear testing was felt to be less practical and less reproducible. However, sectility hardness testing is an empirical test which does not give fundamental data. If fundamental data was required, for xample, in the calculation of apparent shear moduli, large eformation testing could be carried out.

n this work sectility hardness testing has been routinely erformed on all samples to gain an impression of hardness and s the preferred test.

CHAPTER SIX

AN INTRODUCTION TO CREEP COMPLIANCE EXPERIMENTATION

This chapter is divided into two parts. In the first part (Part A) the effect of varying the duration of creep compliance experiments is examined. In the second part (Part B) experimental length is kept constant and the creep responses of butters manufactured from cream subjected to different cream cooling techniques are observed.

PART A

6A.1. EXPERIMENTAL

Two Fritz butters, MAN May 87 and TUI Mar 87 were subjected to creep compliance testing of varying duration; 8, 15 and 25 hours for MAN May 87, and 5, 8 and 19 hours for TUI Mar. 87. All samples were allowed to recover after creep compliance testing.

6A.2. RESULTS

A typical creep and recovery curve is shown in Figure 4.7. Creep compliance parameters (instantaneous compliance, retarded compliances and viscosity) were found for the creep response using the non-linear least squares curve fitting program NONLIN (Chapter 4, Section 6.1.2). Instantaneous responses, the sum of compliances and viscosity terms for the recovery curve were found directly from the recovery curve (Chapter 4, Section 6.2). Data, along with percentage recovery of compliance values are presented in Table 6.1. Full results are included in Appendix 2.

The sum of compliances found for the creep experiments did not vary much as experimental length changed. The sum of the compliance values found on recovery were much less than those

Table 6.1: Rheological parameters found for creep and recovery experiments of differing length.

Sample	MAN May 87			TUI Mar 87		
Duration (hours)	8	15	25	5	8	19
J_{ocreep}	9 (.1)	7 (.1)	7 (.5)	4 (.1)	4 (.1)	3 (.1)
$J_{Rcreep}{}^{a}$	55 (2)	54 (1)	56 (5)	38 (1)	38(.5)	34 (16)
$\Sigma J_{creep}{}^{b}$	64 (2)	61 (1)	63 (5)	42 (1)	42 (.6)	37 (17)
J_{orec}	5 (.5)	3 (.5)	2 (.5)	2 (.5)	2 (.5)	2 (.5)
J_{Rrec}	10 (2)	12 (2)	7 (2)	10 (2)	6 (2)	6 (2)
ΣJ_{rec}	15 (3)	15 (2)	9 (2)	12 (2)	8 (2)	8 (2)
% ΣJ rec.	24 (5)	26 (4)	14 (4)	29 (6)	18 (5)	22 (9)
η_{Ncreep}	29 (10)	38 (9)	33 (15)	18 (2)	19 (1)	15 (6)
η_{Nrec}	4 (.5)	12 (2)	16 (2)	4 (.5)	7 (1)	7 (1)

(a) Retarded compliances.
(b) Sum of all compliances.

() Standard error.

Units

J_o, J_R, ΣJ x 10^{-8} Pa^{-1}
η_N x 10^{10} Pa.s

calculated for the creep response. Only 15 - 30% of the original creep response was recovered. In contrast with the sum of compliances found for the creep curve, the sum of the compliance values recovered showed a tendency to change as duration of the experiment changed. As a consequence percentage recovery also changed (decreased) as experimental length increased.

In all cases the viscosity term obtained from creep was larger than the viscosity term found from the recovery curve. The viscosity terms calculated for the creep curves show little variation with changing experimental length. However, the viscosity terms found from the recovery curve show some tendency to increase as the duration of the experiment increases.

6A.3. DISCUSSION

The variation seen in some creep compliance parameters as experimental length changes demonstrates the need for creep compliance experiments to be carried out over a constant length of time. This must be done to enable meaningful comparisons of data obtained from different experiments.

In addition, the results of the creep and recovery experiments performed raise some questions about the nature of butters' response. The instantaneous recovery of a model viscoelastic material should be equal to the instantaneous elastic response seen on the application of stress. Likewise, the retarded elastic response during recovery should equal that observed during creep (Chapter One, Section A.6.1.1.1).

Neither the instantaneous nor the retarded elastic responses from recovery approach the values obtained from the creep curve. On the removal of stress only 30 - 50% of the instantaneous elastic response and only 15 - 25% of the retarded elastic response is being recovered.

In a true viscoelastic material, a region of pure viscous flow is eventually reached and viscosity remains constant after that time (see, for example, Fig. 1.5). If the duration of an experiment is such that a state of pure viscous flow is not reached, the viscosity can be calculated from the recovery curve, as unrecovered strain is indicative of the permanent deformation caused by viscous flow (Chapter 4, Section 4.6.2).

The variation in the viscosity values obtained from the creep curves as length of experiment increases may indicate a region of viscous flow is not being reached during an experiment. However, viscosity values calculated from the recovery curve should be constant, regardless of length of experiment. This was found not to be so, with viscosity terms tending to increase as experimental length increased. Viscosity values calculated from the creep and recovery curves (for experiments of the same length) should also be approximately the same, whereas they are not (see Chapter Seven, Section 2.3.1).

Results for elastic recovery are at odds with the generalized Kelvin viscoelastic model, as is the viscosity term found from recovery changing with time. Observed creep and recovery behaviours of butter are not being accounted for by this viscoelastic model. These observations and the questions arising from them will be further addressed in Chapter Seven where creep/recovery experiments are extended to more than one load cycle.

Less than 100% recovery of the instantaneous response has previously been reported by DeMan *et al* (1985), who failed to see full recovery on removing stress from a sample (for example, only 10% recovery was seen after an experiment 10 minutes in duration). DeMan *et al* (1985) also reported a decline in the percentage retarded elasticity recovered (for example, 20% recovery after a 10 minute experiment). Percentage recovery of the instantaneous and retarded elasticity both decreased as experimental duration increased. In contrast with the results presented here, they found the percentage retarded elastic term recovered more than the instantaneous term over all experimental lengths.

DeMan *et al* thought the network structures of plastic fat products were showing an initial elastic response to stress, but, as experimental length increased the structure was collapsing, resulting in increasing permanent deformation. These authors used the rapid decrease in the recovery of instantaneous elasticity as evidence for a rapid collapse of the network structure under a stress greater than the yield value. If the samples tested by DeMan *et al* were showing yield type behaviour, they were obviously not acting as linear viscoelastic materials. It is possible the force being used was too large for viscoelastic theory to apply (Chapter 1, Section B.2.1).

PART B
BUTTERS MANUFACTURED USING DIFFERENT CREAM COOLING TECHNIQUES

6B.1. EXPERIMENTAL

The hardness of butter can be manipulated by altering cream cooling procedures (Chapter 1, Section C.2.3.4). Butter was manufactured from Alnarp cooled cream, slowly cooled and rapidly cooled cream, as detailed in Chapter Two.

Sectility hardness testing was carried out. The initial creep responses of the three butters were observed over a period of 17 hours.

6B.2. RESULTS

Sectility hardness results at 10^{o}C are presented in Table 6.2. Creep compliance parameters were found for the creep response using the non-linear least squares curve fitting program NONLIN (Chapter 4, Section 6.1.2). The parameters fitted to the first creep compliance response are presented in Table 6.3. Full creep compliance results are given in Appendix 2.

The sectility hardness value found for the sample made from

Alnarp treated cream had the lowest sectility value, while the sample made from slow cooled cream and the sample made from rapidly cooled cream had approximately the same sectility hardnesses.

The creep compliance results indicate the butter made from Alnarp cooled cream showed the greatest response, ie., had the largest sum of compliances. The butter manufactured from slow cooled cream displayed a creep response somewhere between those of the butters made from Alnarp and rapidly cooled cream, while the butter prepared from rapidly cooled cream showed the smallest creep response. The viscosity term found for the butter prepared from slowly cooled cream is higher than would be expected, however, a large error is involved in this term.

6B.3. DISCUSSION

It is widely recognised Alnarp treatment of cream produces a softer product (Chapter 1, Section C.2.3.4) and that rapid or shock cooling of cream produces a harder product.

Butter made from Alnarp treated cream is softer and creeps further than butter made from slow cooled cream which in turn is softer and creeps further than butter made from rapidly cooled cream. From these results it appears creep compliance response is directly related to sectility hardness. This relationship will be explored further in the following chapters.

Table 6.2: Sectility hardness values at 10^{o}C found for butters manufactured from cream subjected to different cream cooling techniques.

Cream cooling	Sectility Hardness (g)
Alnarp	1425
Slow	1650
Rapid	1700

Table 6.3: Creep compliance parameters fitted to the creep response of butters manufactured from cream subjected to different cream cooling techniques.

	Alnarp	Slow	Rapid
J_o	5.7 (.5)	5.6 (.4)	5.5 (.5)
ΣJ^a	70.4 (.6)	56 (5)	43 (5)
η_N	47 (1)	73 (20)	54 (7)

(a) Sum of compliances

() Absolute error

<u>Units</u>

J_i x 10^{-8} Pa^{-1}

η_N x 10^{10} Pa.s

CHAPTER SEVEN

THEORY

7.1. INTRODUCTION

Analysis of the creep compliance of butter assumes butter behaves as a viscoelastic material. The generalized Kelvin viscoelastic model (Chapter 1, Section A.6.1.1.2) has been used by many workers to explain the rheological responses of butter and related fat systems. This same model is fitted by the least squares non-linear curve fitting program to experimental data in this work and creep compliance parameters are obtained. However, some preliminary work (Chapter 6) indicates butter may not be acting as a viscoelastic material.

This chapter has been divided into three sections:

1) Load cycling, where the appropriateness of the generalized Kelvin viscoelastic model is tested by extending the observation of creep compliance behaviour to a second cycle of stress and recovery.
2) Reworking, where the creep compliance of reworked butters are observed during load cycling.
3) Development of a theory to explain observed behaviour.

7.2. LOAD CYCLING

7.2.1. Experimental

Three samples of Fritz butter and three samples of Ammix butter collected throughout the dairying season were chosen to give a range of sectility hardnesses and solid fat contents. Samples were subjected to creep compliance testing for 17 hours, then allowed to relax for 7 hours. The creep/recovery cycle was then repeated.

7.2.2. Results

The samples subjected to creep and recovery cycling are also examined in Chapter Nine, where the relationships between creep response, sectility hardness and solid fat content are explored. Sectility hardness results and solid fat contents are given in Table 7.1. All samples gave the same general response curve illustrated in Figure 7.1. Creep compliance parameters were found for both the first and second creep responses (C1 and C2 respectively) using a non-linear least squares curve fitting program (Chapter 4, Section 6.1.2). Three retardation mechanisms were fitted to the first creep curve and two were fitted to the second creep curve. Instantaneous responses, the sum of compliances and viscosity terms for the first and second recovery curves (R1 and R2 respectively) were found directly from the recovery curves (Chapter 4, Section 6.2). Continuous retardation spectra found for the first and second creep responses of TUI Apr. 87 and TT Apr. 87 are shown in Figures 7.2a and b and 7.3a and b.

Results in the form of instantaneous compliance, sum of the compliances and viscosity terms for the first and second creep and recovery responses are presented in Table 7.2. Table 7.3 gives the overall creep responses found in terms of total distance crept or recovered while Table 7.4 shows the correlation coefficients calculated between various parameters.

On the first application of stress the usual creep compliance response is seen. On the removal of stress some recovery takes place, as described in Chapter Six. On a second application of stress a creep response of approximately the same magnitude as the first recovery is observed (softer samples crept a little further). If the stress is then removed a second recovery, very similar to the first, is observed (Fig.7.1). From the general shapes of the observed curves it seems butter may be behaving in a viscoelastic manner after the initial creep response.

Between 30 and 50% of the initial instantaneous compliance was recovered on the removal of stress. Instantaneous compliance

Table 7.1: Sectility hardnesses and solid fat contents of selected determined at 10^{o}C.

	Sectility Hardness (g)	Solid Fat Content
TUI Oct 87	1850	54.2
TT Oct 87	1700	53.7
TUI Jan 87	2400	61.2
TT Jan 87	1850	57.5
TUI Apr 87	1450	55.9
TT Apr 87	1325	53.6
TUI Mar 87	1700	57.8
Reworked TUI Mar 87	575	-
TT Feb 87	1650	54.3
Reworked TT Feb 87	600	-

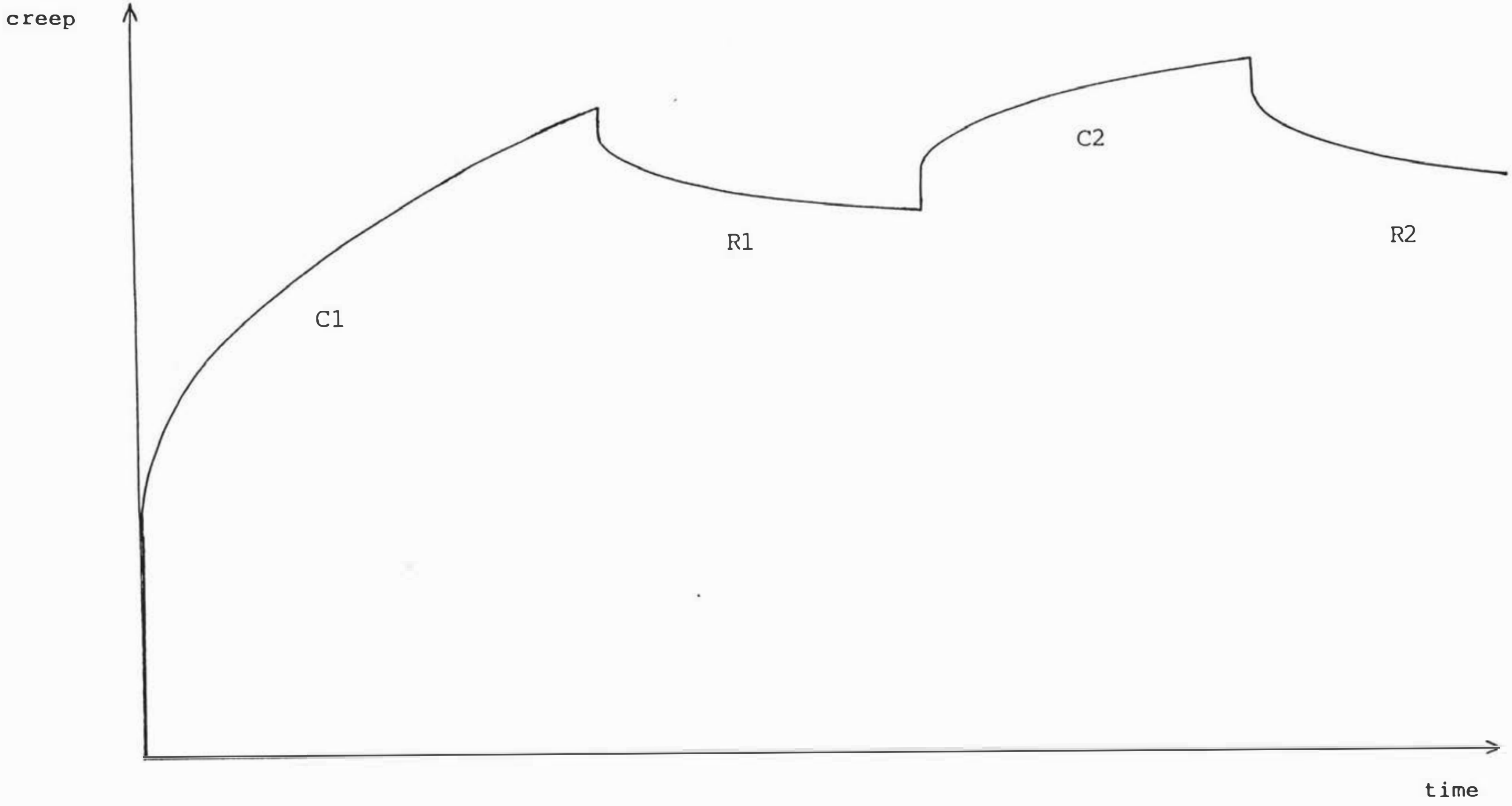
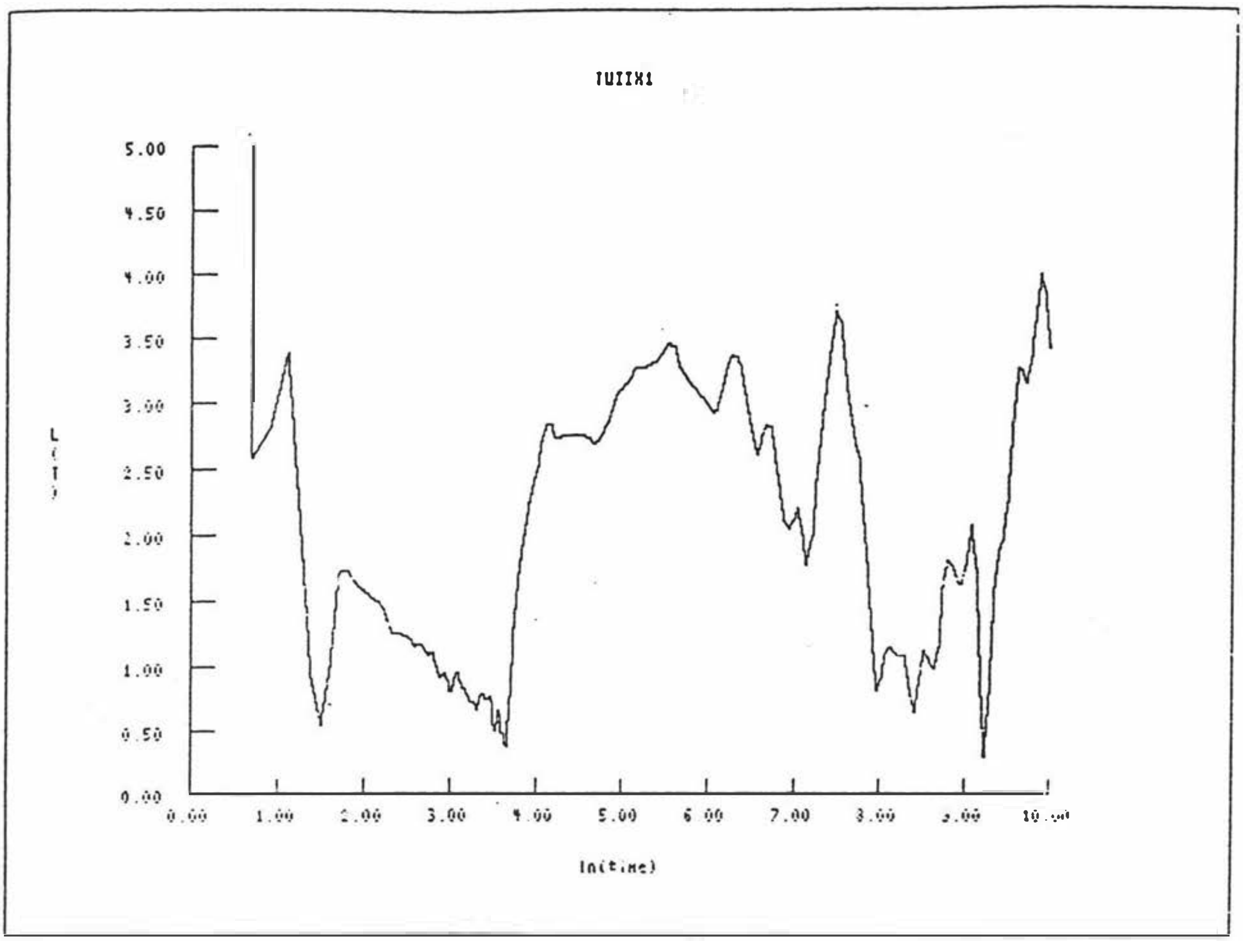
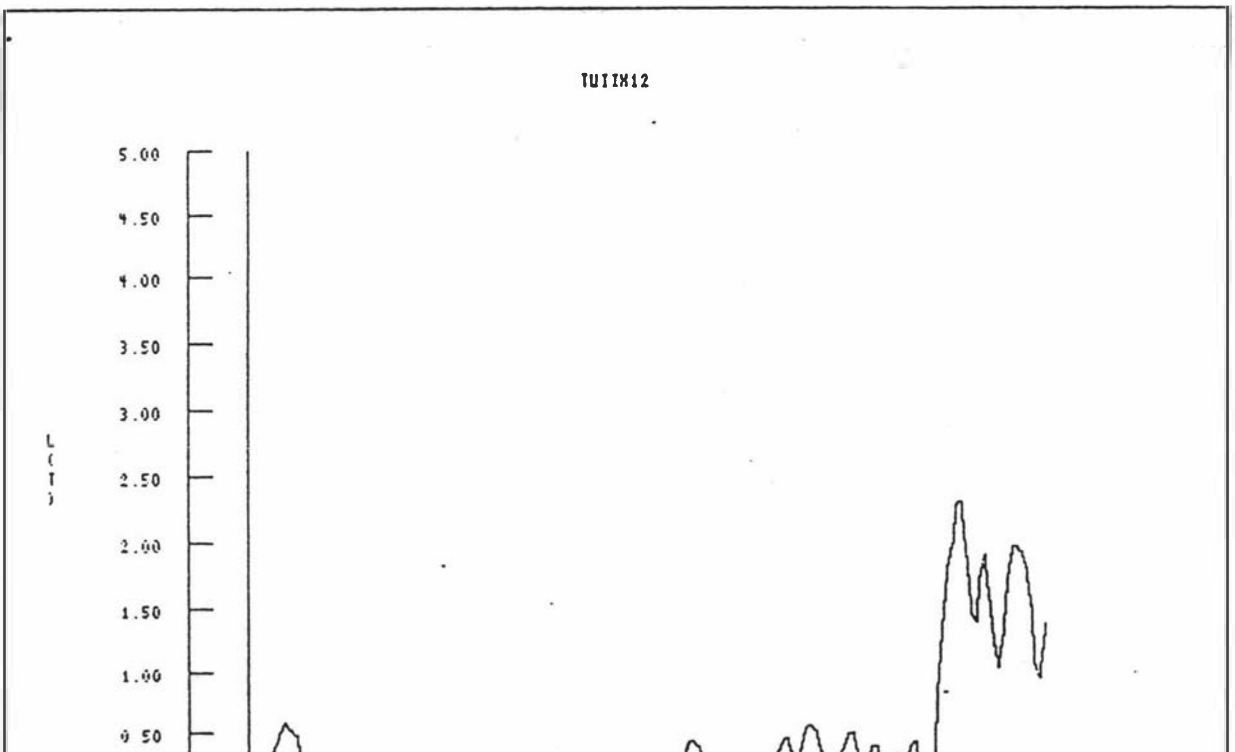


Figure 7.1: Typical creep compliance curve seen on repeatedly applying and removing stress.



(a)



(b)

Figure 7.2: Continuous retardation spectra found for the sample TUI April 1987, a) first creep response, b), second creep response.

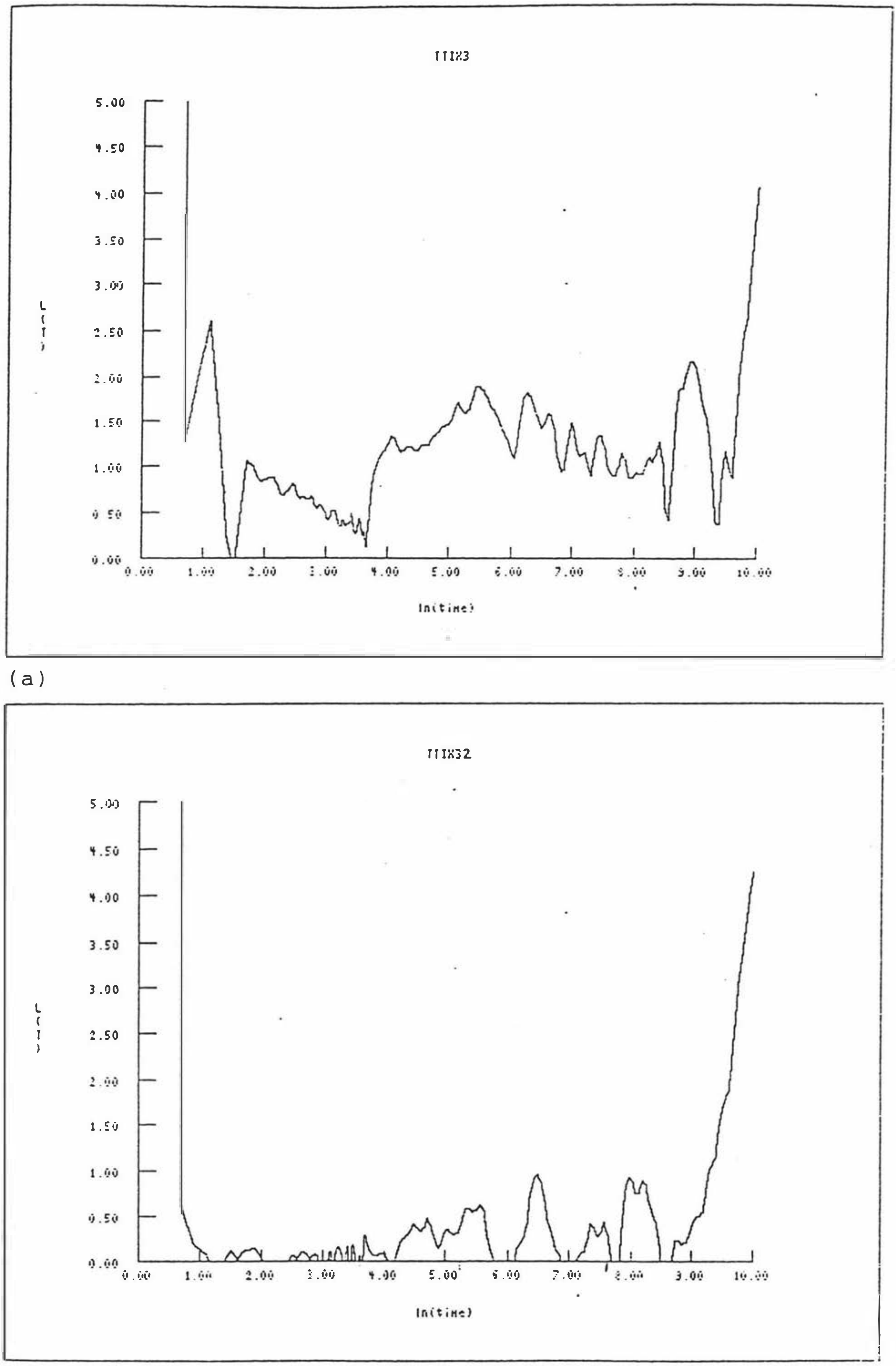


Figure 7.3: Continuous retardation spectra found for the butter TT April 1987, a), first creep response, b), second creep response.

Table 7.2: Creep compliance parameters for samples collected throughout the year.

	TUI Oct 87	TT Oct 87	TUI Jan 87	TT Jan 87	TUI Apr 87	TT Apr 87
Creep 1						
J_o	4.1 (.3)	4.8 (.4)	3.3 (.3)	4.0 (.5)	5.3 (.3)	5.2 (.3)
J_r^a	34 (2)	30 (3)	24 (2)	27 (4)	40 (1)	27 (2)
ΣJ^b	38 (2)	35 (3)	27 (2)	31 (5)	46 (1)	32 (2)
η_N	110 (22)	34 (7)	88 (14)	66 (7)	24 (2)	29 (3)
Recovery 1						
J_o	2.1 (.5)	2.2 (.5)	1.4 (.5)	1.4 (.5)	2.7 (.5)	2.5 (.5)
J_r	4.9 (.5)	7 (1)	4.6 (.5)	5 (1)	8 (2)	11 (2)
ΣJ	7 (1)	9 (2)	6 (1)	6 (2)	11 (3)	14 (3)
η_N	16 (2)	30 (3)	22 (3)	19 (1)	11 (3)	20 (4)
Creep 2						
J_o	1.9 (.3)	2.2 (.4)	1.4 (.4)	1.6 (.6)	1.1 (.3)	2.3 (.5)
J_r	2.5 (.1)	0.8 (.6)	0.8 (.1)	2.4 (.4)	7.1 (.1)	5.7 .5
ΣJ	4.4 (.4)	3 (1)	2.2 (.5)	4 (1)	8.2 (.4)	8 (1)
η_N	140 (40)	55 (5)	110 (28)	180 (88)	65 (30)	40 (10)
Recovery 2						
J_o	2.5 (.5)	2.2 (.5)	-	1.4 (.5)	2.7 (.5)	2.7 (.5)
J_r	5.5 (.5)	7 (1)	3 (1)	6.6 (.5)	7 (1)	7.3 (.5)
ΣJ	8 (1)	9 (2)	3 (1)	8 (1)	10 (2)	11 (1)
η_N	120 (30)	170 (30)	500 (100)	-	160 (80)	88 (14)
% rec J_o	50 (15)	46 (14)	42 (18)	34 (16)	51 (12)	47 (12)
% rec J_r	14 (4)	15 (8)	17 (9)	17 (10)	20 (10)	42 (18)
% rec ΣJ	18 (3)	25 (2)	20 (5)	19 (9)	25 (7)	43 (12)

(a) Retarded compliance.

(b) Sum of compliances.

( ) Standard error.

Units:

J_o, J_r, ΣJ x 10_{-8} Pa^{-1}

η_N x 10^{10} Pa s.

Table 7.3: Overall creep response displayed by samples collected throughout the year (x 10^{-8} Pa^{-1}).

	TUI Oct 87	TT Oct 87	TUI Jan 87	TT Jan 87	TUI Apr 87	TT Apr 87
Creep 1	43.7	44.7	37.5	37.3	65.1	43.8
Rec. 1	6.7	8.9	5.5	5.8	11.4	13.7
Creep 2	11.1	16.4	5.9	7.3	13.7	18.8
Rec. 2	8.3	10.9	4.7	7.5	9.9	11.6

Table 7.4: Correlation coefficients found between various creep compliance parameters and sectility hardness for samples of butter collected throughout the year.

	$\Sigma J_{C}1$	η_{NC1}	ΣJ_{R1}	η_{NR1}	ΣJ_{C2}	η_{NC2}	ΣJ_{R2}	η_{NR2}	%recΣJ	%recJ_{o}
Solid fat	-0.46	0.39	-0.62	-0.06	-0.47	0.11	-0.87	0.28	-0.48	-0.53
Sect. hard.	-0.57	0.74	-0.88	0.26	-0.86	-0.27	-0.98	0.14	-0.69	-0.44
ΣJ_{C1}	-	-0.34	0.40	-0.59	0.58	0.80	0.55	-0.31	-0.05	0.69
η_{NC1}	-	-	-0.80	-0.08	-0.60	-0.29	-0.62	0.12	-0.66	-0.18
ΣJ_{R1}	-	-	-	-0.17	0.86	0.18	0.84	-0.44	0.89	0.55
η_{NR1}	-	-	-	-	-0.63	-0.21	-0.26	0.04	0.08	0.30
ΣJ_{C2}	-	-	-	-	-	0.51	0.82	-0.18	0.66	0.47
η_{NC2}	-	-	-	-	-	-	0.18	0.00	-0.22	0.31
ΣJ_{R2}	-	-	-	-	-	-	-	-0.15	0.66	0.47
η_{NR2}	-	-	-	-	-	-	-	-	-0.33	0.95
%recΣJ	-	-	-	-	-	-	-	-	-	0.66

then remains approximately constant during the subsequent creep and recovery cycle. Similarly, very little recovery of the retarded response was observed (Table 7.2). Consequently, the sum of compliances (ΣJ) recovered is much less than the sum of compliances seen for the initial creep.

The sum of compliances found for the second creep responses appear to be smaller than those calculated for the first and second recoveries (Table 7.2). A consideration of the total creep movement (Table 7.3) shows the overall second creep response to be larger than either of the two recovery responses. The two findings are contradictory, however, the apparent discrepancy is probably due to the fact that the overall creep responses includes a viscous flow element whereas the overall recovery responses do not. The first recovery can also be seen to be the same as, or larger than the second.

While the recovery responses do not contain a viscous flow term, the responses can be used to calculate the Newtonian viscosity of the preceeding creep response. Viscosities calculated from the first recovery curve are less than those found for the first creep response (Table 7.2). However, the viscosities found for the first creep responses are similar in magnitude to those obtained from the second creep and recovery. The viscosities found for the second creep and recovery tend to be greater than those seen for the first creep.

7.2.2.1.Retardation Spectra

A comparison of the retardation spectra for the first and second creep curves shows the spectra are not alike (Figs. 7.2a, 7.2b and 7.3a, 7.3b). The retardation spectra for the second creep curves are much reduced in magnitude. The first creep curves have a far greater contribution to overall response from retardation mechanisms between ln time 3.5 and 8.5, while retardation mechanisms contribute very little to the second creep curve until long times. This can also be seen on comparing the creep curves observed (Fig. 7.4).

The necessity of fitting a reduced number of retardation mechanisms to second creep curves becomes obvious, given the much reduced contribution of such retardation mechanisms at short and medium times. The time constants fitted tended to be in the regions of approximately ln time 6.5 and 8.5. These constants also indicate a loss of retardation mechanisms at short times. The great difference between the spectra obtained for first and second creep responses also illustrates the 75 - 90% decrease seen in retarded elastic response.

7.2.2.2. Correlations

The sums of compliances found for the first recovery (ΣJ_{R1}), the second creep (ΣJ_{C2}) and the second recovery (ΣJ_{R2}) are all highly correlated with each other. In addition, these sums of compliances are all highly correlated with sectility hardness (Table 7.4). In contrast, the sum of compliances found for the first creep response (ΣJ_{C1}) is not highly correlated any other sum of compliance, neither is it highly correlated with sectility hardness (Table 7.4).

The viscosity found for the first creep response (η_{NC1}) shows a good correlation with sectility hardness. η_{NC1} also shows a high negative correlation with the sum of compliances found for the first recovery (ΣJ_{R1}) implying the more viscous a sample, the less it recovers. This contradicts established viscoelastic theory which predicts greater recovery would be seen for increasingly viscous samples. No obvious trends or patterns can be seen for other viscosity terms.

7.2.3. Discussion

7.2.3.1. General Observations

A situation seems to exist where butter is behaving as something other than a viscoelastic material. This was initially seen on allowing butter samples to recover after

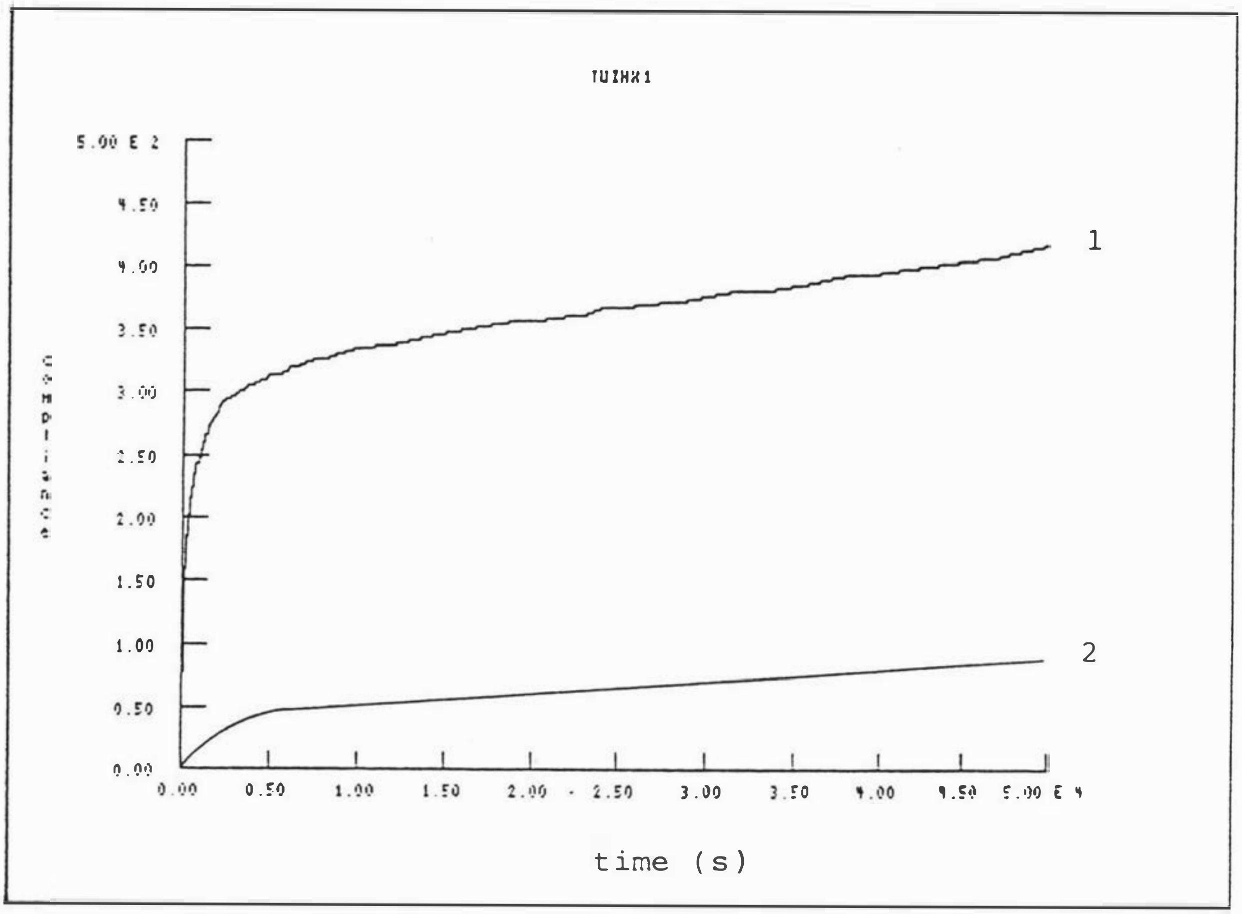


Figure 7.4: First and second creep curves observed for the butter TUI March 1987.

creep testing (Chapter 6). On extending creep experiments to a second creep/recovery cycle the expected response of a viscoelastic material to such treatment (as outlined in Chapter One) was not observed. The butters examined failed to recover all the instantaneous and retarded elastic responses and, on a second application of stress, failed to show a creep response similar to that shown on the first application of stress.

The continuous retardation spectra should remain constant for a viscoelastic system. However, retardation spectra found for the first and second creep are not the same. This can be seen in Figures 7.2a, 7.2b, 7.3a and 7.3b, which show continuous retardation spectra for the first and second creep responses for April 87 TUI and TT butter samples. The number of retardation mechanisms fitted should also remain constant from the first creep to the second. As mentioned previously, it was found a two retardation mechanism model was more appropriate to fit the second creep results. The change in the number of retardation mechanisms fitted suggests the structural elements which responded in a certain way on the first application of stress have been altered or destroyed.

The viscosity found from the first recovery (η_{NR1})is always less than that found from the first creep. However, as the viscosity from the first recovery is calculated from the total unrecovered strain (Chapter 4, Section 6.2), any permanent deformation caused by something other than viscous flow will be included in the term and effectively decrease the apparent viscosity seen. In a true viscoselastic system the viscosities calculated from both creep and recovery should be the same.

The calculation of the viscosity for the first recovery from total unrecovered strain has other effects. This viscosity is inversely correlated with the sum of compliances seen for the first creep. As the unrecovered strain includes a large proportion of the initial creep response, this is not surprising.

Table 7.2 indicates a recovery of between 30 to 50% of the instantaneous elastic response is being seen after 17 hours creep. The instantaneous elastic response differs in comparison with the retarded elastic responses in that the proportion of the original elastic response (J_{OC1}) recovered is greater than that recovered by the retarded compliances.

The percentage recovery of the instantaneous response is inversely related to solid fat content and sectility hardness. A better correlation is seen for solid fat content than sectility hardness (Table 7.4), however, neither correlation is high. In contrast, the sum of compliances found for the first and second creeps and recoveries, and percentage recovery of the sum of compliances are less well correlated with solid fat content, compared to sectility hardness. This suggests solid fat content influences the instantaneous response, while the retarded compliances may be measuring the same property as sectility hardness.

7.3. REWORKING

7.3.1. Experimental

A sample of Fritz butter and a sample of Ammix butter (TUI Mar. 87, hardness 1700g and TT Feb. 87, hardness 1650g) were reworked to investigate the effect of reworking on creep compliances. Creep compliance responses were observed for two 17 hour creep/7 hour recovery cycles.

7.3.2. Results

The non-linear least squares curve fitting program (Chapter 4, Section 6.1.2) was used to fit parameters to the creep responses for both original and reworked butters. Three retardation mechanisms were fitted to the initial creep response, while only two were fitted to the second creep response. These results, along with instantaneous compliances, sum of compliances and viscosites found for the first and second recoveries are presented in Table 7.5. Full results are

Table 7.5: Creep compliance parameters fitted to original and reworked butter pairs.

	TUI Mar 87	RWTUI Mar 87	TT Feb 87	RWTT Feb 87
Creep 1				
J_o	5.7 (.4)	19 (3)	4.8 (.5)	9 (1)
J_r^a	40 (5)	168 (4)	28 (2)	124 (7)
ΣJ^b	46 (5)	187 (7)	33 (3)	133 (8)
η_N	34 (7)	6.3 (.3)	23 (4)	10 (3)
Recovery 1				
J_o	2.7 (.5)	4.6 (.5)	1.3 (.5)	7.1 (.5)
J_r	5 (.3)	52 (15)	4.9 (.5)	24.1 (.5)
ΣJ	8.6 (.8)	55 (16)	6 (1)	31.5 (1)
η_N	14 (.4)	2.1 (.1)	18 (2)	3 (.5)
Creep 2				
J_o	1.8 (.3)	8.2 (.2)	-	6 (1)
J_r	6 (2)	22 (6)	7 (3)	16 (1)
ΣJ	8 (2)	30 (6)	7 (3)	22 (2)
η_N	68 (10)	17 (4)	80 (10)	24 (7)
Recovery 2				
J_o	2.5 (.5)	8.2 (.5)	-	6.8 (.5)
J_r	5 (.5)	31.9 (.5)	7 (1)	15 (1)
ΣJ	8 (1)	30 (1)	7 (1)	22 (2)
η_N	122 (20)	25 (3)	250 (40)	30 (10)
% rec J_o	47 (12)	51 (13)	28 (13)	77 (14)
% rec J_r	13 (4)	27 (10)	15 (8)	20 (2)
% rec ΣJ	19 (4)	28 (4)	19 (5)	23 (2)
Sect. hard. (g)	1700	575	1650	600

(a) Retarded compliance.

(b) Sum of complainces.

( ) Standard error.

<u>Units:</u>

J_o, J_r, $\Sigma J \times 10^{-8}$ Pa^{-1}

$\eta_N \times 10^{10}$ Pa.s

included in Appendix 2. Percentage recoveries are also presented in Table 7.6. Sectility hardnesses and solid fat contents are shown in Table 7.1.

Both the original and reworked samples showed the same general response curve (Fig. 7.1) on being subjected to two cycles of creep and recovery.

Hardness decreased considerably on reworking, 66% for the Fritz butter and 64% for the Ammix butter.

Initial Creep

On comparing the initial creep response of original and reworked butters, it can be seen that instantaneous compliance values increased from 5.7 to 18.9 Pa^{-1} (320%) for Fritz butter, and from 4.5 to 9.2 Pa^{-1} (190%) for Ammix butter. The sums of compliance increased by approximately 400% for both butters. The third retarded compliance term was found to increase more on reworking than the instantaneous compliance and the first and second retarded terms (Table 7.6).

The viscosity of the reworked Fritz butter decreased by 76%, compared to that of the original butter, while that of the Ammix butter decreased by 60%.

First Recovery

The percentage of the instantaneous term recovered was greater than that recovered by the retarded compliances for both original and reworked samples. The reworked Ammix sample recovered a greater percentage of the instantaneous term, compared to the original samples. The percentage of the sum of compliances recovered was approximately the same for the original and reworked samples (Table 7.5).

Second Creep

The sum of compliance terms found for the second creep responses of the reworked butters were much greater than those

Table 7.6: Percentage changes seen in creep response on the reworking of butter samples.

	TUI Mar. 87	TT Feb. 87
First creep		
% inc J_o	320	190
% inc ΣJ	380	408
% inc J_1	305	430
% inc J_2	415	440
% inc J_3	460	480
% dec η_N	76	60
Second creep		
% inc ΣJ	630	210
% dec η_N	70	70

Table 7.7: Pecentage change found in selected parameters on comparing first and second creep responses.

	TUI Mar 87	Reworked TUI Mar. 87	TT Feb 87	Reworked TT Feb. 87
% dec J_o	77	57	-	37
% dec ΣJ	92	86	78	89
% dec J_r	90	89	80	92
% inc η_N	54	64	71	60

found for the original samples, six times greater in the case of the Fritz butter, and twice as large in the case of the Ammix butter.

The viscosities found for the second creep response of both reworked butters showed a 70% decrease on the viscosities found for the original samples (Table 7.6). These findings are in line with the changes seen during the initial creep response of the original and reworked butters.

Second Recovery

The second recovery was, in general, smaller than the first recovery.

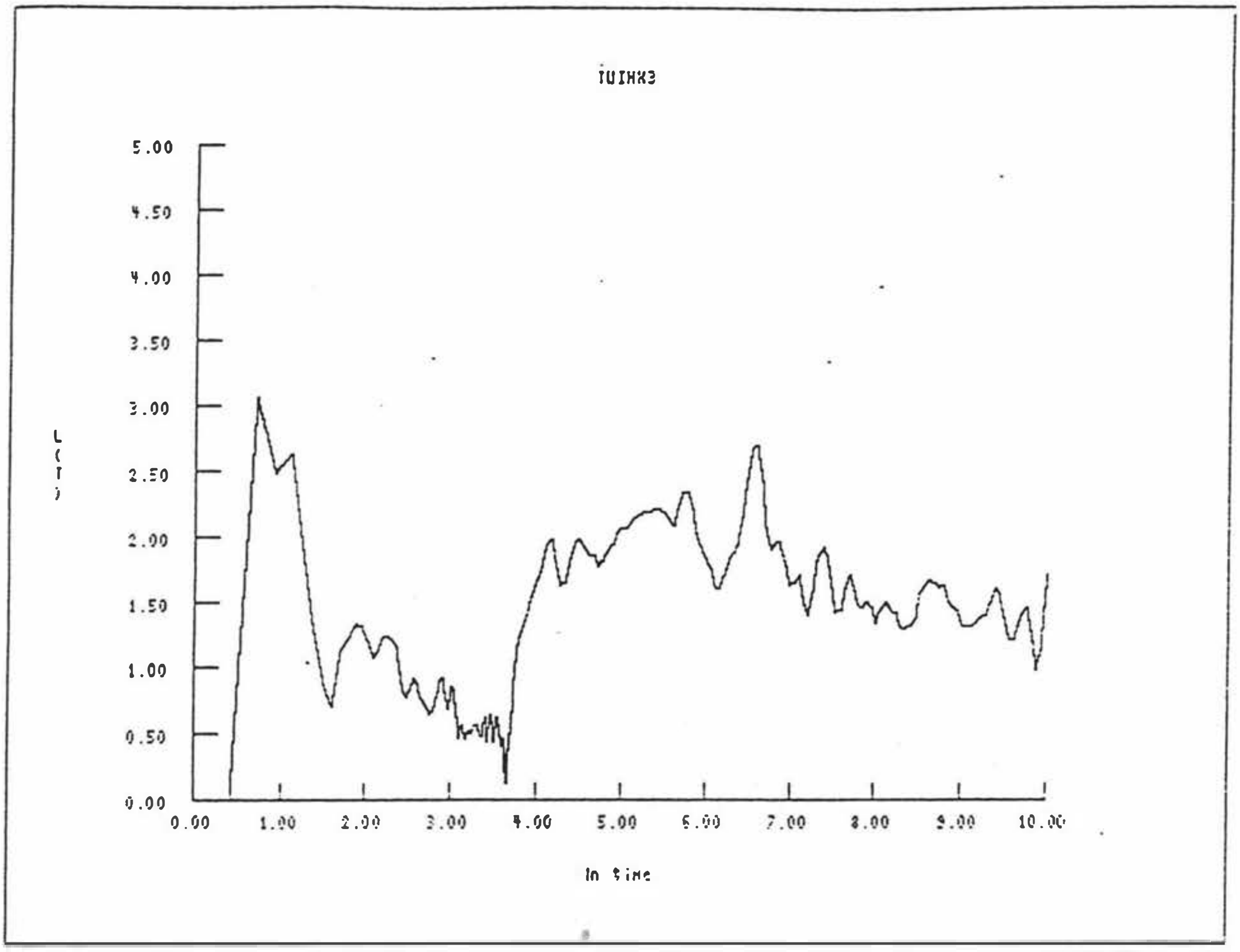
7.3.2.1. A Comparison of the First Creep Response with the Second

A comparison of the first and second creep responses for original and reworked butter shows the percentage decrease observed from the first to second creep in instantaneous compliance was less for the reworked butter. In contrast the percentage decrease in the sum of compliances for original and reworked butters was approximately the same (Table 7.7). Viscosity increased from the first to second creep, in line with those results previously seen (Section). However, there was little difference in the increases seen on comparing original and reworked butter.

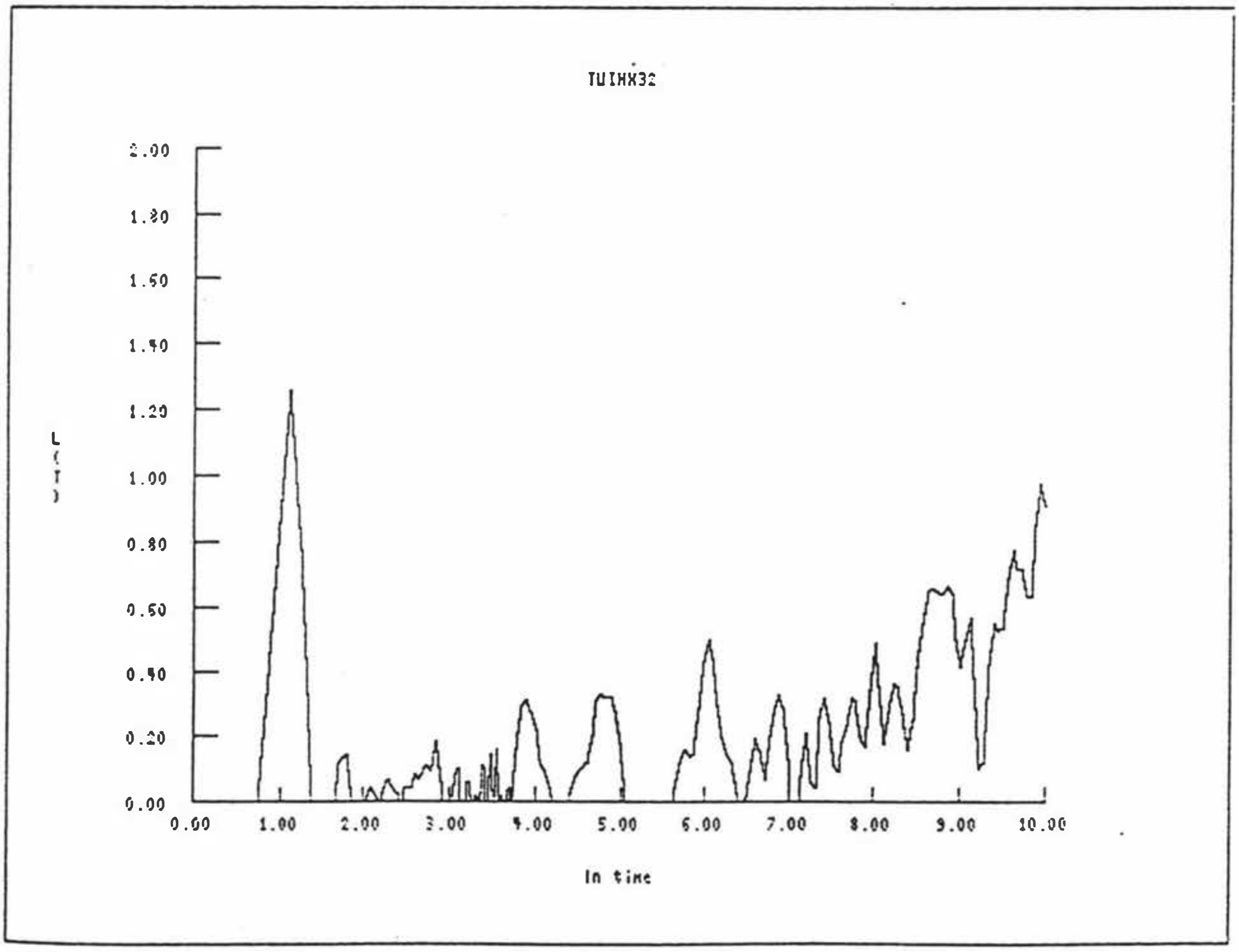
7.3.2.2. Retardation Spectra

Retardation spectra for the initial creep of the original and reworked pairs are shown in Figures 7.5a and 7.6a, and Figures 7.7a and 7.8a. The spectra found for the reworked butters have changed in shape and are smoother. The bulk of the spectra seems to lie at lower times. This trend is reflected in the shortening of retardation times fitted by the curve fitting program NONLIN (Table 7.8).

Figures 7.5b, 7.6b, 7.7b and 7.8b show the retardation spectra found for the second creep response for the original and

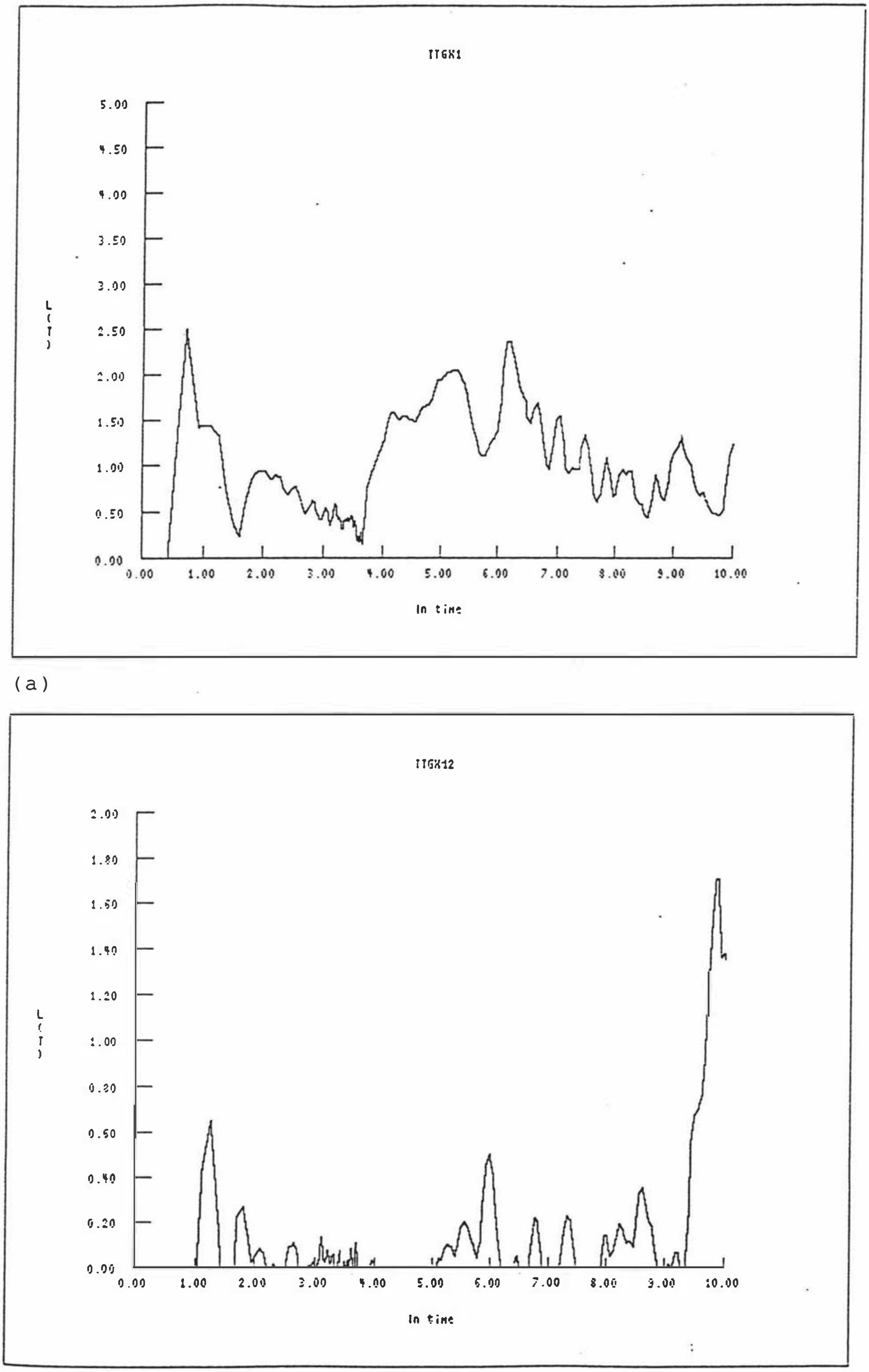


(a)



(b)

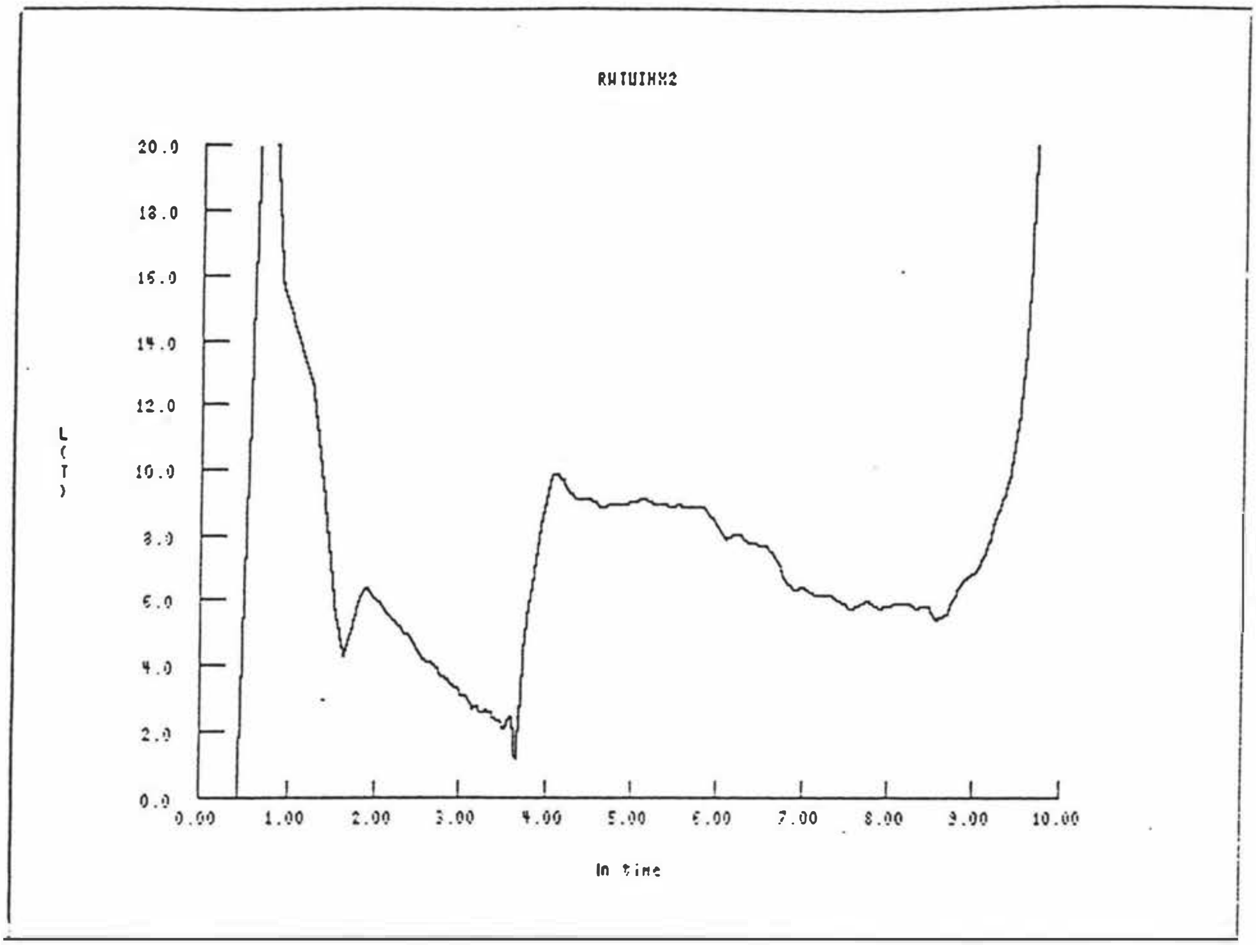
Figure 7.5: Continuous retardation spectra found for the butter TUI March 1987, a) first creep response, b), second creep response.



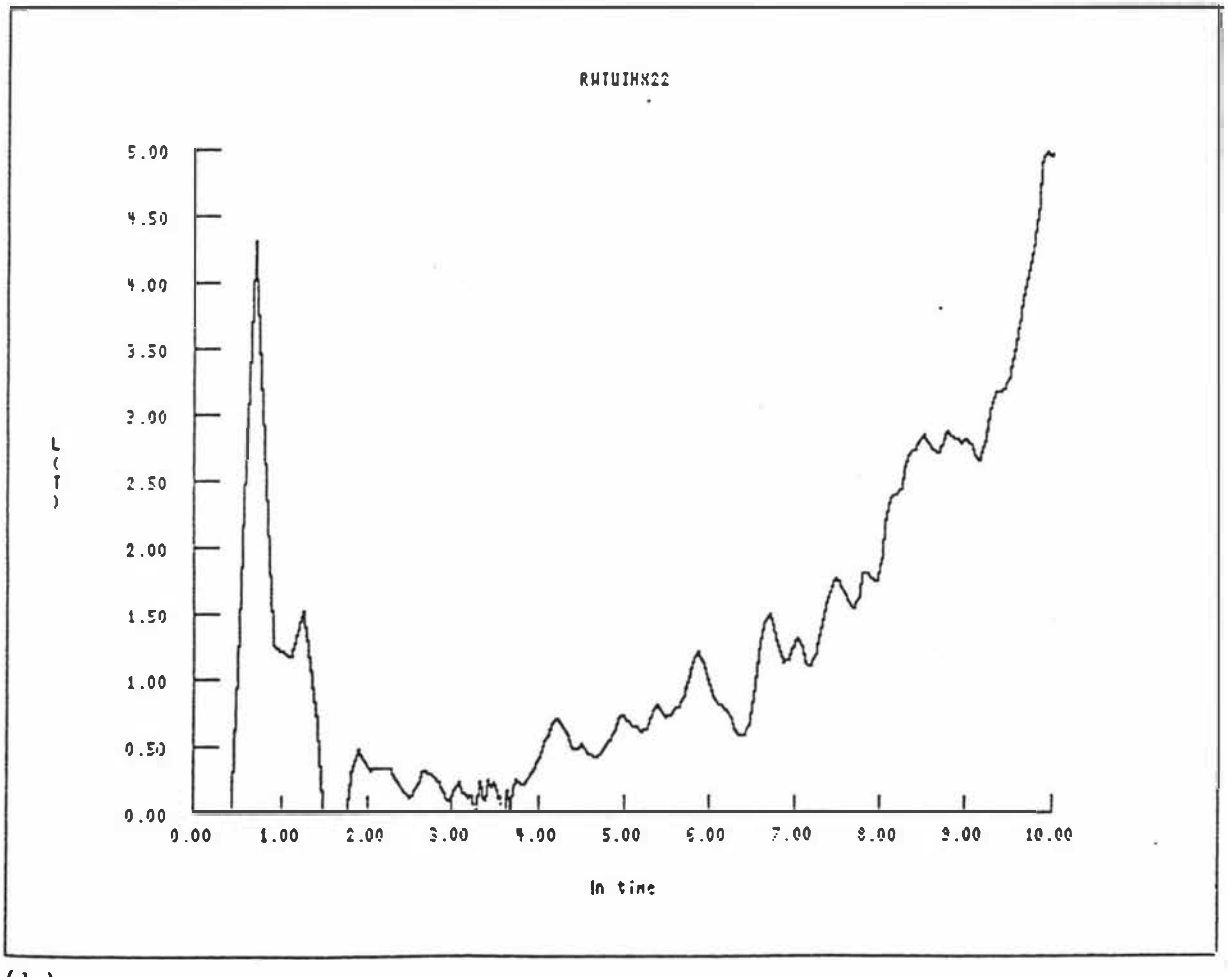
(a)

(b)

Figure 7.6: Continuous retardation spectra found for the butter TT Feb. 1987, a), first creep response, b), second creep response.



(a)



(b)

Figure 7.7: Continuous retardation spectra found for the reworked butter TUI March '87, a) first creep response, b), second creep

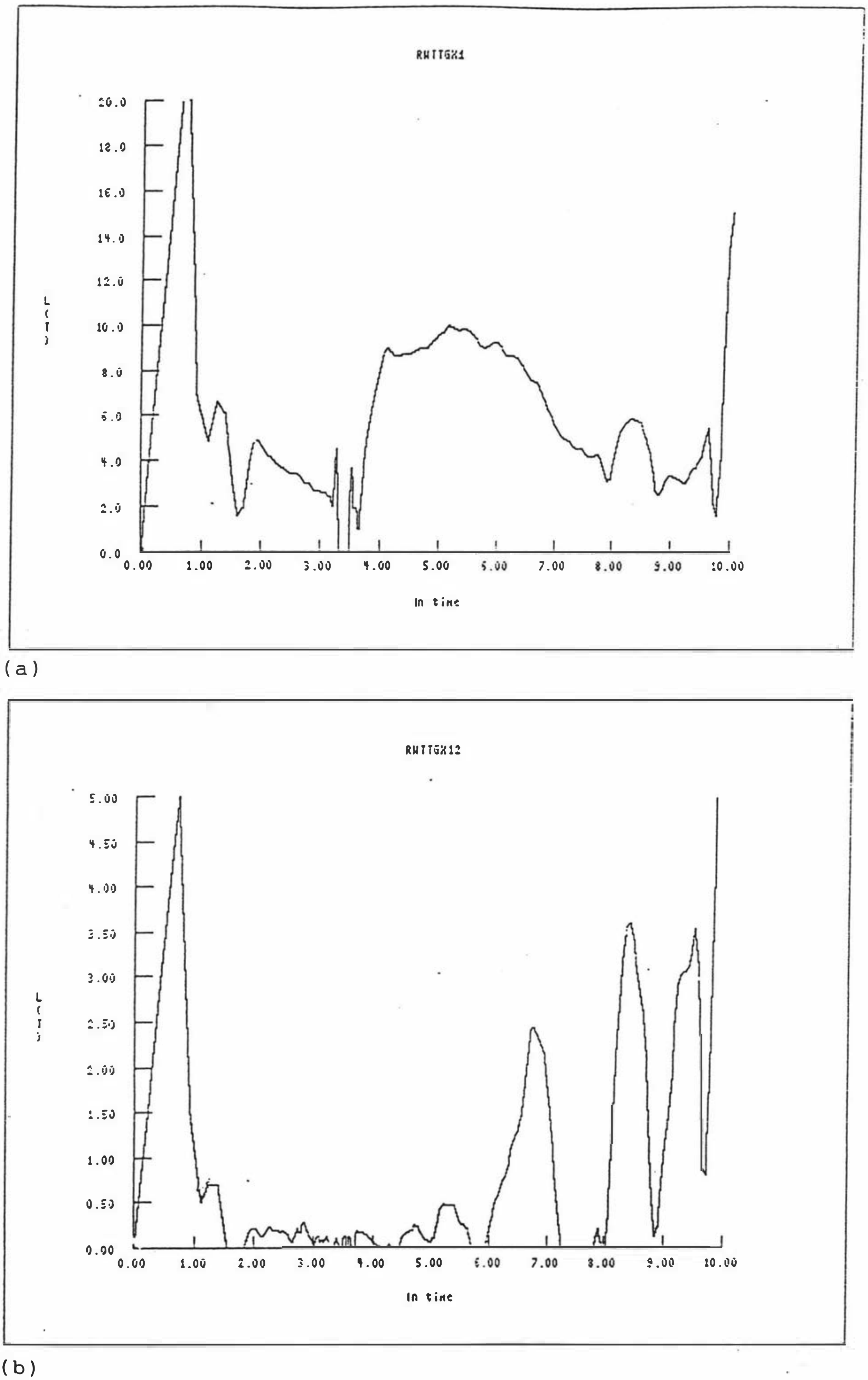


Figure 7.8: Continuous retardation spectra found for the reworked butter TT Feb, '87, a) first creep response, b), second creep response.

Table 7.8: Retardation times found for original and reworked butters.

	TUI Mar 87	Reworked TUI Mar. 87	TT Feb 87	Reworked TT Feb. 87
τ_1 (s)	28	20	29	15
τ_2 (s)	315	190	319	100
τ_3 (s)	2000	1600	3740	1000

reworked pairs. In contrast to the original butters, the reworked butters have a greater contribution to the spectra at long times.

7.3.3 Discussion

Reworking a butter results in a major disruption of any crystalline structures present. Crystals, or small clumps of crystals, will be disturbed and relocated throughout the sample. When the process of reworking is complete, crystal networks will reform. However, owing to the breaking of bonds and the disruption of structural units, these units will no longer be in their most probable configuration. This process is also thought to break 'strong' bonds or linkages between the structural elements of butter. It is thought that once these bonds are broken a large proportion either do not reform, or only partially reform over a long period of time (Haighton, 1965). For these reasons reworking results in a permanent reduction in hardness.

Both samples decreased in hardness on reworking. Creep compliance parameters have been found to correlate with sectility hardness (see later, Chapter 9, Section B.3), therefore these parameters would be expected to change for reworked butters.

Initial Creep

Instantaneous Response

The elastic compliance responses seem to be dependent on the number of strong 'bonds' present. As these are broken during reworking, the instantaneous compliance term should increase for reworked butter. The reworked Fritz butter has a third of the hardness of the original butter, and shows an instantaneous response three times greater than the original butter. The hardness of the reworked Ammix butter is 40% that of the unworked butter, with an instantaneous response twice as great as that seen for the unworked butter (Table 7.6).

Retarded Response

Retarded compliance responses should also increase because the reworking process has reduced the number of strong 'bonds' present. Retarded compliances of reworked butters are four to five times larger than those seen for the original butter. These increases are larger than would be predicted by sectility hardness alone. This suggests reworking affects elastic compliances in ways other than just breaking strong 'bonds'. The less favourable configurations of elements of the crystal lattice may make deformation easier and explain the increases seen.

Retardation times are also affected by reworking in that they decrease. It seems that as deformation becomes easier, it becomes faster (Table 7.8). It also appears some 'bonds' at medium to long times are lost on reworking. This may happen as structural units are forced from their most probable positions. On reformation of crystal networks these 'bonds' may not reform or reform very slowly. These changes are reflected in the retardation spectra.

Viscosity

The decrease in viscosity seen for reworked butter is expected. With strong 'bonds' being broken during reworking fewer bonds would need to break for particles or crystals to be able to flow.

Interestingly, the percentage decrease in viscosity is close to the percentage decrease in sectility hardness. As mentioned, sectility hardness has been found to correlate well with viscosity, and less well with solid fat content for a range of butters (see later, Chapter 9, Section B.3). Solid fat content is not affected by the breaking of strong bonds during reworking. From the observations made here it seems the viscosity (and sectility hardness) of a sample are highly dependent on the number of strong bonds present, rather than solid fat content.

Other Workers

Shama and Sherman (1970) and Gupta and DeMan (1985) observed a reduction of approximately 60% in viscosity on reworking. This figure is very similar to the reduction in viscosity seen here. Changes in the sum of compliances seen after reworking of approximately 50% were reported by these workers. This is somewhat less than the 75% seen here.

7.4. DEVELOPMENT OF A THEORY TO EXPLAIN OBSERVED BEHAVIOUR

7.4.1. Introductory comments.

The major structural component of butter is crystalline fat which forms a network or series of networks. The network is held together by a range of 'bonds' of varying strengths, ranging from actual crystal-crystal linkages to very weak attractive van-der-Waals forces (Chapter 1, Section C.2.2). Liquid oil is held within the solid fat network. Ways in which the network might deform under a shear stress must now be considered. The hypothesis must explain the observed behaviour, namely that after the initial creep response samples do not seem to undergo any further permanent changes and appear to behave in a viscoelastic fashion.

7.4.2 Theory A - The Breaking of Bonds

If, as viscoelastic theory assumes, the instantaneous response is due to strong 'bonds' or crystal-crystal linkages stretching (Sherman, 1970), the failure to recover all, or even most of the instantaneous elastic response may indicate some of these 'bonds' are being broken.

The tendency of the instantaneous responses seen after the first creep response to remain approximately the same (Table 7.2) suggests that once an initial rupture has occurred the number of remaining 'bonds' or crystal-crystal linkages does not decrease further.

The breaking of 'bonds' may continue during the retarded elastic response. The percentage recovery of the retarded compliances is less than the percentage recovery of instantaneous compliance (Table 7.2). This suggests most change in structure occurs in the retarded compliance region of the initial creep curve. This is supported by the difference in retardation spectra seen for the first and second creep responses. The differences indicate the loss of whole regions of retardation mechanisms suggesting a drastic change in structure has occurred.

In a viscoelastic system the retarded elastic response is thought to be due to the breaking and reforming of the weak van-der-Waals 'bonds' holding the crystal network together, as suggested in Chapter One, Section C.2.2. If the reformation of van-der-Waals 'bonds' is completely reversible this should lead to a complete recovery of retarded compliances. Alternatively, if van-der-Waals 'bonds' are reforming without recovering strain the second creep response should still be similar in magnitude to the first creep response. The observed creep response of butter does not fit either of these scenarios. Although van-der-Waals 'bonds' are likely to be present, there must be some other factor which is responsible for observed behaviour. This may be the breaking of bonds, as suggested above.

7.4.2.1 Criticism of Theory A

The suggestion has been made above that strain is not recovered after creep compliance due to the breaking of bonds on the application of stress. These bonds are not thought to reform on the time scale of the experiment.

The reworking of butter involves the disruption of strong bonds, leading to a permanent softening effect (Haighton, 1965). The creep response of a reworked butter has been found to show an elastic response approximately four times that seen for an unworked butter (Section 3.2 above). If, as in reworking, strong 'bonds' are broken during the first creep response, the second creep response would be expected to be greater than the first, even if recovery was small. If the number of bonds broken was small in comparison to reworking a second creep response at least similar to the first would be expected.

The viscosity of reworked butter is approximately 60 - 80% lower than that of unworked butter (Table 7.6). Analogously, viscosity should also be affected by bonds breaking and failing to reform during the initial creep response. The viscosity seen for the second creep should indicate the sample has become less viscous. In fact, the viscosities found for the first and second creep responses are of similar magnitude, with the viscosity term for the second creep (η_{NC2}) tending to be higher.

The above discussion suggests that while the possibility some bonds may break during creep compliance cannot be ruled out, the observed behaviour does not seem to be due to bonds breaking and failing to reform.

7.4.3. Theory B - Deformation of the Crystalline Network

The possibility that the bonds holding the network together are broken and not reformed during creep compliance now seems less likely, consequently a further explanation of observed behaviour appears necessary.

On the application of a shear stress, as in creep compliance, the network may behave in a way similar to polymers under stress (Mandelkern, 1964). The network may deform along the axis of applied stress. As this happens elements of the crystal network would be distorted from their most probable configurations. In polymers this results in a decrease in configurational entropy and may also be happening here. As deformation is maintained, crystal, or structural units would become increasingly orientated along the axis of shear.

As the network, or parts of the network become more orientated and become aligned with each other, opportunities for the formation of a range of bonds will arise. Weak bonds and/or van-der-Waals attractive forces will break and reform and, as duration of the experiment increases, increasingly strong 'bonds' will break and reform. Additional strong 'bonds', or crystal-crystal linkages may also be formed during this process.

The net result of forming new linkages and the continuous breaking and reforming of van-der-Waals bonds as the network becomes increasingly deformed, will be to gradually 'lock' the network into a deformed state. Not only will the deformation of the network be permanent, the deformed state will be more ordered and therefore have reduced entropy. As a result little recovery will be seen on the removal of stress. If the structure becomes locked into a more ordered state, subsequent application of stress would be expected to cause little further deformation.

7.4.3.1. Explanation of General Creep Response in Relation to This Proposed Theory

To investigate whether or not the theory of network deformation accounts for the creep and recovery behaviour during creep compliance testing of the butter, it is now appropriate to consider the responses of original and reworked butter samples with varying sectility hardnesses and solid fat contents.

Initial Creep, Instantaneous Response

On the application of stress an instantaneous elastic response is seen. This can be thought of as the instantaneous elastic deformation of the network. The instantaneous response increases as solid fat content decreases. As percentage solid fat decreases the crystalline network will be less rigid because of a smaller number of 'bonds', and there will be a smaller mass of crystals to deform. This, and the possibility of increased liquid fat acting as a lubricant will not only make deformation easier, but will increase the magnitude of the deformation. Similarly, in reworked butters which contain fewer strong 'bonds', the crystalline network will be less rigid and will deform more easily.

Retarded Response

The retarded elastic response can be thought of as the network continuing to deform, with deformation becoming slower as time goes on. Bonds will be breaking and new bonds will be forming, including some new strong 'bonds'. The network will also be becoming more orientated in the direction of shear. The degree of deformation will be reflected in the compliances seen.

Solid fat content has been seen to have an effect on the retarded elastic compliances. Less crystalline fat not only means fewer crystals present to participate in the network and fewer 'strong bonds', but also a smaller number of crystals to deform. Overall, this will result in a less rigid network, which is easier to deform.

The large increase in retarded compliances seen for reworked butters presumably results in part from fewer strong 'bonds' being present in the structure. As noted previously (Section 3.3) an additional factor may be involved, namely the less favourable configuration of structural elements resulting from reworking.

Viscosity

Viscous flow will eventually occur as particles break free and are able to move. This will also help orientation of structural units in the direction in which stress is applied.

Viscosity is correlated with sectility hardness, and solid fat content to a lesser extent. As sectility hardness and solid fat content decrease fewer strong 'bonds' will be present.

Presumably, with fewer strong 'bonds' to be broken before flow occurs, a greater viscous response would be seen. This is especially marked for butters in which strong 'bonds' have been broken on reworking. Increased amounts of liquid fat would also facilitate flow, and both factors would contribute to increased orientation of structural units.

First Recovery

On the removal of stress, little recovery of strain is seen as the deformed network has been 'locked' into place. Some instantaneous recovery (30 - 50%) of the original elastic response is seen as the whole network relaxes when stress is removed. The instantaneous recovery increases as solid fat content decreases. A much smaller recovery of original retarded elasticity is seen (15 - 20%). This presumably occurs as parts of the network relax further, at a slower pace.

A greater recovery of the instantaneous compliance is seen for reworked butters (Table 7.5), possibly indicating the reduction in the number of strong 'bonds' and the less rigid structure resulting from reworking enables greater relaxation on the removal of stress. The recovery of sums of retarded compliances is also greater for reworked butters. This may also indicate the reduction of the number of strong 'bonds' enables the deformed structure to relax more.

Second Creep and Recovery

On a second application of stress the instantaneous response is similar to that seen previously on recovery. It can be thought of as the network 'taking the strain' again. Similarly, retarded elastic responses are of the same order as the strain recovered. A greater response than that seen for recovery may be observed for the second creep, especially in softer butters, as further orientation takes place.

The second recovery is frequently smaller than that seen for the first recovery, also indicating the network has become more orientated and more 'locked' into a new, ordered state during the second creep. Eventually an equilibrium will be reached after which very little irreversible deformation will take place.

Retardation Spectra

The retardation spectra found for the second creep responses tend to support the idea that deformation is still occurring at long times. Very little deformation seems to be occurring at short times. This may indicate the deformed network is reasonably stable after one creep-recovery cycle. However, a problem with scale exists as the second creep responses are very small. This may be obscuring the spectra at short times.

CHAPTER EIGHT

BUTTER AND ANHYDROUS PRODUCTS MADE FROM THE SAME FAT

8.1. INTRODUCTION

Creep compliance experiments on butter in which stress is applied and removed in a cyclic fashion (load cycling) indicate samples being tested are not acting as viscoelastic materials. Permanent structural changes seem to be occurring on the application of stress. This is thought to be due to the crystalline network deforming along the axis of applied stress. A combination of new strong bonds and the relocation of weak bonds increasingly lock the network into a new, possibly more ordered state. This was discussed in the previous chapter.

8.2. EXPERIMENTAL

Three samples, a plasticized milkfat, a milkfat/oil blend and a butter were prepared from the same milkfat source in order to investigate the effect of the presence of water and the influence of solid fat content on creep compliance behaviour. The samples were manufactured using an Ammix type process, details of which are found in Chapter Two. All three samples were later reworked.

Sectility hardness values at 10°C were obtained for both the original and reworked samples. Solid fat contents were found by NMR. The solid fat contents of the anhydrous products (original and reworked plasticized milkfat and milkfat/oil blend) were determined directly from the products themselves. Samples were loaded cold at 5°C. The solid fat content of the milkfat extracted from the butter was also determined. Melting thermograms were obtained by differential scanning calorimetry for the original and reworked anhydrous products.

Samples were loaded cold at 5^{O}C. All samples were subjected to creep compliance testing for 17 hours then allowed to recover for 7 hours. The creep/recovery cycle was then repeated.

8.3 RESULTS

Sectility hardness results are presented in Table 8.1, and solid fat contents in Table 8.2. Figure 8.1a and b illustrate the melting thermograms obtained for the plasticized milkfat both before and after reworking, with Figure 8.2a and b showing the melting curves of the milkfat/oil blend before and after reworking.

The creep response of the samples was very similar to that seen and described in Chapter Seven, Figure 1. Creep compliance parameters were found for both the first and second creep responses (C1 and C2 respectively) using a non-linear least squares curve fitting program (Chapter 4, Section 6.1.2). Three retardation mechanisms were fitted to the first creep curve and two were fitted to the second creep curve. Instantaneous responses, the sum of compliances and viscosity terms for the first and second recovery curves (R1 and R2 respectively) were found directly from the recovery curves (Chapter 4, Section 6.2). Results are presented in Table 8.3. Full creep results are given in Appendix 2. Table 8.4 gives the correlation coefficients found between various creep compliance parameters and sectility hardness.

Continuous retardation spectra for the first and second creep responses for the original samples are presented in Figures 8.3 (plasticized milkfat), 8.4 (butter) and 8.5 (milkfat/oil blend). The retardation spectra found for the first and second creep responses for the reworked samples are presented in Figures 8.6 (plasticized milkfat), 8.7 (butter) and 8.8 (milkfat/oil blend).

8.3.1. Sectility Hardness and Solid Fat Content

The original plasticized milkfat and butter manufactured from the same milkfat have approximately the same sectility

Table 8.1: Sectility hardness results, $10^{o}C$.

	Sample	Sectility Hardness (g)	% red'n hardness
Original	PMF	1800	-
	Butter	1825	-
	MF/oil	1512	-
Reworked	PMF	550	69
	Butter	750	59
	MF/oil	485	68

Table 8.2: Solid fat contents as determined by NMR.

	Temperature (^{o}C)							
	0	5	10	15	20	25	30	35
Original								
PMF	48.0	43.4	35.8	28.9	18.4	8.7	3.8	0.4
MF/oil	39.1	34.8	28.7	22.3	13.2	6.2	2.5	-
Reworked								
PMF	49.7	45.6	40.2	32.1	20.2	9.1	3.6	0.7
MF/oil	41.6	37.9	33.3	25.6	14.7	6.5	2.7	0.8
Butter*	59.6	55.8	48.8	33.2	16.6	8.5	4.0	1.1

* Extracted fat.

PMF = plasticized milkfat.
MF/oil = milkfat/oil blend.

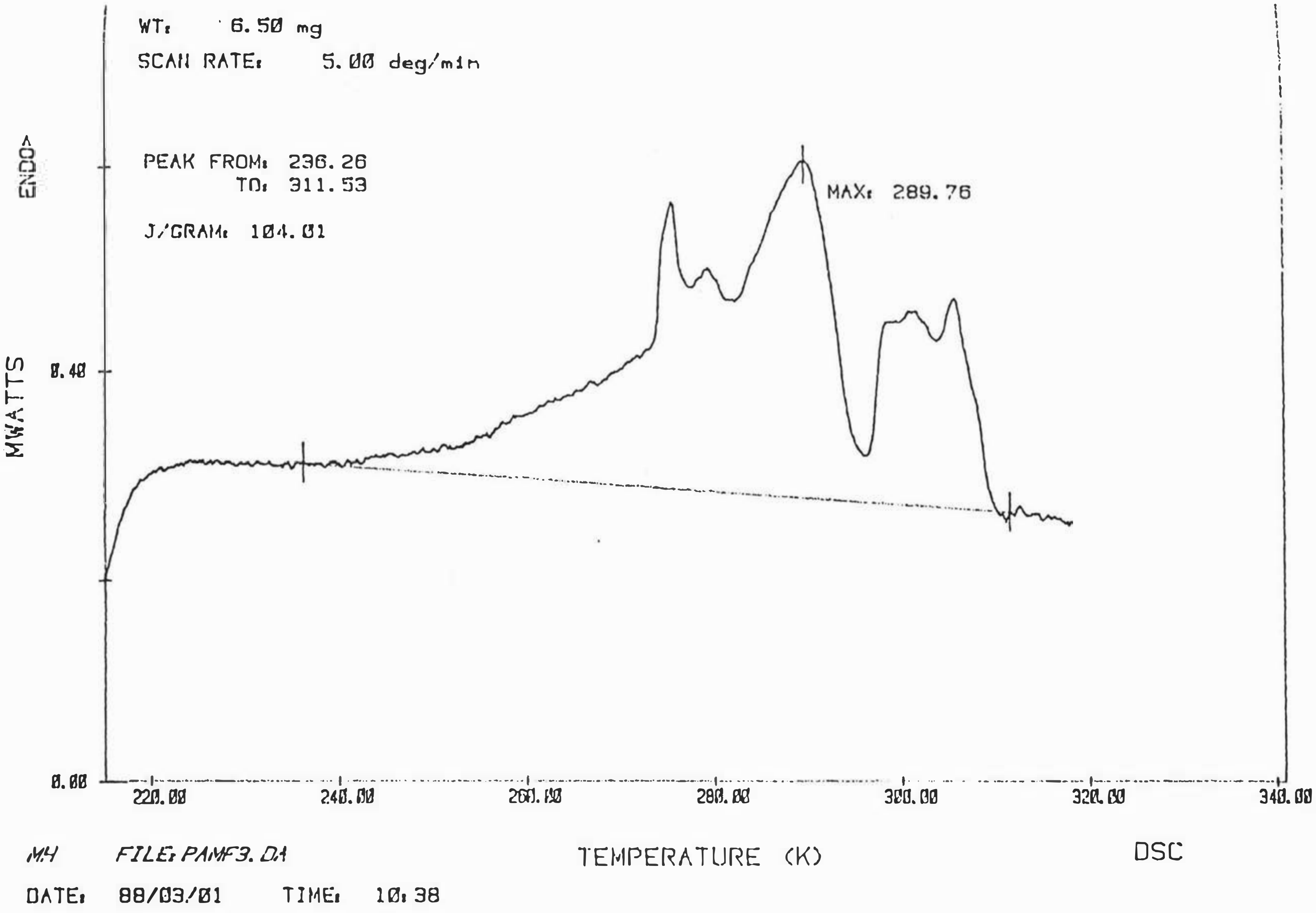


Figure 8.1a: Differential scanning calorimetry melting thermogram found for original plasticized milkfat.

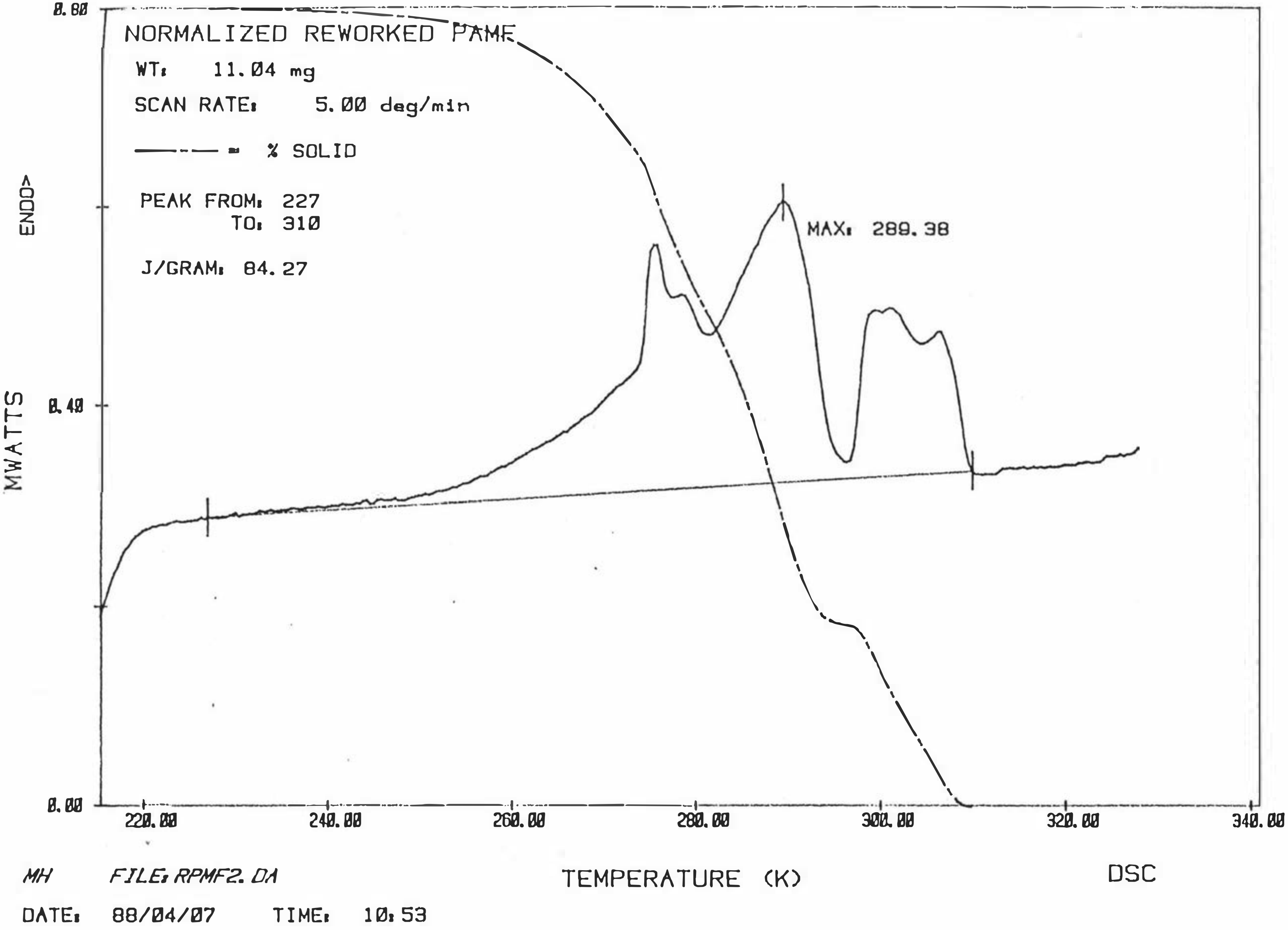


Figure 8.1b: Differential scanning calorimetry melting thermogram found for reworked plasticized milkfat.

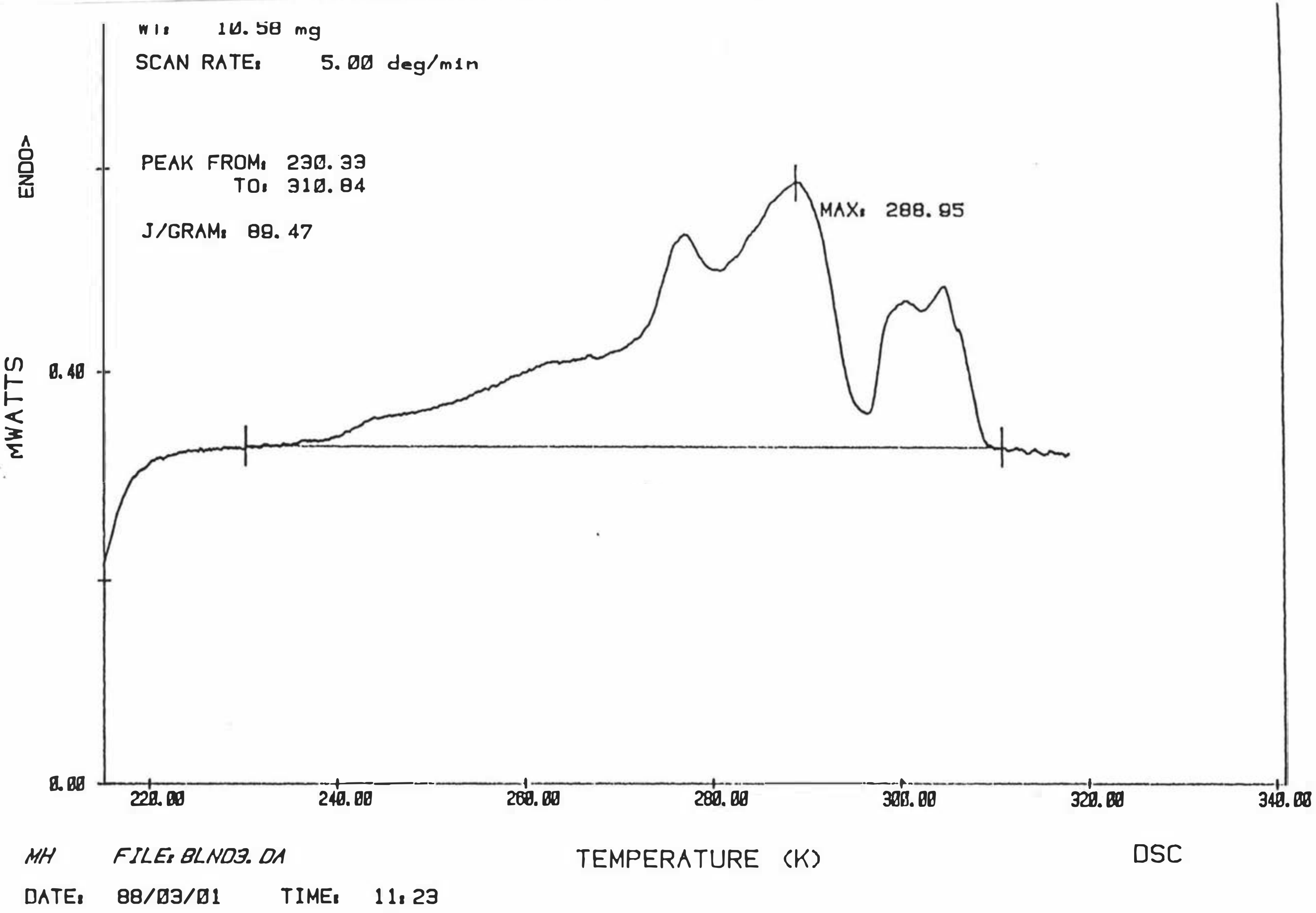


Figure 8.2a: Differential scanning calorimetry melting thermogram found for original milkfat/oil blend.

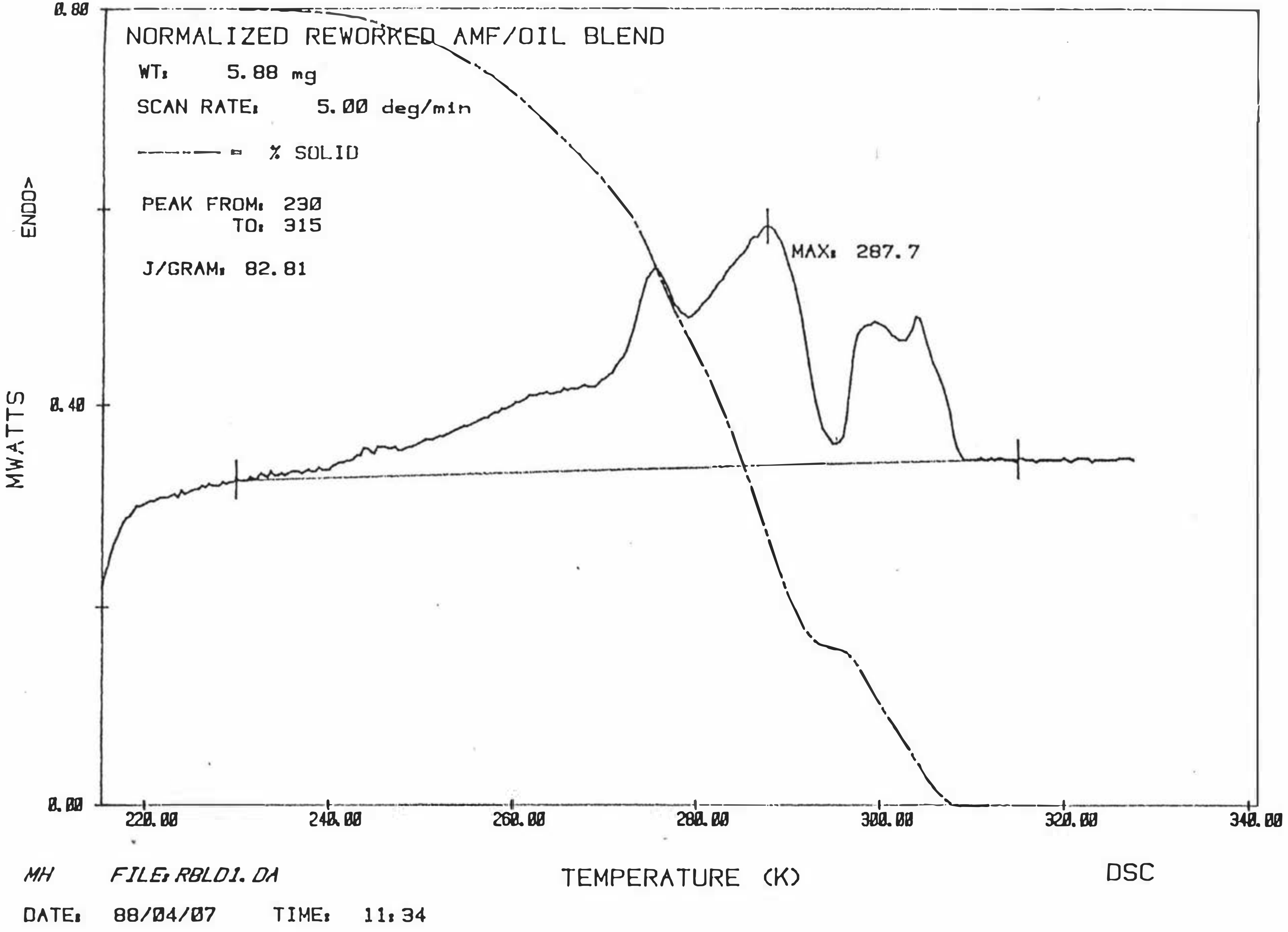


Figure 8.2b: Differential scanning calorimetry melting thermogram found for reworked milkfat/oil blend.

Table 8.3 Creep compliance parameters for original and reworked samples of butter, plasticized milkfat and a milkfat/oil blend manufactured from the same fat source.

		Original			Reworked	
	Butter	PMF	MF/oil	Butter	PMF	MF/oil
Creep 1						
J_o	4 (.3)	4 (.3)	7 (2)	11 (1)	12 (.1)	22 (3)
J_r[a]	19 (1)	21 (3)	46 (5)	104 (4)	131 (13)	160 (22)
ΣJ[b]	23 (2)	25 (3)	53 (9)	115 (5)	143 (13)	182 (25)
η_N	70 (4)	30 (3)	37 (3)	9.6 (.6)	6 (1)	4.0 (.1)
Recovery 1						
J_o	2 (.5)	2 (.5)	3 (.7)	6 (.8)	6 (.5)	14 (.5)
J_r	5 (1)	6 (1)	5 (.3)	15 (5)	32 (3)	52 (2)
ΣJ	7 (1)	8 (1)	8 (1)	21 (6)	38 (3)	66 (2)
η_N	33 (6)	20 (1)	21 (3)	5.1 (.2)	3.2 (.1)	1.8 (.1)
Creep 2						
J_o	1.1 (.4)	1.4 (.2)	2.5 (.3)	4.2 (.3)	5.5 (.4)	8.9 (.1)
J_r	3 (.1)	1.6 (.8)	3 (.7)	12 (.2)	11 (.4)	15 (3)
ΣJ	4 (.5)	3 (1)	6 (1)	16 (.5)	16 (.8)	24 (3)
η_N	300 (20)	70 (10)	90 (10)	20 (.5)	11 (1)	8 (3)
Recovery 2						
J_o	2.1 (.4)	2.1 (.5)	3 (.7)	6.8 (.5)	6.8 (.5)	12 (.5)
J_r	2.3 (.1)	4.9 (.5)	3 (.3)	14 (5)	26 (3)	35 (6)
ΣJ	4.4 (.5)	7 (1)	6 (1)	21 (6)	33 (4)	48 (7)
η_N	1100 (300)	270 (50)	98 (14)	23 (5)	25 (6)	18 (4)
% rec J_o	48 (15)	58 (18)	46 (24)	50 (12)	46 (5)	64 (11)
% rec J_r	25 (13)	28 (13)	10 (7)	14 (7)	25 (6)	33 (8)
% rec ΣJ	29 (7)	32 (8)	15 (5)	18 (6)	27 (4)	36 (6)

(a) Retarded complaince.
(b) Sum of compliances.
( ) Standard error.

Units:

J_o, J_r, ΣJ $\times 10^{-8}$ Pa^{-1}.
η_N $\times 10^{10}$ Pa.s.

Table 8.4: Correlation coefficients found between various creep compliance parameters and sectility hardness for original and reworked butters, plasticized milkfat and milkfat/oil blend manufactured from the same fat.

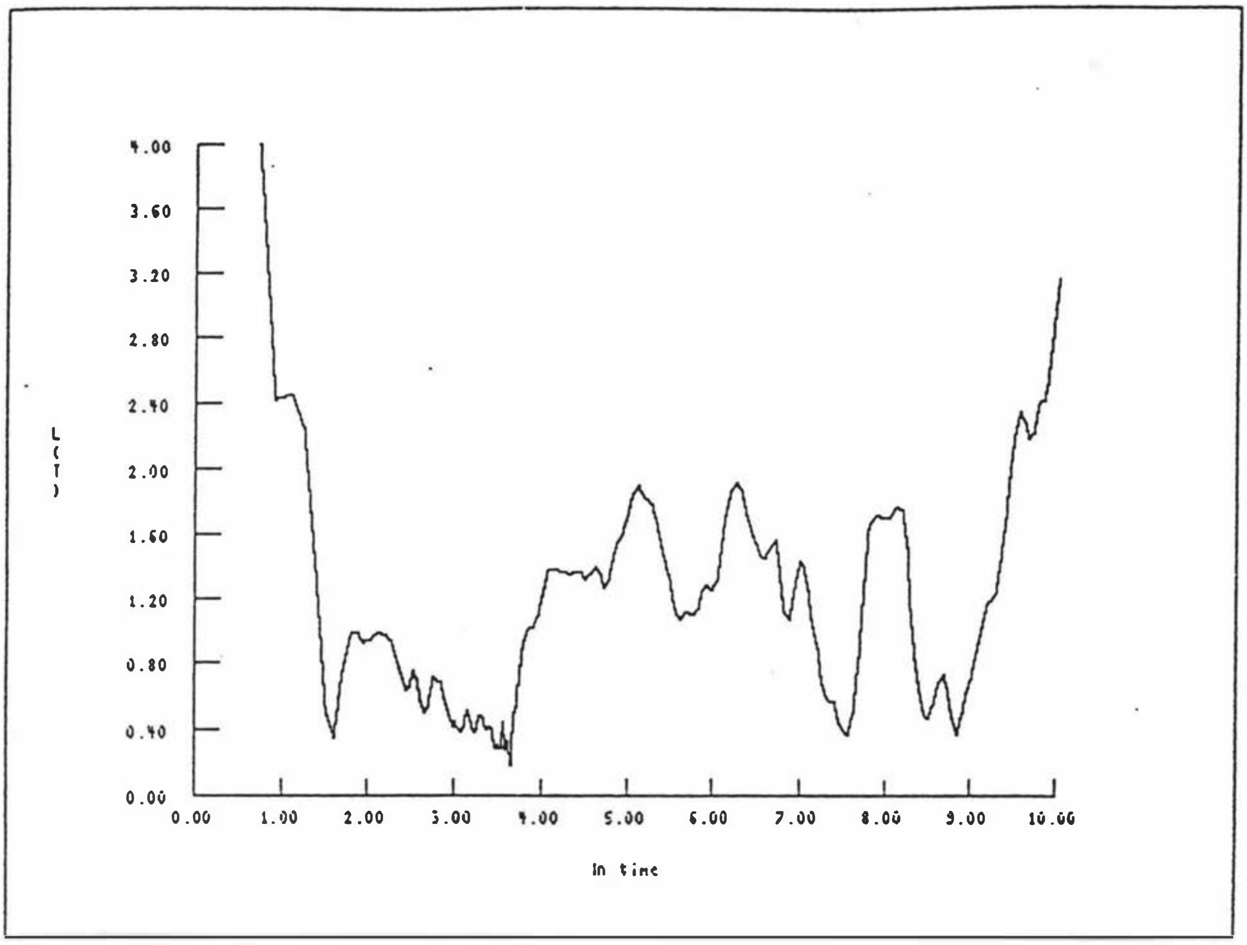
	ΣJ_{C1}	η_{NC1}	ΣJ_{R1}	η_{NR2}	ΣJ_{C2}	η_{NC2}	ΣJ_{R2}	η_{NR2}	%recΣJ
Sect hard	-0.98	0.87	-0.86	0.95	-0.96	0.74	-0.91	0.68	0.08
ΣJ_{C1}	-	-0.84	0.94	-0.91	0.99	-0.71	0.97	-0.65	0.22
η_{NC1}	-	-	-0.73	0.98	-0.79	0.97	-0.78	0.91	-0.06
ΣJ_{R1}	-	-	-	-0.79	0.95	-0.59	0.99	-0.49	0.52
η_{NR1}	-	-	-	-	-0.89	0.91	-0.86	0.84	-0.09
ΣJ_{C2}	-	-	-	-	-	-0.65	0.97	0.58	0.25
η_{NC2}	-	-	-	-	-	-	-0.65	0.98	-0.03
ΣJ_{R2}	-	-	-	-	-	-	-	-0.56	0.44
η_{NR2}	-	-	-	-	-	-	-	-	0.21

hardness, while the milkfat/oil blend is softer. On reworking the hardness of all samples is reduced. The hardness of the two anhydrous products decreased by approximately 70% while the hardness of the butter decreased by approximately 60%.

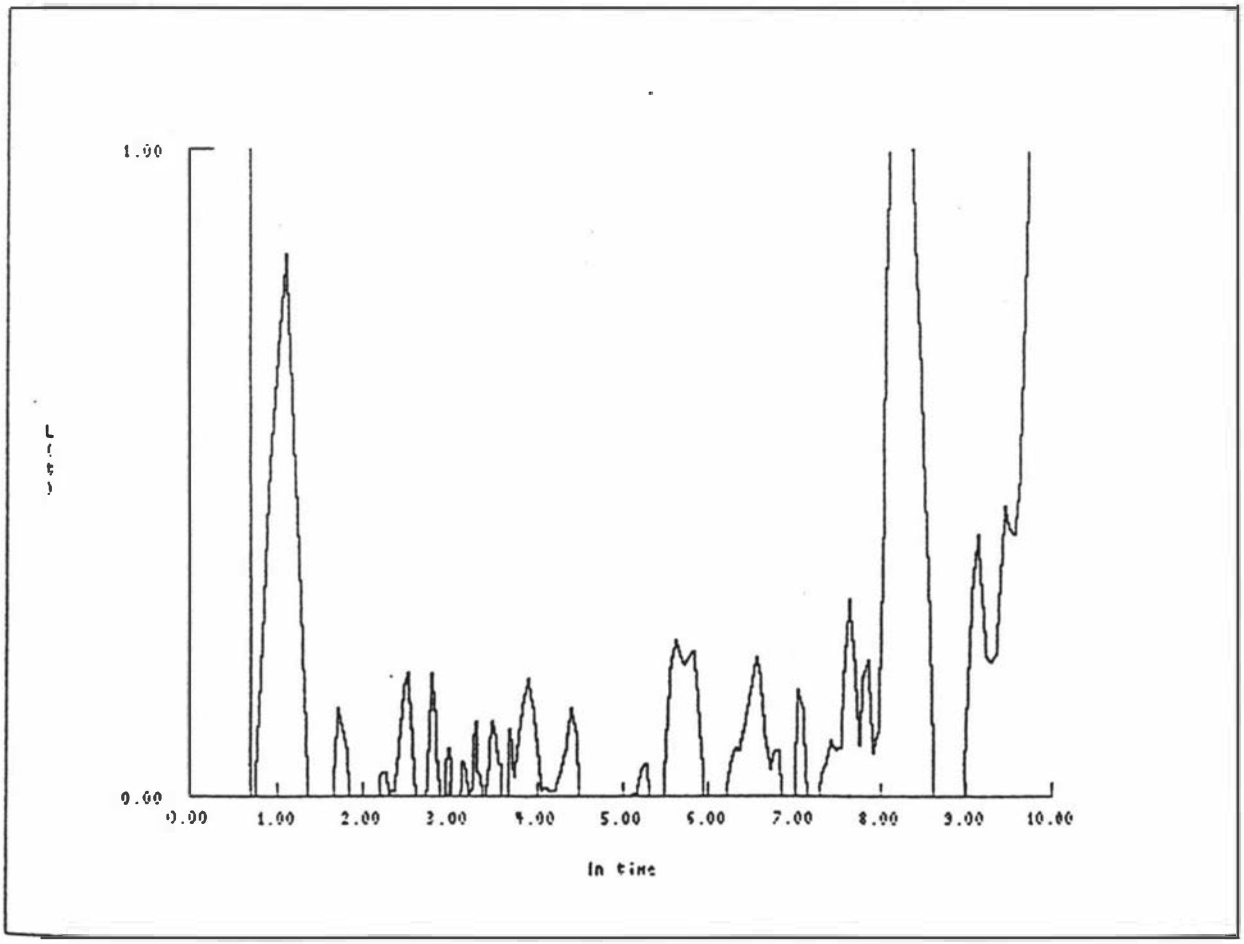
As expected solid fat contents indicate the original milkfat/oil blend has less solid fat than the original plasticized milkfat. On reworking the solid fat contents of the anhydrous products increases slightly (2 - 4%) around 10 - 15°C. This phenomenon has been noted before (Bissell, 1988). This suggests temperature during reworking may have reached about 15°C, causing some of the fat to melt and subsequent recrystallization has increased the amount of solid fat.

A meaningful comparison of the solid fat content of butter and the anhydrous products can not be made because fat was initially extracted from the butter before measurement.

The melting thermograms determined by differential scanning calorimetry (Figures 8.1 and.8.2) give a visual picture of the way in which the anhydrous products respond to increasing temperature. It can be seen that the milkfat/oil blend has a greater proportion of liquid fat at low temperatures. The thermograms show a main peak at 16°C preceeded by a smaller peak at 5°C. The plasticized milkfat exhibits a sharp water peak at 0°C, which distorts the smaller peak. The magnitude of the peak suggests the product contains approximately 1% moisture. The main peak is followed by a sharp dip and a large, broad peak. This feature suggests the high melting triglycerides may be crystallizing separately during manufacture rather than forming solid solutions with the intermediate melting triglycerides (Taylor et al, 1978). On reworking the main features of the melting thermograms did not change.



(a)



(b)

Figure 8.3: Continuous retardation spectra found for plasticized milkfat; (a) initial creep resonse, (b) second creep response.

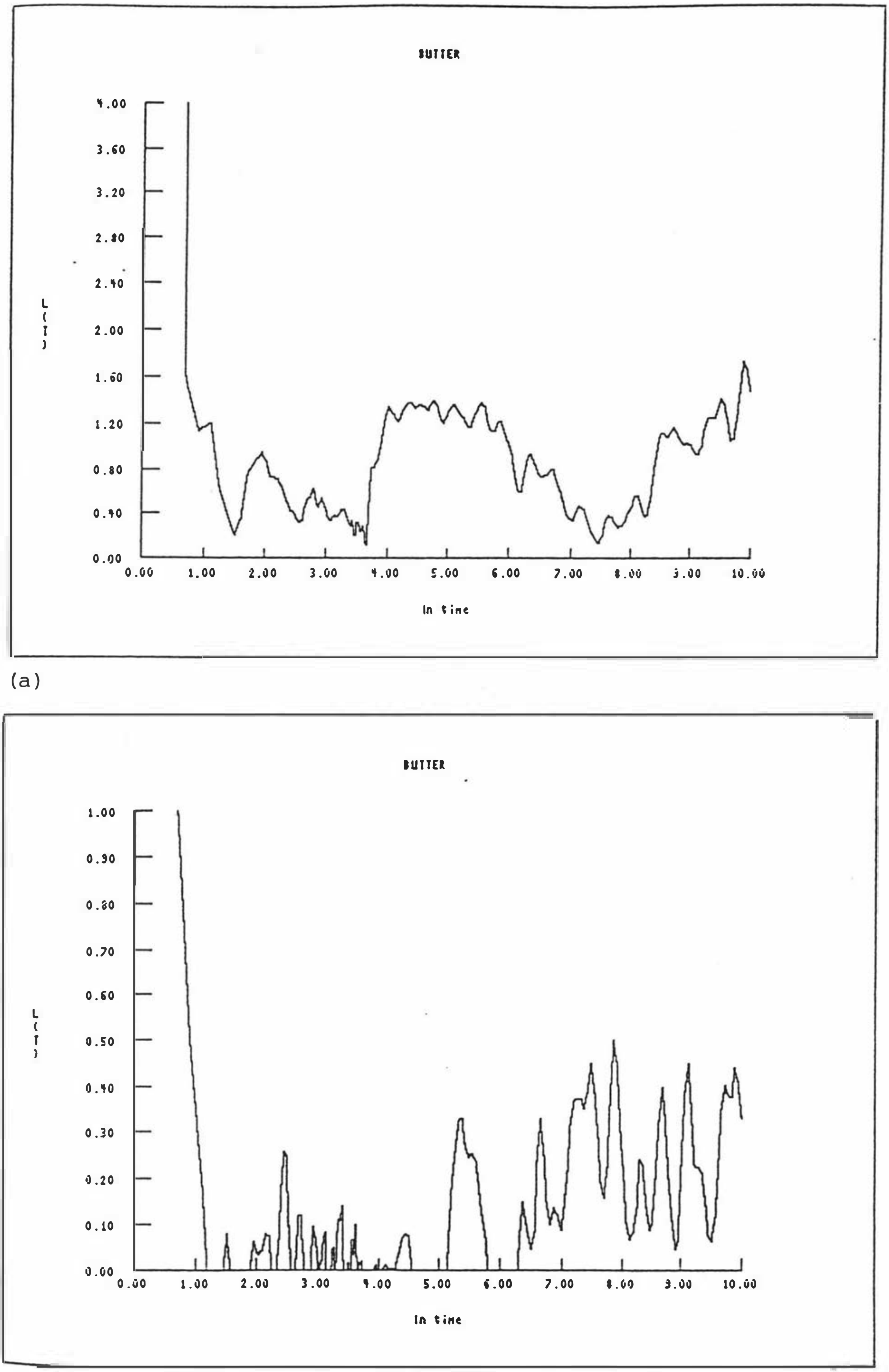


Figure 8.4: Continuous retardation spectra found for butter: (a) initial creep response, (b) second creep response.

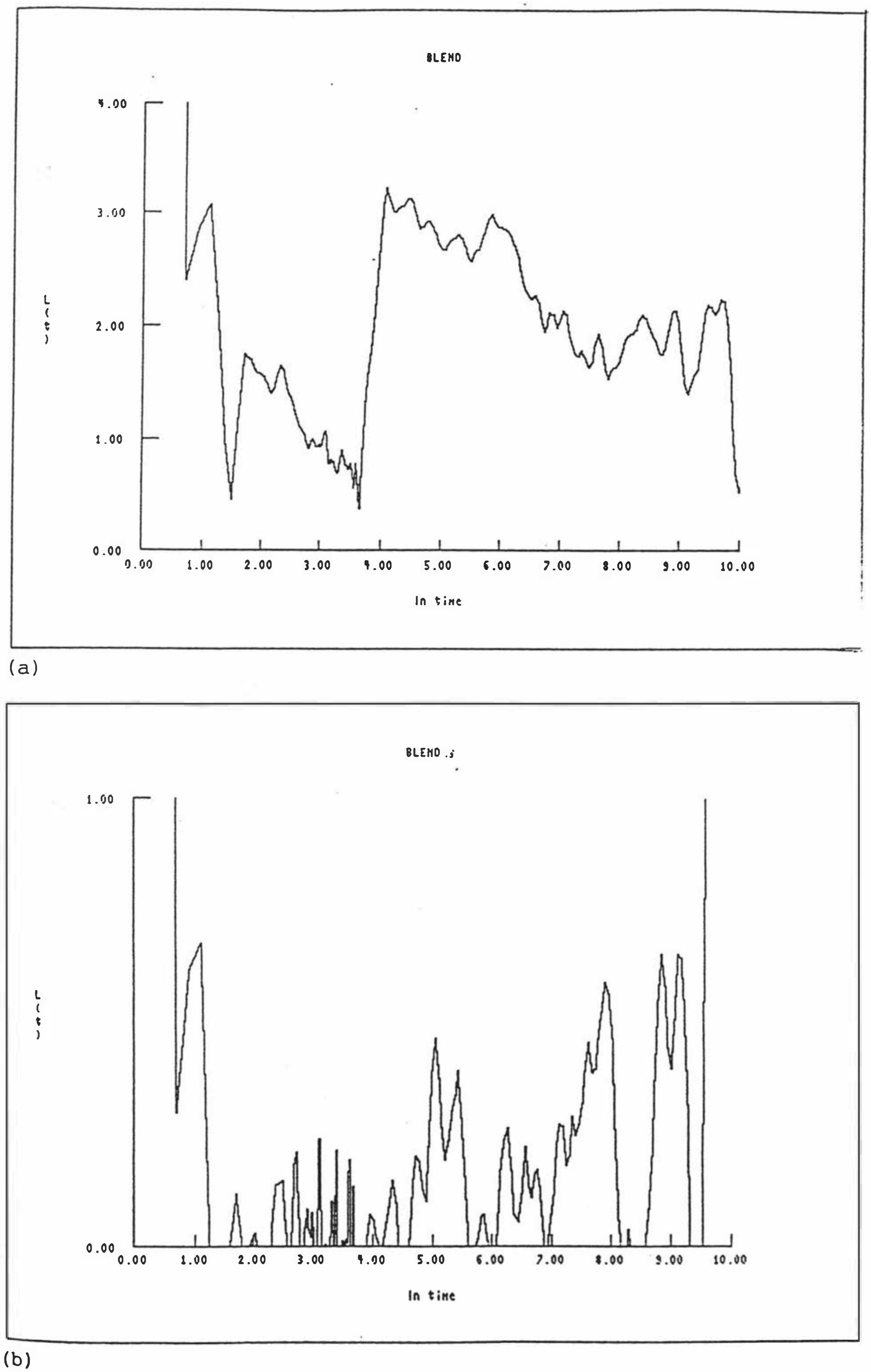


Figure 8.5: Continuous retardation spectra found for milkfat/oil blend; (a) initial creep response, (b) second creep response.

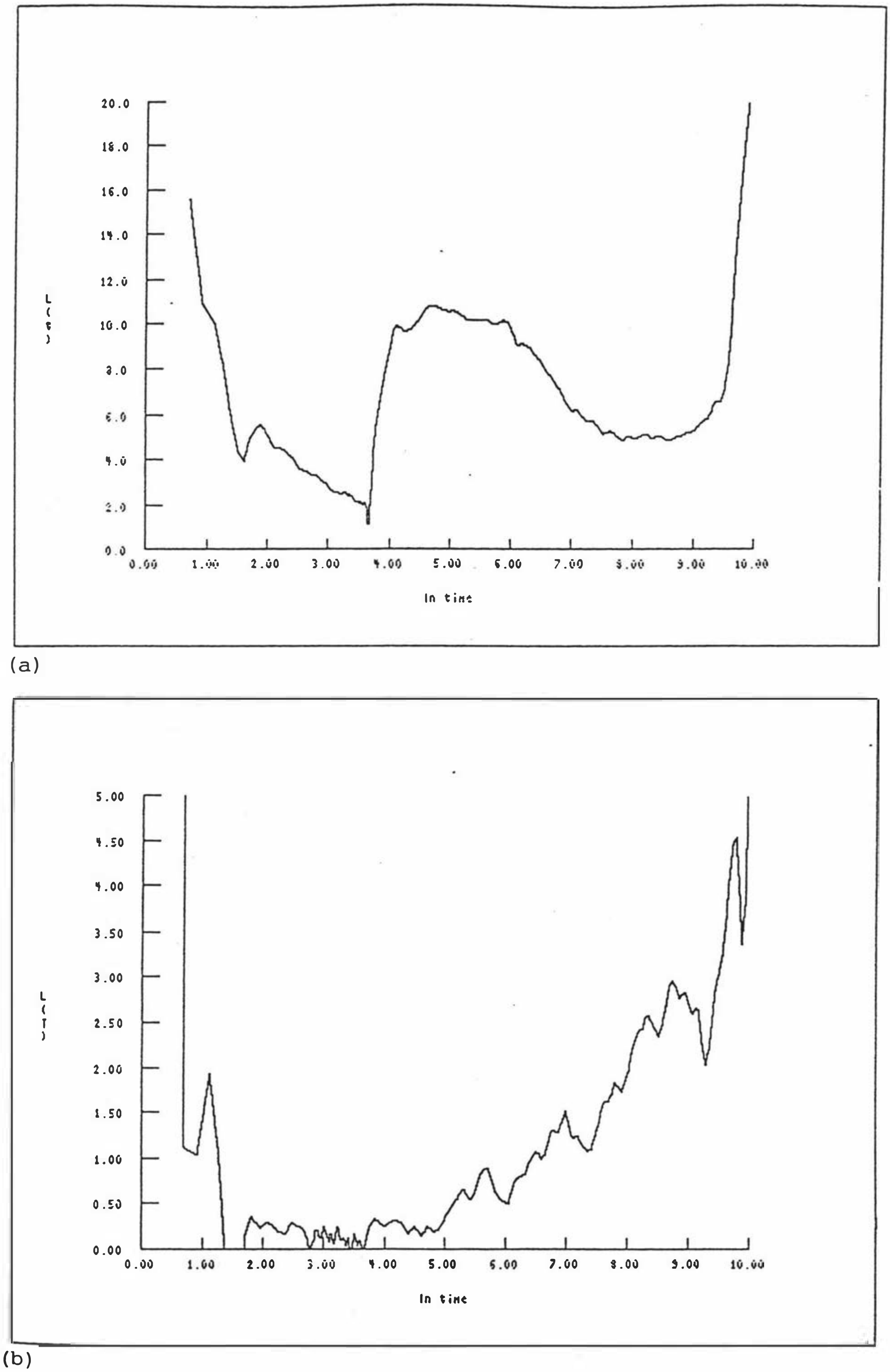


Figure 8.6: Continuous retardation spectra found for reworked plasticized milk-fat; (a) initial creep response, (b) second creep response.

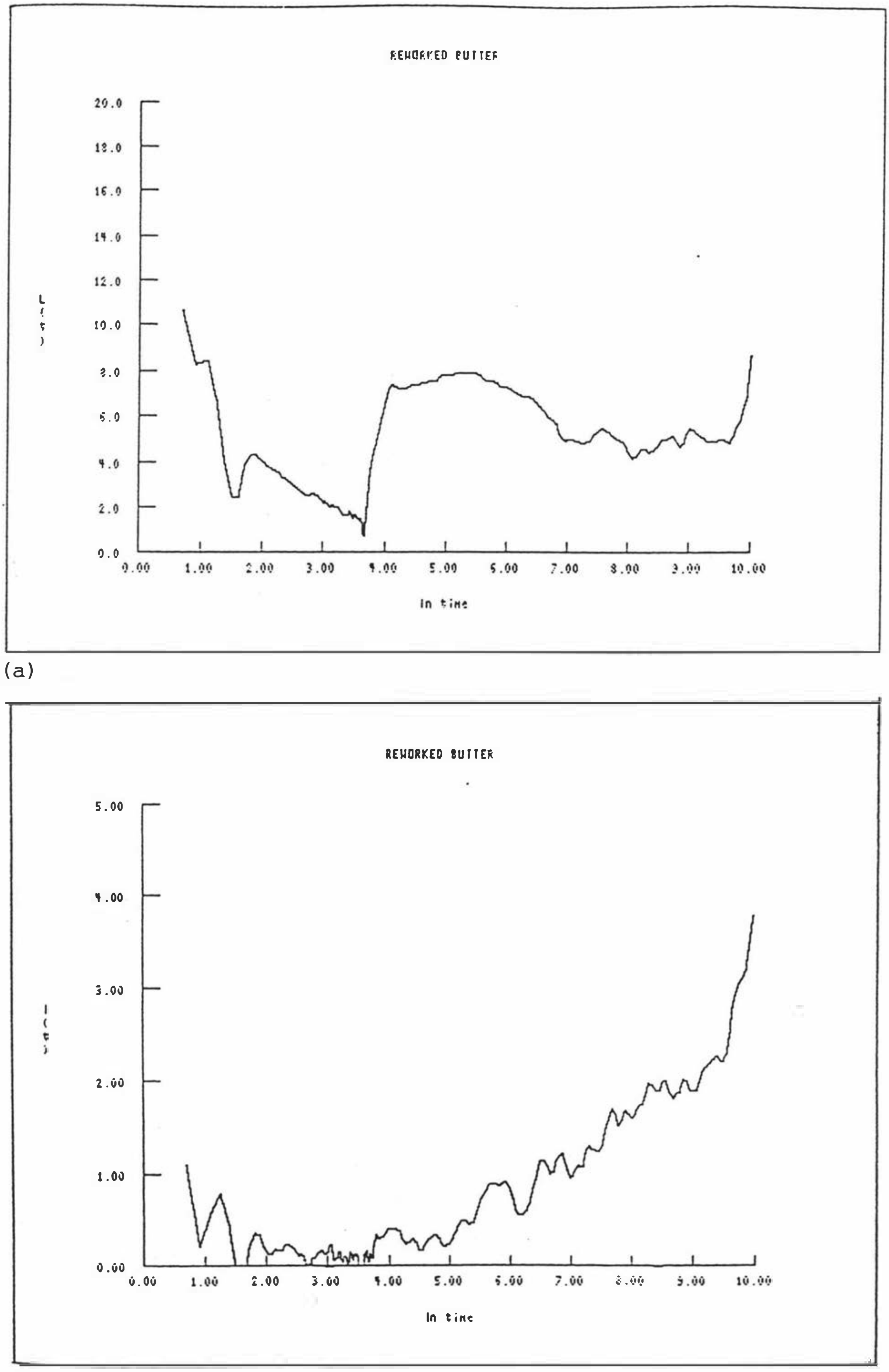


Figure 8.7: Continuous retardation spectra found for reworked butter; (a) initial creep response, (b) second creep response.

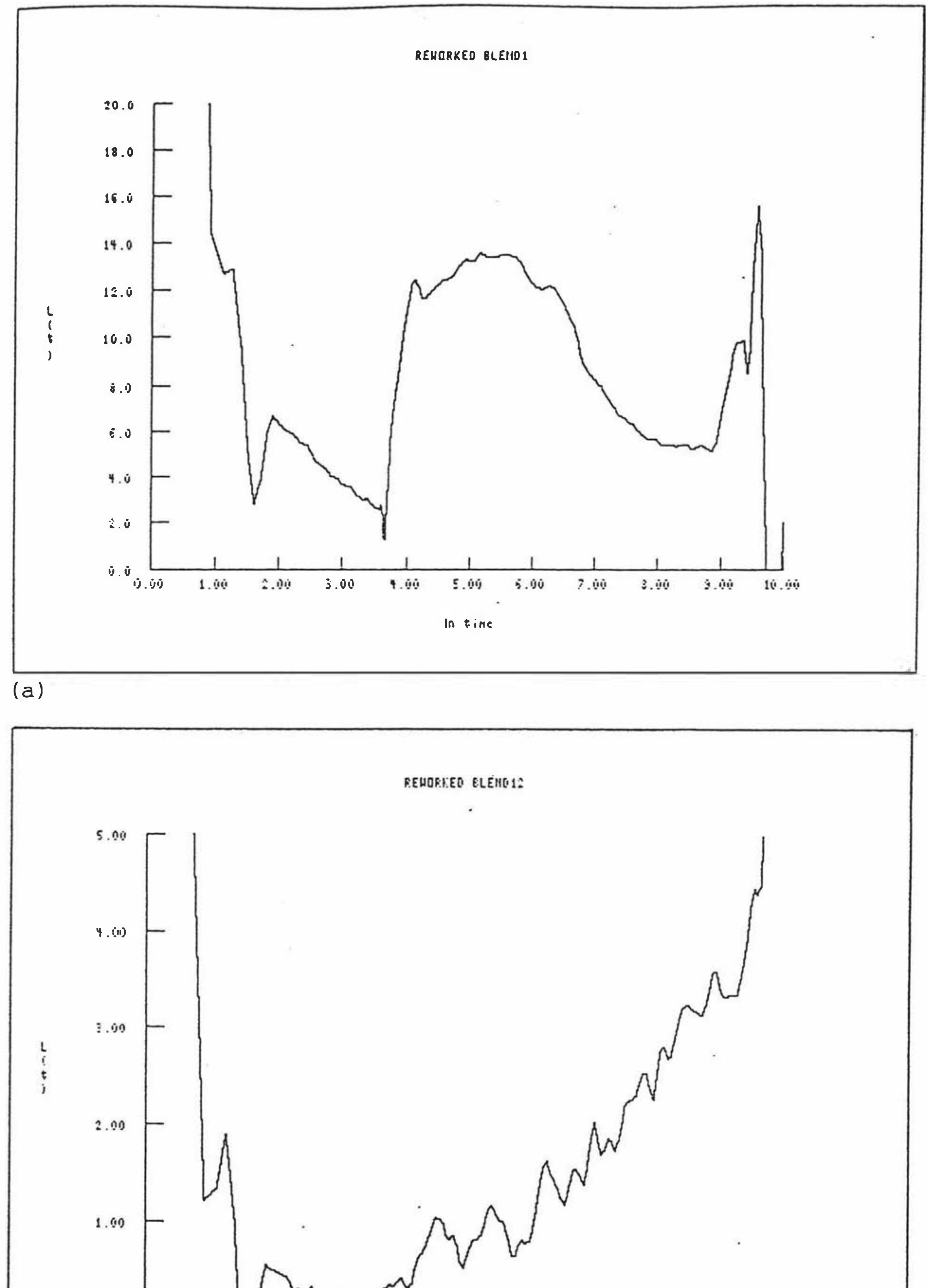


Figure 8.8: Continuous retardation spectra found for reworked milkfat/oil blend; (a) initial creep response, (b) second creep response.

8.3.2. Creep Compliance Responses

8.3.2.1. A Comparison of the Three Samples.

a) Initial Creep

The initial instantaneous response and sum of compliances of the original milkfat/oil blend is greater than that seen for the other two samples (Table 8.3). The instantaneous compliance response and the sum of compliances found for the plasticized milkfat sample is approximately the same as that found for the butter. The viscosities of the two shortenings are approximately the same, while the viscosity found for butter is twice as large.

As for the original samples, the reworked milkfat/oil blend showed the greatest creep response (Table 8.3). The sum of compliances seen for the reworked plasticized milkfat was less than that of the milkfat/oil blend, with the reworked butter showing the smallest response. The viscosity of the reworked butter is once again greater than the viscosities seen for the other two samples.

b) First Recovery

The percentage recovery of instantaneous compliance and the sum of compliances seen after the first recovery are also presented in Table 8.3. The original plasticized milkfat and butter showed approximately the same percentage recovery of the sum of compliances (about 30%) while the milkfat/oil blend showed a smaller recovery (15%).

An examination of the percentage recoveries of the sum of compliances seen after the initial creep for the reworked samples (Table 8.3) shows the blend to have recovered most, followed by the plasticized milkfat and butter. This trend is the reverse of that seen for the original samples.

A greater proportion of the instantaneous term is recovered for both original and reworked samples, compared with the sum of compliances recovered.

c) Second Creep

The magnitude of the second creep response of all samples was much less than that seen for the first creep. The original milkfat/oil blend displayed a greater creep response than the other two samples during the second load cycle (Table 8.3). The viscosity of butter was again greater than that of the anhydrous products.

On considering the reworked samples it can be seen that once again the blend showed the greatest response. Both the reworked butter and reworked plasticized milkfat had approximately the same sum of compliances. The viscosity seen for butter is approximately twice that seen for the two reworked shortenings.

d) Second Recovery

The sum of compliances found for the second recovery of the original and reworked samples are slightly less than those seen for corresponding samples during the first recovery. Viscosity terms found were larger than those seen for the second creep.

8.3.2.2. A Comparison between Original and Reworked Samples

a) Initial Creep

The creep response seen for the reworked samples is much greater than that seen for the original samples. On comparing the initial creep response of the original and reworked samples it can be seen that the plasticized milkfat, the butter and the reworked milkfat/oil blend all showed approximately the same increase in instantaneous compliance (300%, Table 8.5). In contrast, the percentage increase in sums of compliances seen for reworked plasticized milkfat (550%) and butter (500%) was greater than that seen for the reworked blend (345%). The second and third retarded compliances were found to increase most [illegible] reworking. In addition, time constants decreased. This follows a trend noted

Table 8.5: Percentage changes seen in various parameters going from original to reworked.

	Butter	PMF	MF/oil
Creep 1			
% inc J_o	260 (40)	330 (3)	335 (140)
% inc J_1	435 (40)	435 (40)	170 (50)
% inc J_2	650 (70)	590 (70)	360 (100)
% inc J_3	530 (50)	740 (180)	530 (130)
% inc ΣJ	500 (70)	550 (110)	345 (100)
%dec η_N	86 (10)	81 (20)	90 (10)
Creep 2			
% inc J_o	390 (160)	400 (90)	200 (30)
% inc ΣJ	410 (60)	610 (230)	450 (130)
% dec η_N	93 (9)	84 (20)	91 (40)

( ) Absolute error.

earlier (Chapter 7, Sections 3.2 and 3.2.2). The viscosity of all three samples decreased by 80 - 90% on reworking.

b) First Recovery

THe reworked samples recovered approximately the same proportion of the instantaneous response, as the original samples (Table 8.3). The reworked milkfat/oil blend recovered a greater percentage of the retarded compliance terms, compared to the original blend. In contrast, the other reworked samples recovered less than the original samples.

c) Second Creep

The sum of compliance terms found for the second creep responses of the reworked samples were much greater than those found for the original samples; six times greater in the case of plasticized milkfat, 4.5 times greater for the blend and four times greater for the butter. These increases are similar to those seen for the initial creep response.

The viscosities found for the second creep of the reworked samples showed a decrease of 80 -90%, compared to the viscosities found for the original samples. These findings are similar to those changes seen on comparing the initial creep response of the original and reworked samples.

d) Second Recovery

The same trends which were seen for the first recovery of the original and reworked samples were evident for the second recovery with the reworked milkfat/oil blend recovering a greater percentage of sums of compliance, compared to the other two samples.

8.3.2.3. A Comparison of the First Creep Response with the Second

A comparison of the first and second creep responses for the original and reworked samples (Table 8.6) shows the percentage decrease observed in the instantaneous response is similar for

Table 8.6: Comparison of second creep response with the first creep response.

	Original			Reworked		
	Butter	PMF	MF/oil	Butter	PMF	MF/oil
% dec J_o	53	61	74	61	61	78
% dec ΣJ	89	90	83	90	86	87
% inc η_N	48	57	77	59	52	50

corresponding pairs of samples. Likewise, the percentage decrease seen in the sum of compliances is approximately the same for both original and reworked butters. Similar results were found for butters reworked butter in Chapter Seven, Section 3.2.1.

Viscosity increases from first to second creep for both original and reworked samples. The percentage increase in viscosity was not as great for the reworked milkfat/oil blend.

Sectility hardness was very highly correlated with all sums of compliances and with the viscosities calculated for the first load/recovery cycle (Table 8.4). Sums of compliances were also well correlated with one another. In this respect the creep behaviour of samples tested can be said to be similar to that shown by the samples examined in Chapter Seven.

8.3.2.4. Retardation Spectra

The retardation spectra of the initial creep curves (Figs. 8.3a, 8.4a and 8.5a) reflect the relative sizes of the creep responses and show the blend had a larger first retarded response than the other two samples. Retardation spectra found for the second creep response (Figs. 8.3b, 8.4b and 8.5b) indicate a loss of retardation mechanisms in short time regions. (This leads to the fitting of a smaller number of retardation mechanisms, two instead of three).

Retardation spectra for the reworked samples (Figs. 8.6a, 8.7a and 8.8a) seem to be smoother and to have changed in shape, compared to the original samples (Figs. 8.3a, 8.4a and 8.5a). The bulk of retardation mechanisms seem to have moved to shorter times. This phenomenon was also seen for reworked butter (Chapter 7, Section 3.2.2). In addition the retardation times calculated by NONLIN are shorter.

Retardation spectra for the second creep of the reworked samples differed to those seen for the original samples, especially at long times. The reworked butters have a much greater contribution to the spectra at long times (compare, for example Figs. 8.3 and 8.6).

8.4. DISCUSSION

This study allows the effects of varying composition and the effect of reworking to be investigated. It should be possible to apply the theory of network deformation discussed in the previous chapter and explain observed behaviour.

8.4.1. The Effect of Varying Composition

8.4.1.1. Sectility Hardness

8.4.1.1.1. Plasticized Milkfat and Butter

Sectility hardness values demonstrate that the plasticized milkfat and butter have approximately the same hardness. On considering the possible structure of the plasticized milkfat it seems likely most, or all of the solid fat present will form extensive crystal networks. In contrast, the butter will contain water droplets which would be expected interrupt the crystal networks. This would decrease the number of strong 'bonds' present and possibly lead to a less rigid structure. As manufacturing conditions were similar (Chapter 2) the butter might be expected to be softer than the plasticized milkfat, however, this is not seen.

It is thought strong 'bonds' are broken on reworking and that a large proportion of these either do not reform, or partially reform over a long period of time (Chapter 1, Section C.2.3.7). The plasticized milkfat, with more extensive crystalline networks, should have more of these types of bonds and should therefore undergo a greater reduction in hardness on reworking. On reworking the plasticized milkfat does in fact show a greater reduction in hardness than the butter, (Table 8.1). This suggests a sample with a large number of strong 'bonds' will undergo a greater permanent reduction in hardness on reworking, compared to a sample which may have approximately the same hardness, but fewer strong 'bonds'.

8.4.1.1.2. Plasticized Milkfat and Milkfat/oil Blend.

In contrast with the plasticized milkfat, the 80:20 milkfat/oil blend has a greater percentage of liquid fat, and a correspondingly smaller amount of solid fat. From 0 - 15°C, the blend has approximately 20% less solid fat as determined by NMR (Table 8.2). Consequently, less solid fat is available to be involved in crystalline networks and fewer strong bonds will have formed. The milkfat/oil blend, therefore, should be softer, and not as strong as the plasticized milkfat. This is reflected in sectility hardness results, with the blend having a hardness approximately 20% lower than that found for the plasticized milkfat.

On reworking, the milkfat/oil blend, with presumably fewer strong bonds, should experience a smaller reduction in hardness, than that seen for the plasticized milkfat. The milkfat/oil blend does experience a smaller reduction in hardness (1000g) compared with 1250g for the plasticized milkfat. However, both samples experience about the same percentage reduction in hardness, 70% for plasticized milkfat and 68% for the milkfat/oil blend. This suggests the same percentage of 'bonds' was broken during working.

Interestingly, even though a marked reduction in sectility hardness is seen, solid fat content seems to have increase slightly on reworking.

8.4.1.2. Creep Compliance

The shortenings and butter made from the same fat have been found to exhibit creep compliance behaviour similar to that seen for the samples examined in Chapter Seven. Comments made about the calculation of the apparent viscous term from the first recovery are applicable here. This term includes unrecovered strain as well as viscosity and hence gives an unreliable indication of viscosity.

8.4.1.2.1. Plasticized Milkfat and Butter

a) Initial Creep

The sum of the initial creep compliance responses of plasticized milkfat and butter were similar. Given that the two samples have approximately the same sectility hardness (and solid fat content) the similarity of the sum of compliances is not surprising. The sum of compliance values (Table 8.3) and retardation times (Appendix 2) imply crystalline networks are being deformed to the same extent and at the same rate in both samples.

The viscosity found for the butter was twice that found for the plasticized milkfat. Experience with a range of butters has shown that sectility hardness correlates with viscosity (Chapter 9, Section B.3). Given this, the dissimilarity in viscosity seen for the two samples is surprising. This suggests factors other than fat composition or method of manufacture are influencing viscosity. The main difference between the two samples is the presence (or absence) of water droplets. The results suggest the presence of water droplets may be affecting the viscosity of the initial creep response. If viscosity is a measure of the ease with which particles can move past one another, this may indicate water droplets impede this flow or movement. Flow may be impeded by water droplets physically preventing flow by disrupting the network and blocking movement of particles. Water droplets may also prevent orientation in the direction in which stress is being applied.

On examining the response of reworked plasticized milkfat and butter the reworked butter sample did not creep as far as the reworked plasticized milkfat (ΣJ butter 115 $\times 10^{-8}$ Pa^{-1}, ΣJ plasticized milkfat 143 $\times 10^{-8}$ Pa^{-1}), ie. the two samples were not deforming to the same extent. This contrasts with the results seen for the original samples which have similar sum of compliance values. The failure of butter to work soften to the same extent as the plasticized milkfat (59% as opposed to

69%) may explain the smaller sum of compliances seen, as creep response is highly correlated with sectility hardness (Table 8.4).

In line with the original samples the viscosity of the reworked butter was higher than that of the reworked plasticized milkfat. Once again it appears the presence of water droplets may be impeding flow.

b) First recovery
On the removal of stress, the plasticized milkfat and butter both recover to approximately the same extent (Table 8.3). The similar recovery seen for the retarded compliances may also indicate the network structures were deformed to the same extent in both samples and that the amount of permanent deformation experienced by both samples is approximately the same.

The instantaneous recovery seen on the removal of stress is approximately the same for both reworked samples, while butter showed a smaller overall recovery of elastic response (20.5 x 10^{-8} Pa^{-1} compared to 38 x10^{-8} Pa^{-1}). The smaller overall recovery of sums of compliance found for butter is probably related to the smaller initial deformation seen.

c) Second Creep
The instantaneous compliance and sums of compliances seen for the second creep response once again suggest the two original samples are deforming to the same extent.

The results for the second creep of the reworked samples (Table 8.3) suggests the sum of compliances seen are approximately the same. This contrasts with the initial creep where the plasticized milkfat showed a greater sum of compliance response.

The original and reworked butters have much greater viscosities than the original and reworked plasticized milkfats. This is in line with the results seen for the initial creep response.

d) Second Recovery

The same trend as seen for the first recovery is also seen for the second recovery. On the removal of stress, the recoveries seen are approximately the same for both original samples. The reworked plasticized milkfat shows a greater recovery than the reworked butter, indicating the network structure of the plasticized milkfat is able to relax more easily when stress is removed.

The viscosity found for the butter is greater than that found for the plasticized milkfat. Unusually, the viscosities found for the reworked samples are approximately the same.

e) General Comments

The original and reworked samples of plasticized milkfat and butter are behaving as would be predicted by the theory developed in the previous chapter. The one departure from predicted behaviour is the consistently higher viscosity found for the butter samples. This is perhaps due to the presence of water droplets in the butter.

It is interesting to note instantaneous compliance values remain approximately the same for original plasticized milkfat, reworked plasticized milkfat, original butter and reworked butter after the initial deformation. This has been noted previously (Chapter 7).

8.4.1.2.2 Plasticized Milkfat and Milkfat/oil Blend

a) Initial Creep

A comparison of the initial creep responses seen for the original plasticized milkfat and the milkfat/oil blend reveals the blend has a greater instantaneous compliance and sum of compliance value and approximately the same viscosity as the plasticized milkfat. Given the main difference between samples is solid fat content this suggests the amount of solid fat present has a large effect on both the instantaneous and retarded elastic compliances. As noted previously, a lower solid fat content would have the effect of decreasing the amount of solid fat in the crystalline network and the number of strong 'bonds' present. This would enable the networks to deform more easily. Lowering the number of fat crystals present should also increase ease of deformation, as should increased amounts of liquid fat, if liquid fat acts as a lubricant (Chapter 7, Section 4.3.1).

Also noted in the previous chapter, a decrease in the number of strong 'bonds' and an increase in liquid fat might also be expected to decrease viscosity. This does not appear to have happened, suggesting the ease with which flow occurs is about the same in both plasticized milkfat and milkfat/oil blend.

On examining the reworked plasticized milkfat and milkfat/oil blend the sum of compliances of the initial creep found for the blend is greater than that seen for the plasticized milkfat. However, the difference between the two responses is not as great as the difference in sums of compliance seen between the original samples. This suggests reworking has had a greater effect on plasticized milkfat, ie. more strong 'bonds' may have been broken, enabling the plasticized milkfat to creep comparatively further than before. This also implies the plasticized milkfat should have work softened more than the blend. This was observed (Section 4.1.1.1).

In contrast to the original samples the viscosity of the reworked blend is slightly less than that seen for the plasticized milkfat. This would be expected, based on differences in solid fat content.

b) First Recovery

The sum of compliances recovered after the initial creep is similar for each sample. Percentage recovery of the sum of compliances shows the blend recovers less, compared to the plasticized milkfat. Given the apparent ease with which the blend deforms during the first creep, the structure should also relax easily, resulting in a greater recovery than is seen. The closeness of the percentage recovery of the instantaneous term to those seen for plasticized milkfat and butter, also suggests the recovery of retarded elastic compliances is much lower than expected.

The reworked milkfat/oil blend shows a greater recovery of the retarded compliances. This would be expected if decreasing amounts of solid fat increase the ease with which relaxation as well as deformation occur as mentioned above. The instantaneous compliance term also shows a greater recovery for the blend. This is also expected, given that the instantaneous term is thought to be dependent on the amount of liquid fat present. These results contrast with those seen for the original samples.

c) Second Creep

Once again the second creep response of the milkfat/oil blend is greater (in terms of sum of compliances) than the plasticized milkfat. This suggests more deformation is taking place. A similar response is seen for the reworked samples.

The viscosities found for each pair of original and reworked samples were similar. This unexpected trend is the same as that seen for the first creep response.

d) Second Recovery

The sums of compliance are seen on recovery for the original samples after the second creep were similar, while the reworked milkfat/oil blend recovered a greater sum of compliances than the plasticized milkfat. This trend is the same as that seen for the first recovery.

e) General Comments

The behaviour of the reworked milkfat/oil blend is in accordance with expectations based on the theory described in the previous chapter, ie. a greater creep and recovery is seen for each cycle, compared with the plasticized milkfat. In contrast, while the original milkfat/oil blend shows greater creep responses than the plasticized milkfat, it does not show the expected greater recovery.

8.4.2. Effects of Reworking

The hardness of all samples decreased on reworking, with the plasticized milkfat showing the greatest decrease in hardness. As noted previously, viscosity and sum of compliances are correlated with sectility hardness (Table 8.4), therefore changes in these parameters are expected for reworked samples.

a) Initial creep

The changes seen in the instantaneous response appear to be directly linked to changes in sectility hardness. The hardness of the reworked milkfat/oil blend and plasticized milkfat are one third of the hardness of the original samples, while the instantaneous responses are three times those of the original samples. The hardness of reworked butter is 40% of the original, with an instantaneous compliance term 2.5 times that of the sample (Table 8.5). A similar relationship between change in hardness and increases in the instantaneous response has been noted for reworked butters (Chapter 7, Section 3.3).

The retarded elastic compliances increase on reworking and are 2 - 7 times greater than those seen for the original samples (Table 8.5). Some of these increases are far greater than changes in sectility hardness would predict. This has also been seen previously for reworked butters (Chapter 7, Section 3.3). It is thought reworking affects elastic compliances in ways other than just breaking strong 'bonds'. The less favourable configurations of elements of the crystal lattice may make deformation easier and explain the increases seen.

The greatest increase in individual retarded compliances on reworking is seen for the second and third compliances. This can be seen on comparing the retardation spectra found for original and reworked samples. Retardation curves for reworked samples are smoother, with the bulk of retardation times shifted to shorter times. The change in retardation spectra and retardation times indicate the number of mechanisms and bonds contributing to the structure of the fats have changed, with the contribution from those at long times being reduced. This suggests bonds etc. which would not ordinarily break until long times have been destroyed by reworking. The changes seen on reworking are similar to those seen for reworked butter (Chapter 7, Section 3.2.2).

The decrease in viscosity seen for reworked samples is expected. As with all reworked samples, the breaking of strong 'bonds' would mean fewer'bonds' would need to break before particles or crystals are able to flow.

Viscosity was reduced on average 86% by reworking. This is a greater percentage reduction than that of approximately 60% seen by Shama and Sherman (1970) and Gupta and DeMan (1985) and a reduction of 60 - 75% seen earlier in this work (Chapter 7, Section 3.3).

The greater reduction in viscosity seen may be due to the manufacturing method ie., rapid cooling and little working, compared to 'normal' butters, would combine to produce a harder product. This product could be expected to contain a greater number of strong 'bonds' and therefore soften more on reworking, leading to the greater reduction in viscosity seen.

b) First Recovery

Reworking does not seem to affect the percentage recovery of the instantaneous term, compared with the original samples. As expected, the reworked blend shows a greater recovery than the other two samples. This contrasts with the behaviour of the original blend which showed less recovery than the other two samples. The reworked plasticized milkfat and butter show a similar or less recovery, compared to the original samples.

c) Second Creep and Recovery

Reworking, leading to a decrease in sectility hardness, would also be expected to result in increased sum of compliances and decreased viscosities being seen during a second load cycle. The responses seen are appropriately increased or decreased (Table 8.5), and are related to sectility hardness (Table 8.4). The parameters increase and decrease in approximately the same ratios as seen when the first creep of original and reworked sample pairs are compared (Table 8.4). This was also seen for reworked butter (Chapter 7, Section 3.2).

CHAPTER NINE

SEASONAL TRENDS IN FRITZ AND AMMIX BUTTER

PART A: ESTABLISHED METHODS

9A.1. INTRODUCTION

In New Zealand, milkfat composition varies in a regular, recurring manner throughout the year. As a result, the rheological behaviour of butter fluctuates with season. Seasonal trends observed in the sectility hardness of patted butter were reported by Dolby, who carried out the first reported survey of the hardness of New Zealand butter (Dolby, 1949). The results showed a large annual variation, with butter softest at the start of the season (August), rapidly becoming harder in October to reach a peak hardness in December. From January, the butter became softer. Using iodine values and softening point as a measure of milkfat composition, Dolby concluded "...that at least 80% of the variation in softness ... can be attributed to variations in the composition of the butterfat ...".

The seasonal trends reported by MacGibbon and McLennan (1987), who undertook a second survey of butter to determine the changes in hardness of New Zealand patted butter, parallel those of Dolby (1949).

In this study the seasonal trends in chemical and physical properties of butter were examined. An attempt was made to establish a relationship between rheological measurements such as sectility hardness and creep compliance (Part B) and melting characteristics and composition of milkfat.

9A.2. EXPERIMENTAL

Samples of Fritz and Ammix butters were collected through the 1985 - 1986 dairy season from October to April, the 1986 -

1987 season from August to April and the 1987 - 1988 season from September to December inclusive. Traditional sectility hardness and solid fat content by NMR were determined for all samples. Differential scanning calorimetry melting thermograms, fatty acid and triglyceride compositions were determined for samples collected in the 1985 - 1986 season. Sample collection is detailed in Chapter Two.

9A.3. RESULTS AND DISCUSSION

9A.3.1. Sectility Hardness

Sectility hardnesses were determined at 10^{o}C for all samples (Table 9.1). Figure 9.1 shows the variation in hardness throughout the year. The results for the '86 - '87 season show a steep rise in hardness in the spring, reaching a peak around November/December, followed by a decrease in the autumn. Autumn hardnesses do not fall as low as spring hardnesses. The '85 - '86 season shows a similar trend, although the Ammix butters had lower sectility values during the summer. Too few samples were collected for the '87 - '88 season to establish any definite trends in hardness.

The trend in sectility hardness throughout the season was similar to that reported by Dolby (1949) and MacGibbon and McLennan (1987).

Butters manufactured by the Ammix method during the sampling period were softer than corresponding butters manufactured using the Fritz process. However, the Fritz and Ammix samples collected monthly are manufactured with cream collected from different sources. The implications of this are discussed later (Section A.3.5).

9A.3.2. Solid Fat Content

Solid fat contents for milkfat extracted from Fritz butter are presented in Table 9.2, with results for milkfat extracted from Ammix butter in Table 9.3.

Table 9.1: The sectility hardness of samples of patted butter determined at 10^{o}C.

FRITZ		AMMIX	
Date	Hardness (g)	Date	Hardness (g)
85 - 86 SEASON			
Oct 1	1725	Oct 2	1100
Nov 5	2100	Nov 1	1400
-	-	Dec 7	1350
Jan 8	1850	Jan 3	1200
Feb 1	1700	Feb 1	1325
Mar 6	1450	Mar 7	1325
Apr 9	1950	Apr 1	1500
86 - 87 SEASON			
Aug 14	900	-	-
Sep 1	1000	-	-
21	1200		-
Oct 22	1900	-	-
Nov 1	2050	Nov 11	1550
Dec 5	2300	-	-
Jan 6	2400	Jan 1	1850
Feb 10	2000	Feb 10	1650
Mar 7	1700	Mar 25	1450
Apr 4	1700	Apr 2	1325
87 - 88 SEASON			
Sep 4	1450	-	-
Oct 5	1850	Oct 7	1700
Nov 1	1725	Nov 1	1700
Dec 7	2150	Dec 7	1400

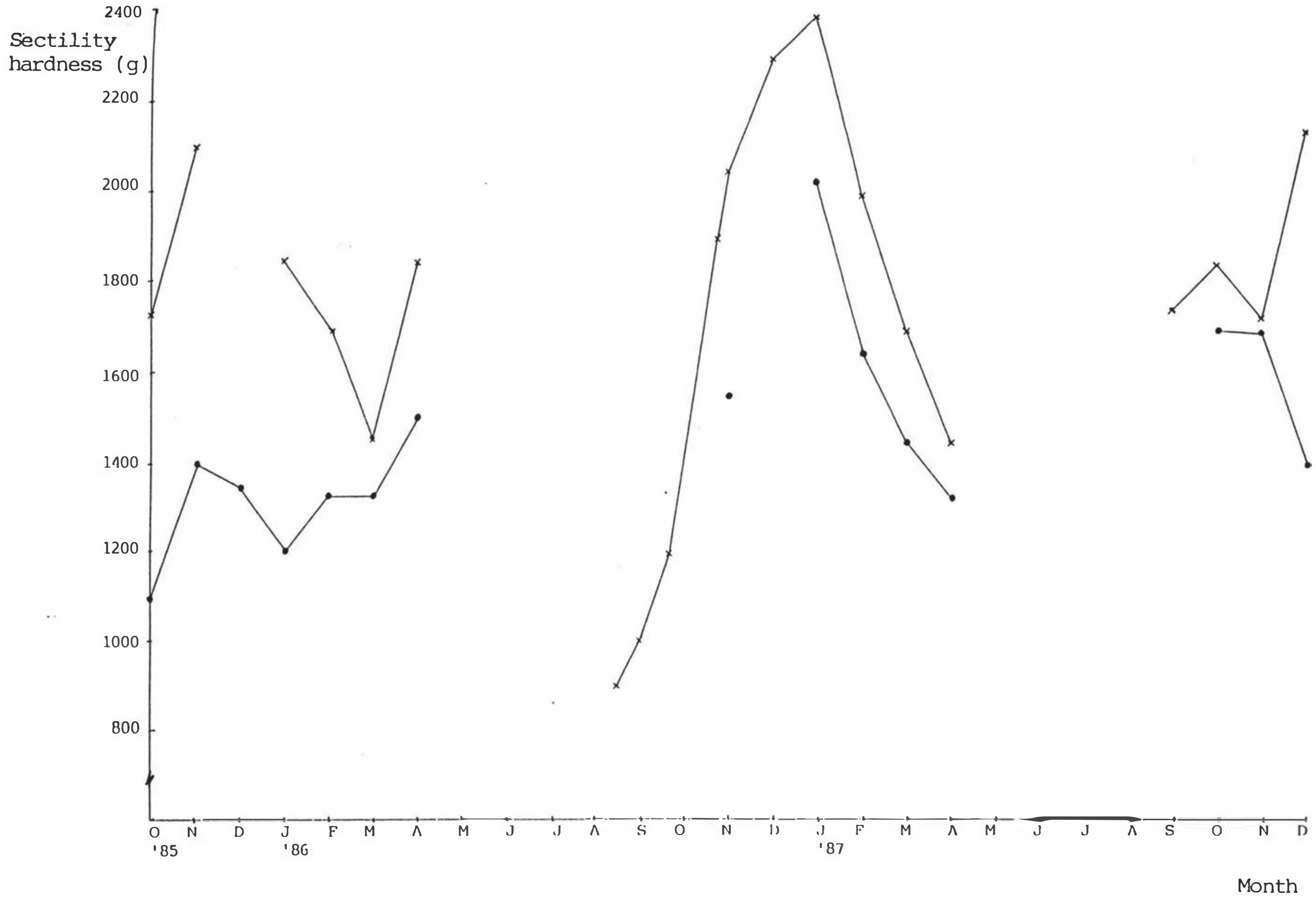


Figure 9.1: The variation of sectility hardness with season; x = Fritz butter, o = Ammix butter.

Table 9.2: Percentage solid fat as determined by NMR for samples of milkfat extracted from Fritz butter.

TEMP.	0	5	10	15 (°C)	20	25	30	35
85-86 SEASON								
Oct 1	66.1	61.8	54.4	37.1	19.7	10.1	4.5	-
Nov 5	69.2	65.0	58.5	42.0	22.0	12.1	5.9	0.4
Dec no sample received								
Jan 8	68.8	65.0	58.5	43.0	24.2	12.1	6.8	1.0
Feb 1	67.4	63.6	57.1	42.3	23.1	12.8	6.4	1.3
Mar 6	66.3	63.3	57.2	42.2	23.0	12.6	6.1	1.3
Apr 9	66.4	63.3	57.1	41.6	22.5	13.0	5.8	1.3
86-87 SEASON								
Aug 14	58.6	55.1	50.3	35.1	19.0	9.5	4.4	1.6
Sep 1	58.7	55.1	48.8	34.9	17.6	8.9	4.5	1.4
Sep 21	60.5	57.1	50.5	35.9	19.0	9.9	4.8	1.6
Oct 22	65.0	61.9	56.1	38.2	20.5	11.4	4.9	0.6
Nov 1	67.0	63.3	56.1	40.4	21.5	11.5	4.4	1.0
Dec 5	70.8	67.3	60.5	45.4	25.4	13.4	7.0	1.6
Jan 6	71.0	67.6	61.2	46.8	27.3	14.0	7.2	1.3
Feb 10	70.6	67.0	61.0	45.8	27.7	14.5	7.2	1.8
Mar 7	67.3	63.9	57.8	42.0	24.4	13.0	6.9	1.5
Apr 4	66.4	62.5	55.9	39.4	21.6	12.3	5.6	0.4
87-88 SEASON								
Sep 4	62.0	57.3	51.0	36.4	18.2	9.4	4.5	0.6
Oct 5	65.0	60.7	54.2	38.6	19.5	10.5	4.6	0.1
Nov 1	68.1	64.1	57.0	41.4	21.4	11.8	5.0	0.4
Dec 7	70.2	66.5	60.0	45.3	24.60	13.4	6.7	0.8

Table 9.3: Percentage solid fat as determined by NMR for samples of milkfat extracted from Ammix butter.

TEMP. (°C)	0	5	10	15	20	25	30	35
85-86 SEASON								
Oct 2	60.5	56.2	48.8	31.8	15.7	8.3	5.0	-
Nov 1	63.8	59.5	52.3	35.2	17.5	9.8	4.4	-
Dec 7	65.6	61.8	54.7	38.6	20.0	11.8	5.1	0.7
Jan 3	65.1	60.9	54.0	37.1	19.7	10.8	4.9	0.6
Feb 1	64.5	60.7	54.1	38.8	19.8	11.7	5.4	0.7
Mar 7	62.2	59.1	52.3	36.5	18.7	10.8	4.8	0.6
Apr 1	62.8	59.5	53.0	36.7	19.1	11.3	5.2	0.9
86-87 SEASON								
Nov 11	65.5	61.8	54.3	37.5	19.9	11.4	4.0	0.3
Dec	No sample received							
Jan 1	67.7	63.7	57.5	42.6	23.8	12.7	6.1	1.3
Feb 10	68.8	64.6	58.4	42.6	24.1	13.2	6.3	1.1
Mar 25	65.1	61.1	54.3	37.2	20.1	11.3	5.6	1.1
Apr 2	64.2	60.2	53.6	36.3	19.1	11.1	4.9	-
87-88 SEASON								
Oct 7	65.4	60.3	53.7	38.7	19.6	10.9	4.9	0.5
Nov 1	67.6	63.8	56.9	40.9	22.1	12.5	5.7	0.8
Dec 7	67.3	63.6	56.4	41.3	21.0	12.0	5.5	0.8

Summer milkfat has a higher solid fat content than either spring or autumn milkfat, especially at temperatures below 20°C.

The seasonal variation in the solid fat content at 10°C is shown in Figure 9.2. A trend similar to that shown by hardness (Fig. 9.1) may be observed, with a rapid increase in solid fat content through spring to summer, followed by a decline in autumn. MacGibbon and McLennan (1987) observed the same seasonal trends for solid fat content as are reported here. MacGibbon and McLennan point out the effect of short term fluctuations in solid fat content are also seen in the solid fat/season curve.

Milkfat extracted from butter made by the Ammix method has consistently lower solid fat levels than that made by the Fritz process. This is discussed further below.

9A.3.3. Comparison between Sectility Hardness and Solid Fat Content

Figure 9.3 illustrates the relationship between sectility hardness at 10 °C and solid fat content at the same temperature for samples of Fritz and Ammix butters collected throughout the season. The correlation was high ($r = 0.81$ for all samples). However, not all the variation in butter hardness is explained by solid fat content ($R^2 = 65.8\%$).

For Fritz butters alone the correlation between solid fat and sectility hardness was $r = 0.82$, while for Ammix butters the correlation was $r = 0.71$. The better correlation shown by Fritz butter may be due to, in part, a wider range of sectility hardness values. Differences in manufacturing method may also affect the correlations. On examining Figure 9.3, the Fritz and Ammix points can be seen to be lying on slightly different lines. Ammix butter appears to be softer than Fritz butter, especially as solid fat content increases.

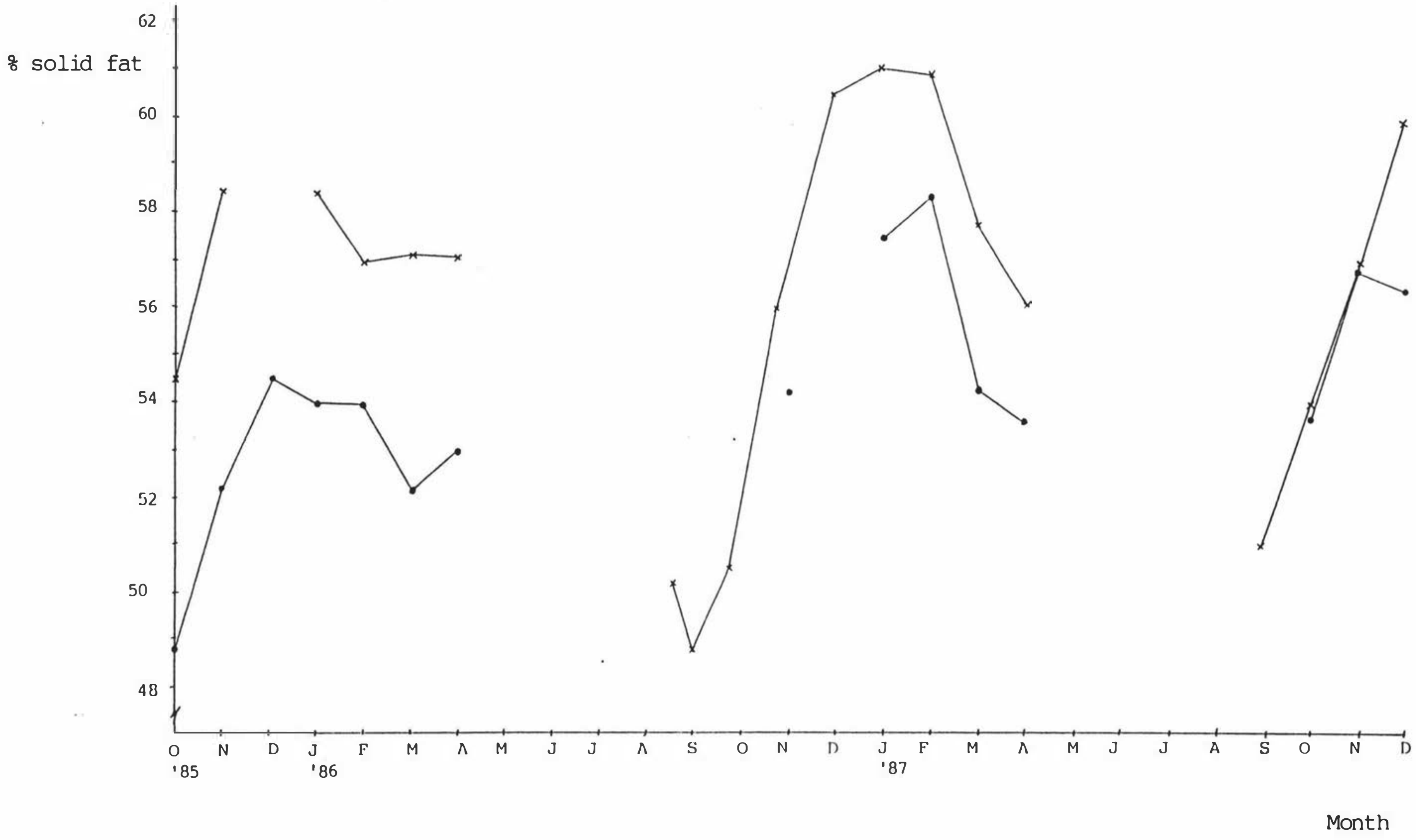


Figure 9.2: The variation of percentage solid fat with season: x = Fritz butter, o = Ammix butter.

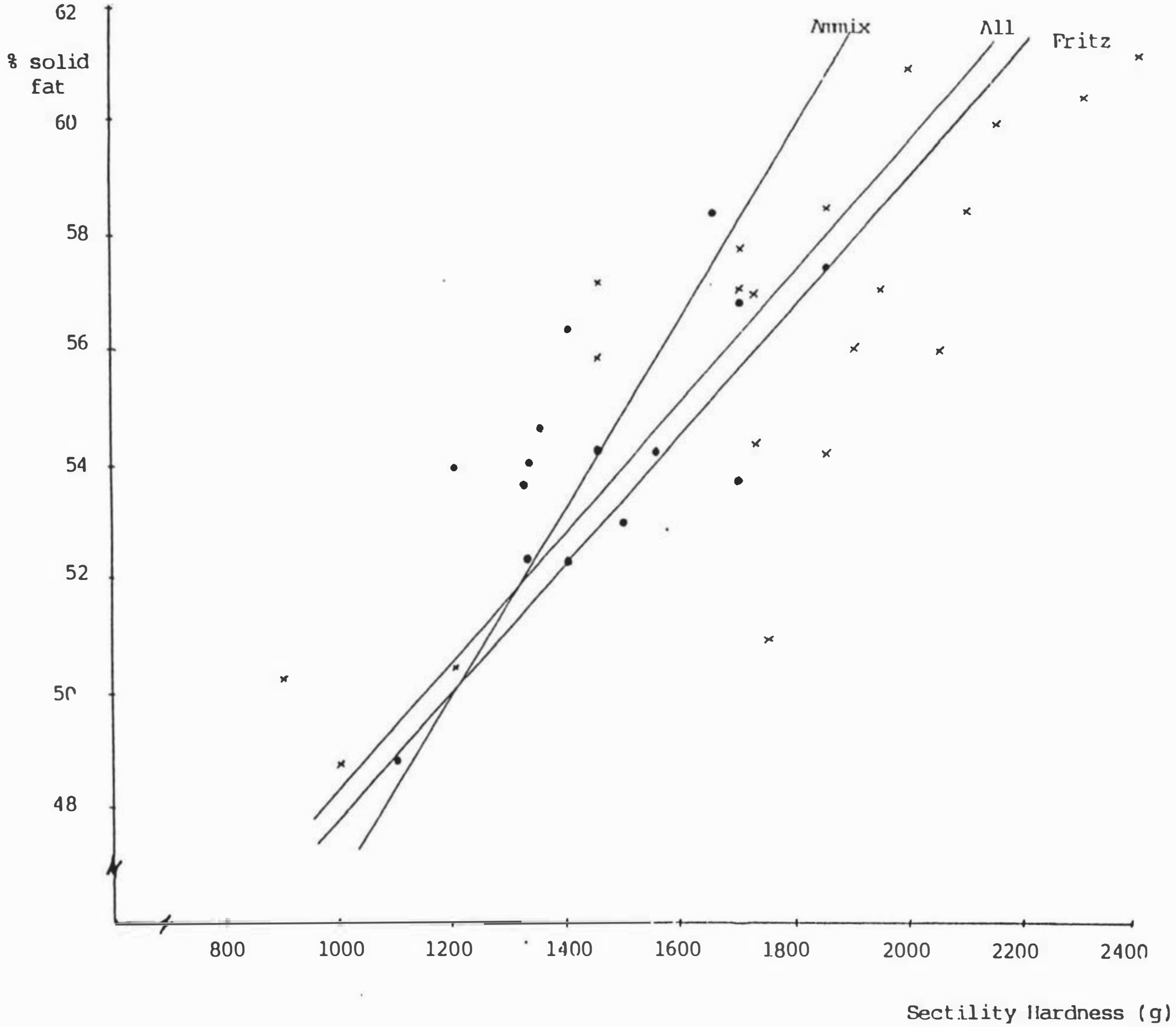


Figure 9.3: Solid fat content plotted against sectility hardness showing lines of best fit for all samples and Fritz and Ammix butters separately. x = Fritz, o = Ammix.

Solid fat content has been found to account for about 66% of variation in butter hardness. This suggests other factors such as manufacturing have some effect on hardness. These factors seem to have more effect on Ammix butter, as solid fat accounts for 57% (R^2 = 56.56%) of the variation in hardness, whereas solid fat accounts for about 67% (R^2 = 67.35%) of the variation in hardness of the Fritz samples. Despite the effects of factors other than solid fat content, it seems Ammix butters are softer than Fritz butters mainly by virtue of lower solid fat content.

Other workers have examined the relationship between solid fat and sectility hardness. Taylor and Norris (1977), for example, found samples with a wide range of sectility hardnesses at 5°C were highly correlated with solid fat content determined by NMR ($r = 0.97$). MacGibbon and McLennan (1987) found the average correlation for the butters from all plants surveyed was $r = 0.55$ (10°C). They point out that the correlation would be expected to improve as the range of sectility values increased and if manufacturing conditions were kept constant.

9A.3.4 Differential Scanning Calorimetry.

Differential scanning calorimetry was used to obtain melting thermograms of milkfat extracted from Fritz and Ammix butters colllected during the '85 - '86 season. These are included in Appendix 3. The shape of the curves obtained is characteristic of milkfat, with a main peak at 17°C, a small shoulder at 12°C and a large plateau between 20 - 37°C. The melting thermograms of early October and December Ammix milkfat are shown in Figure 9.4. All curves obtained lie between the October and December curves. Thermograms of early season samples show a less pronounced low temperature shoulder associated with a smaller main peak and a less pronounced plateau.

Differential scanning calorimetry provides information in the form of a melting curve over the entire melting range. Changes in the melting thermograms with season were similar to those

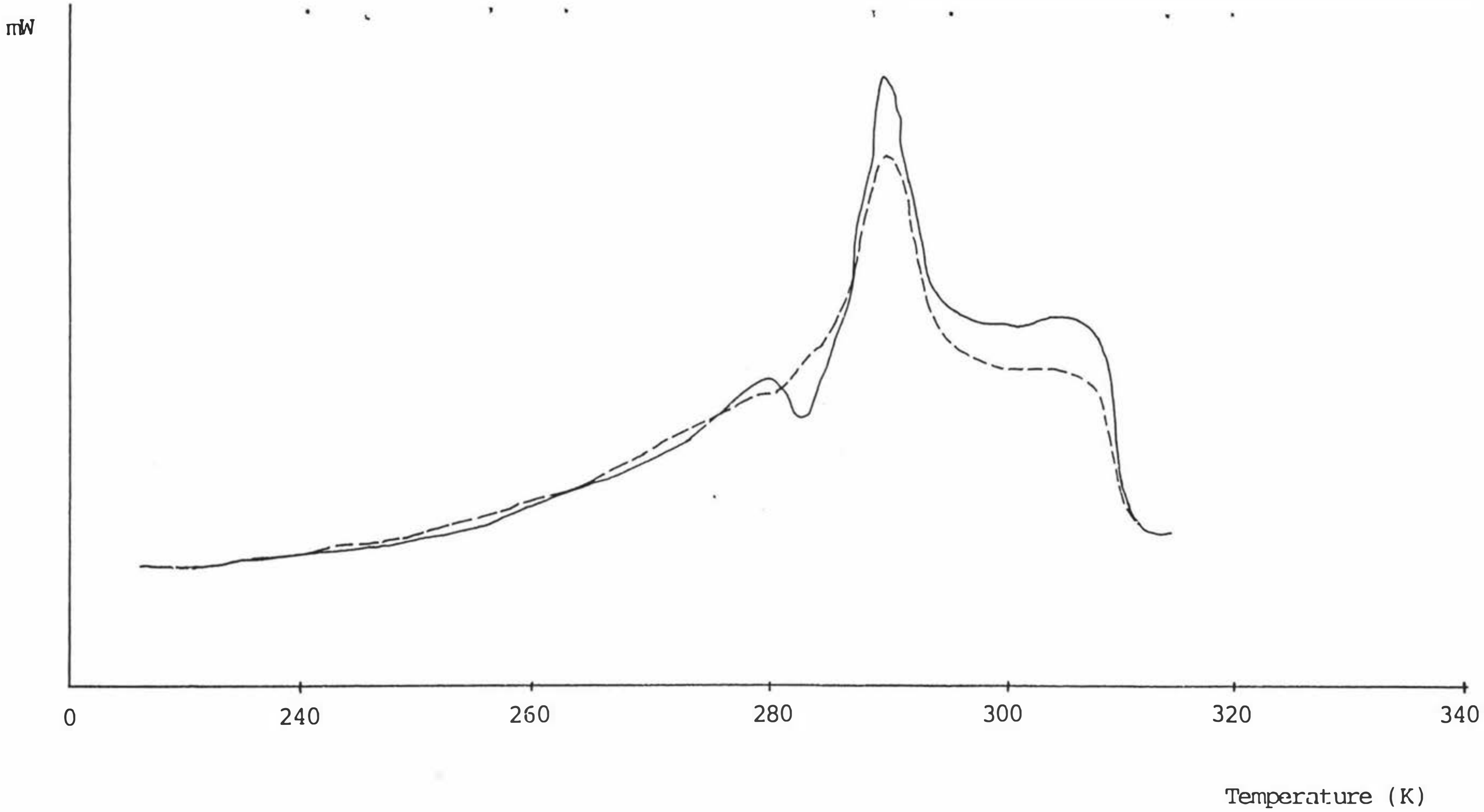


Figure 9.4: Differential scanning melting thermograms found for October (dotted line) and December (solid line) Ammix butters.

seen by Norris *et al* (1973). Melting thermograms obtained showed the July sample to have the most liquid fat, and the November sample to have the least. All other samples had intermediate liquid fat contents.

Comparison of the differential scanning calorimetry curves for Fritz butters with those of Ammix butters collected at the same time reveals differences in the curves. The curves show Fritz butters have a greater proportion of higher melting fat. This finding is consistent with differences in solid fat content and sectility hardness noted above.

9A.3.5 Fatty Acid Composition

The Fritz and Ammix samples collected during the '85 - '86 season were analysed by gas chromatography to ascertain their fatty acid composition. Results for Fritz butter are presented in Table 9.4 and results for Ammix butter are presented in Table 9.5.

Butyric acid levels do not seem to show any particular seasonal trend. Short chain fatty acids, caproic ($C_{6:0}$) and caprylic ($C_{8:0}$), show a slight rise during October-November then a general decline throughout the season. Medium chain acids, $C_{10:0}$, $C_{12:0}$ and $C_{14:0}$, rise to a peak in late November, then decline until the end of the season. Palmitic acid ($C_{16:0}$) increases from a minimum value in spring to peak in the summer, with a small decline in the autumn. $C_{18:0}$ and $C_{18:1}$ are at high levels at the beginning of the season, fall to a minimum in December and rise again in the autumn. Palmitic acid was found to vary inversely with stearic acid ($C_{18:0}$).

Gray (1973) studied the seasonal variation of fatty acid composition of New Zealand milkfat samples collected during the 1969-70 dairying season using gas-liquid chromatography. He found the levels of various fatty acids varied with season in much the same way as described above. Short chain fatty

Table 9.4: Fatty acid composition of Fritz butters collected during the 1985 - 1986 season.

Fatty acid	Fatty acid composition (wgt %)					
	OCT	NOV	JAN	FEB	MAR	APR
4:0	3.3	4.0	4.5	4.0	4.3	4.1
6:0	2.2	2.7	2.4	2.3	2.2	2.2
8:0	1.3	1.7	1.4	1.4	1.3	1.3
10:0	2.9	4.1	3.0	3.0	2.8	3.0
12:0	3.6	4.5	3.4	3.3	3.1	3.3
14:0	10.6	13.2	10.8	10.7	10.2	10.5
14:1	1.8	1.0	1.3	1.4	1.4	1.5
15:0	1.4	1.3	1.5	1.5	1.4	1.5
16:0	25.4	28.2	27.8	28.7	27.3	27.0
16:1	3.6	1.9	3.0	3.1	3.2	3.4
17:0	1.0	0.5	1.1	1.04	1.0	1.1
17:1	0.5	0.4	0.4	0.4	0.4	0.4
18:0	9.8	11.4	11.5	11.1	11.0	11.0
18:1	27.1	19.6	21.2	21.4	22.9	23.1
18:2	2.6	1.4	2.5	2.3	2.5	2.7
18:3	2.3	2.1	2.4	2.5	2.6	2.5

Table 9.5: Fatty acid compossiton of Ammix butters collected during the 1985 - 1986 season.

Fatty acid	Fatty acid composition (wgt %)						
	OCT	NOV	DEC	JAN	FEB	MAR	APR
4:0	3.4	4.7	4.1	4.0	4.0	4.8	4.0
6:0	2.5	2.6	2.2	2.3	2.3	2.1	2.0
8:0	1.6	1.6	1.4	1.4	1.3	1.2	1.2
10:0	3.5	3.9	3.1	3.0	2.8	2.7	3.0
12:0	3.8	4.2	3.5	3.3	3.1	2.9	2.6
14:0	10.9	11.3	10.9	10.8	10.3	9.9	9.9
14:1	1.4	1.5	1.5	1.5	1.5	1.5	1.5
15:0	1.4	1.6	1.6	1.6	1.5	1.4	1.5
16:0	24.5	24.9	26.4	26.8	27.0	25.6	25.5
16:1	3.2	3.2	3.2	3.2	3.3	3.4	3.4
17:0	1.1	1.2	1.1	1.2	1.2	1.0	1.1
17:1	0.4	0.5	0.5	0.5	0.5	0.4	0.4
18:0	11.4	11.2	11.0	10.6	10.6	10.6	10.9
18:1	24.3	22.9	22.6	22.6	22.9	24.7	25.3
18:2	2.3	2.2	2.4	2.5	2.6	2.9	2.7
18:3	2.5	2.5	2.6	2.7	2.8	3.0	3.0

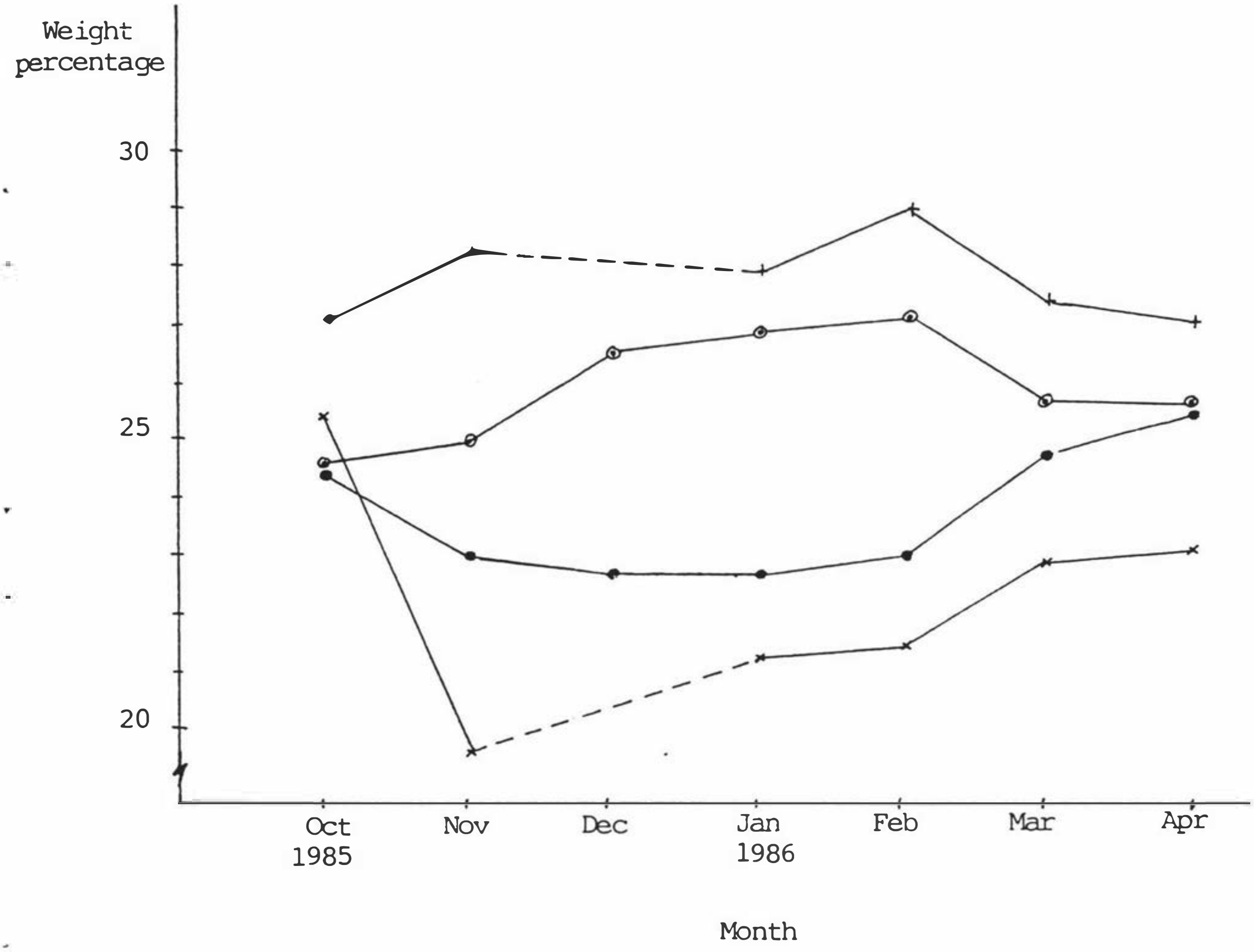


Figure 9.5: Weight percentages of $C_{16:0}$ and $C_{18:1}$ for Fritz and Anmix butters collected over the '85 - '86 season.

+ $C_{16:0}$ Fritz.

x $C_{18:1}$ Fritz.

⊙ $C_{16:0}$ Anmix.

● $C_{18:1}$ Anmix.

acids were found to be highly correlated with one another and showed significant negative correlation with palmitic acid ($C_{16:0}$) and significant positive correlation with stearic acid ($C_{18:0}$).

Parodi (1970) also used gas-liquid chromatography to survey seasonal changes in the fatty acid composition of Australian butters. His findings parallel those of Gray (1973).

Results in the present study are in accordance with those of Gray and Parodi, with the exception of butyric acid levels.

Figure 9.5 illustrates the change in $C_{16:0}$ and $C_{18:1}$ levels for both Fritz and Ammix samples as the season progresses. The Ammix samples consistently have a smaller proportion of $C_{16:0}$ and a greater proportion of $C_{18:1}$. Furthermore, the amount of $C_{16:0}$ and $C_{18:1}$ present in the Ammix sample does not seem to vary as much with season as fatty acid levels in corresponding Fritz samples.

Differences seen in the fatty acid compositions of Fritz and Ammix butters explain the difference in solid fat contents of the two types of butter. The lower levels of $C_{16:0}$ and higher levels of $C_{18:1}$ seen in milkfat extracted from Ammix butter would lead to a lower solid fat content.

On considering factors which could cause differences in the fatty acid composition of milkfat extracted from Fritz and Ammix butters, two major differences stand out; method of manufacture and different cream sources. The method of manufacture does not affect the fatty acid composition of milkfat in butter, therefore differences in cream source must be a princpal factor.

The obvious difference between cream sources which are used for the manufacture of the Fritz and Ammix butter samples is a geographical one. The two sources are widely separated within

New Zealand. In connection with this, MacGibbon and McLennan (1987) found butter from five of the six plants they surveyed to have approximately the same sectility hardnesses at the same time of the year. As a result regional differences were not thought to affect solid fat content or milkfat composition.

However, fatty acid composition suggests a difference in cream produced in the two regions. Aside from geographical differences, a large amount of artificial irrigation is carried out in the region which supplies the cream which is manufactured into Ammix butter, especially in the summer. This would lead to pasture growth similar to that of spring, with pasture plants containing more un-saturated lipids (McDowall *et al*, 1961). Thus, the fatty acid compostion of milkfat produced by cows grazed on irrigated pastures would be expected to be different from the fatty acid composition of milkfat of cows grazed on non-irrigated pastures. The solid fat content would be expected to be lower in the former case because of incresed amounts of un-saturated fats.

In addition, continued spring-like pasture growth should lead to a diminished fluctuation on the levels of various fatty acids. Figure 9.5 shows levels of $C_{16:0}$ and $C_{18:1}$ do not vary as much for Ammix samples compared to Fritz samples.

9A.3.6. Triglyceride Composition

The triglyceride composition of Fritz and Ammix butters collected during the '85 - '86 season were also ascertained by gas chromatography. Triglyceride analysis results are presented in Tables 9.6 and 9.7 for Fritz and Ammix butters respectively. Lower molecular weight triglycerides, C36 and under, increase until November/December then slowly decline through the autumn. The percentage of high molecular weight triglycerides, C50 and above, decline to a minimum in November and increase again in the autumn. Triglycerides between C36 and C48 tend to decline slightly as the season progresses.

Table 9.6: Triglyceride composition of Fritz butters collected during the 1985 - 1986 season.

C*	OCT	NOV	JAN	FEB	MAR	APR
28	0.63	0.8	0.5	0.5	0.4	0.4
30	1.4	1.5	1.1	1.0	1.0	1.1
32	2.7	3.0	2.1	2.2	1.9	2.0
34	5.9	6.2	5.5	5.5	4.8	4.9
36	11.2	12.1	11.3	11.02	10.4	10.3
37	1.1	0.7	1.3	1.4	1.3	0.8
38	14.2	13.8	14.0	13.6	13.4	12.9
40	11.0	11.1	10.6	10.2	10.4	10.3
42	7.2	8.5	6.9	6.6	6.0	6.8
44	6.6	7.4	6.0	5.8	5.6	6.4
45	0.4	0.5	0.5	0.5	0.5	0.4
46	6.4	7.3	6.4	6.3	6.2	6.9
47	0.6	0.5	0.7	0.8	0.8	0.7
48	7.1	7.3	7.9	7.7	8.0	8.6
49	0.8	0.4	1.0	1.1	1.2	1.1
50	8.8	7.8	10.0	10.1	10.7	11.1
52	8.7	7.2	9.3	9.1	10.4	10.6
54	4.0	2.9	3.6	3.5	4.5	4.4

(C*) Carbon number of triglycerides.

Table 9.7: Triglyceride composition of Ammix butters collected during the 1985 - 1986 season.

C*	OCT	NOV	DEC	JAN	FEB	MAR	APR
28	0.6	0.9	0.7	0.6	0.5	0.5	0.5
30	1.4	1.6	1.2	1.3	1.0	1.0	1.0
32	2.7	3.1	2.5	2.6	2.0	2.1	2.0
34	5.4	6.2	5.8	6.1	4.8	5.2	4.7
35	0.7	0.7	0.5	0.8	0.7	0.4	0.0
36	10.8	11.7	10.8	12.0	10.2	9.9	9.7
37	1.5	1.4	0.7	1.3	1.4	0.7	1.4
38	14.2	14.5	12.4	14.7	12.9	12.5	12.7
40	12.2	11.0	9.9	10.7	10.3	10.7	10.3
42	7.4	7.6	6.7	7.0	6.3	6.4	6.3
44	6.0	6.5	6.3	6.3	5.5	5.8	5.4
45	0.4	0.5	0.5	0.4	0.5	0.4	0.5
46	5.9	6.3	6.7	6.5	6.1	6.4	6.0
47	0.5	0.4	0.8	0.5	0.8	0.6	0.8
48	6.6	6.8	8.0	7.5	7.8	8.1	7.8
49	0.8	0.5	1.2	0.5	1.2	1.1	1.2
50	8.8	7.3	10.1	8.3	10.8	11.7	10.5
52	9.2	7.3	9.4	8.4	10.2	10.9	11.2
54	4.4	3.7	4.3	3.9	4.5	5.4	5.5

(C*) Carbon number of triglycerides.

Taylor and Hawke (1975a) analysed the triglycerides present in samples of September, January and March milkfats. The September sample contained a higher proportion of unsaturated triglycerides than the January and March samples. They concluded differences in the triglyceride composition between September, and the January and March samples were the result of differences in the proportions of the different types of triglycerides, and not differences in the composition of the major triglyceride species.

The seasonal changes in fatty acid composition and triglyceride levels seen here are in accord with Taylor and Hawke's (1975b) observation that fatty acid composition affects the relative proportions of constituent triglycerides. The percentages of low molecular weight triglyerides vary throughout the season in the same way as short and medium chain fatty acids. High molecular weight triglycerides follow the same seasonal trends as C_{18} acids. Changes in the proportion of triglycerides are clearly related to changes in fatty acid composition and depend on those factors which influence fatty acid composition.

9A.4. CONCLUSION

The major physical property of butter considered in Part A, hardness, has been found to be highly correlated to solid fat content. Solid fat content in turn is dependent on fatty acid and triglyceride composition.

The relationship between solid fat content and composition has been discussed by Gray (1973) and Norris *et al* (1973). The composition of milkfat is affected by a number of factors, including type of feed, stage of lactation and plane of nutrition. These factors, and others, interact in a complex manner. In New Zealand, spring calving and spring pasture growth contribute to higher levels of short chain and unsaturated fatty acids, and hence lower solid fat contents. As pastures mature, the level of saturated fats rise, increasing solid fat content. Fresh autumn pasture growth leads to the production of milkfat with a lower solid fat content, but not as low as that found in spring.

The physical properties of butter are very dependent on the chemical composition of milkfat and thus will vary as chemical composition varies. Other factors, such as manufacturing variables will have some effect on physical properties, however, the solid fat content of milkfat has been found to be the major contributory factor to the physical properties of butter.

PART B: CREEP COMPLIANCE

In addition to established methods of physical and chemical testing the creep compliance behaviour of a range of samples was examined.

9B.1. EXPERIMENTAL

Fritz and Ammix butters from the months of October, January and April were chosen to give samples with a wide range of sectility hardness and solid fat contents. Creep compliance testing of 17 hours duration was carried out on October, January and April samples from the 1985 - 1986 season, while January, April and October samples from 1987 were subjected to load cycling experiments where samples were subjected to creep compliance testing for 17 hours, then allowed to relax for 7 hours. The creep/recovery cycle was then repeated.

9B.2. RESULTS

a) First Creep Response

Sectility hardness, solid fat content and creep compliance results for the first creep response are presented in Table 9.8. Creep compliance parameters were found for the first creep response using a non-linear least squares curve fitting program (Chapter 4, Section 6.1.2). Three retardation mechanisms were fitted. Instantaneous response, the sum of compliance and viscosity term were found directly from the recovery curve (Chapter 4, Section 6.2). Full creep compliance parameters are listed in Appendix 2.

In general, the sum of the compliance values decreases as sectility hardness and solid fat content increase. Viscosity values tend to increase as hardness and solid fat content increase.

The correlation coefficients found between sectility hardness and solid fat content and various creep compliance parameters for all butters, and Fritz and Ammix separately, are presented in Table 9.9. For all butters the sum of the compliance values correlates with sectility hardness (r = -0.77) and solid fat content (r = -0.80). Viscosity correlates well with sectility hardness (r = 0.81), and less well with solid fat content (r = 0.56). Hardness accounts for 66% of the variance in viscosity (R^2 = 66.1%) and for 60% of the variance in the sum of the compliances (R^2 = 59.8%). Solid fat content has a large effect on sum of compliances but little effect on viscosity (R^2 = 64.6% and 31.4% respectively).

A separate examination of the creep results found for the Fritz and Ammix butters shows Ammix butter to have a high correlation between sum of compliances and sectility hardness (r = -0.75), as does Fritz butter (r = -0.86). Ammix butter shows a higher correlation between solid fat content and sum of compliance (r = -0.85) than Fritz butter (r = -0.70).

The viscosities found for both Fritz and Ammix butters are correlated with sectility hardness (r = 0.66 and 0.84 respectively). Ammix butter also shows a high correlation between viscosity and solid fat content (r = 0.80), in complete contrast to Fritz butter (r = 0.11).

Table 9.8: Creep compliance parameters fitted to butters.

	Sectility hardness (g)	Solid fat %	Sum of the compliances ($\times 10^{-8}$ Pa^{-1})	Viscosity η_N ($\times 10^{10}$Pa.s)
FRITZ				
TUI April 87	1450	55.9	45	24
TUI Oct 85	1725	54.4	40	62
TUI Oct 87	1850	54.2	38	110
TUI April 86	1950	57.1	26	73
TUI Jan 87	2400	61.2	27	88
AMMIX				
TT Oct 85	1100	48.8	68	19
TT Jan 86	1200	54.0	49	28
TT April 87	1325	53.6	32	29
TT April 86	1500	53.0	47	49
TT Oct 87	1700	53.7	35	34
TT Jan 87	1850	57.5	31	66

b) Load Cycling

Creep compliance results for load cycled samples are presented in Table 9.10. This data was presented previously in Chapter Seven. The instantaneous compliance values and sums of compliances observed for recovery and creep after the initial creep response tend to decrease as sectility hardness and solid fat increase, while no trends are discernible for the viscosities.

The sum of compliances recovered after the first creep, ΣJ_{R1}, is highly negatively correlated with sectility hardness (r = -0.88). (All correlation coefficients are presented in Table 9.9.) The sum of compliances recovered does not correlate as well with solid fat content (r = -0.62). Hardness accounts for 78% of variation in the sum of compliances recovered (R^2 = 78.0%), while solid fat accounts for only 38% (R^2 = 38.3%).

The creep and recovery observed for the second load cycle correlate highly with sectility hardness (r = -0.86 and -0.99 respectively), with sectility hardness accounting for 73% of the ΣJ_{C2} response (R^2 = 73.5%) and 97% of the ΣJ_{R2} response (R^2 = 97.1). In contrast, solid fat content does not correlate as well, r = -0.47 for the sum of creep compliances and r = -0.87 for the sum of the recovery compliances.

The percentage of the instantaneous compliance value recovered after the initial creep decreases as sectility hardness and solid fat content increase (Table 9.10). However, a better correlation is seen for solid fat content (r = -0.51), compared to sectility hardness (r = -0.40).

Similarly, the percentage of the sum of compliances recovered after the first creep generally decreases as sectility hardness increases and shows a reasonable correlation with sectility hardness (r = -0.68). Regression analysis shows sectility hardness accounts for about 46% (R^2 = 46.1%) of the percentage recovery seen. Solid fat content does not correlate as well (r = -0.43).

Table 9.9: Correlation coefficients found between sectility hardness and solid fat content and creep compliance parameters for a number of butters.

		All Butters (11)	Fritz Butters (5)	Ammix Butters (6)
	ΣJ vs. SH	-0.77	-0.86	-0.75
C1	ΣJ vs. sfc	-0.80	-0.70	-0.85
	η_N vs. SH	0.81	0.66	0.84
	η_N vs. sfc	0.56	0.11	0.80
		(6)		
R1	ΣJ vs. SH	-0.88	-	-
	ΣJ vs. sfc	-0.62	-	-
C2	ΣJ vs. SH	-0.86	-	-
	ΣJ vs. sfc	-0.47	-	-
R2	ΣJ vs. SH	-0.99	-	-
	ΣJ vs. sfc	-0.87	-	-

Figures in brackets = number of samples.
SH = Sectility hardness.
sfc = Solid fat content.
ΣJ = Sum of compliances.
η_N = Viscosity.
C1 and C2 = first and second creep.
R1 and R2 = first and second recovery.

Table 9.10: Creep compliance parameters for samples collected throughout the year.

	TUI Oct 87	TT Oct 87	TUI Jan 87	TT Jan 87	TUI Apr 87	TT Apr 87
Creep 1						
J_o	4.1 (.3)	4.8 (.4)	3.3 (.3)	4.0 (.5)	5.3 (.3)	5.2 (.3)
J_r^a	34 (2)	30 (3)	24 (2)	27 (4)	40 (1)	27 (2)
ΣJ^b	38 (2)	35 (3)	27 (2)	31 (5)	46 (1)	32 (2)
η_N	110 (22)	34 (7)	88 (14)	66 (7)	24 (2)	29 (3)
Recovery 1						
J_o	2.1 (.5)	2.2 (.5)	1.4 (.5)	1.4 (.5)	2.7 (.5)	2.5 (.5)
J_r	4.9 (.5)	7 (1)	4.6 (.5)	5 (1)	8 (2)	11(2)
ΣJ	7 (1)	9 (2)	6 (1)	6 (2)	11 (3)	14 (3)
η_N	16 (2)	30 (3)	22 (3)	19 (1)	11 (3)	20 (4)
Creep 2						
J_o	1.9 (.3)	2.2 (.4)	1.4 (.4)	1.6 (.6)	1.1 (.3)	2.3 (.5)
J_r	2.5 (.1)	0.8 (.6)	0.8 (.1)	2.4 (.4)	7.1 (.1)	5.7 .5
ΣJ	4.4 (.4)	3 (1)	2.2 (.5)	4 (1)	8.2 (.4)	8 (1)
η_N	140 (40)	55 (5)	110 (28)	180 (88)	65 (30)	40 (10)
Recovery 2						
J_o	2.5 (.5)	2.2 (.5)	-	1.4 (.5)	2.7 (.5)	2.7 (.5)
J_r	5.5 (.5)	7 (1)	3 (1)	6.6 (.5)	7 (1)	7.3 (.5)
ΣJ	8 (1)	9 (2)	3 (1)	8 (1)	10 (2)	11 (1)
η_N	120 (30)	170 (30)	500 (100)	-	160 (80)	88 (14)
% rec J_o	50 (15)	46 (14)	42 (18)	34 (16)	51 (12)	47 (12)
% rec J_r	14 (4)	15 (8)	17 (9)	17 (10)	20 (10)	42 (18)
% rec ΣJ	18 (3)	25 (2)	20 (5)	19 (9)	25 (7)	43 (12)

(a) Retarded compliance.
(b) Sum of complainces.
( ) Standard error.

Units:

J_o, J_r, ΣJ x 10_{-8} Pa^{-1}
η_N x 10^{10} Pa s.

9B.3. DISCUSSION

For all butters examined, the sum of compliances seen during the initial creep response, during recovery on the removal of stress, and when stress is applied and removed again, have all been seen to correlate well with sectility hardness. In addition, the correlation between sum of compliances and sectility hardness improves after the initial creep response (Table 9.9).

Solid fat content correlates well with the sum of compliances found for the first creep response. However, solid fat content does not correlate as well as sectility hardness with the sums of compliances found for the first recovery, or the sum of compliances found for the subsequent load cycle (Table 9.9).

The viscosity terms found for the initial creep response correlate well with sectility hardness, and less well with solid fat content (Table 9.9).

A separate examination of the relationships between sum of compliances found for the Fritz and Ammix samples and sectility hardness shows a good correlation for both butters (Table 9.9), with Ammix butter showing a higher correlation.

The viscosities of Fritz and Ammix butter show reasonable correlations with sectility hardness. In complete contrast, the viscosity of the Fritz butter shows almost no correlation with solid fat content, while the correlation between the viscosity of Ammix butter and solid fat content is good (Table 9.9).

Given that solid fat content has been seen to correlate well with sectility hardness, for example, r = 0.81 for the butter samples reported on in Part A, Section 3.3, it is not unreasonable to expect sectility hardness and solid fat content to be correlated with various creep and recovery parameters to the same extent. However, this is not seen in every case. On considering all samples together, it is apparent the correlation between solid fat content and viscosity is much lower than that found for sectility hardness and viscosity. This is especially apparent if the Fritz samples are considered separately. Sums of compliances found for recovery and the second creep response also fail to correlate as well with solid fat content.

The poorer correlation seen between solid fat content and viscosity, compared to that seen between viscosity and sectility hardness is not unexpected. Both creep and sectility hardness testing are performed on butter directly while solid fat content is determined from extracted fat which has undergone a cooling and tempering procedure. Preparation of samples in such a manner would eliminate any contribution which manufacturing method or structure may have had on hardness. This may partially explain the very low correlation seen between solid fat content and viscosity for Fritz butter, however, the low correlation seen may also be (partially) accounted for by the difficulty experienced in obtaining accurate viscosity values.

In general these results suggest both sectility hardness and solid fat content have approximately the same effect on the initial sum of compliances, while sectility hardness plays a greater part in determining the initial viscous response and subsequent creep and recovery responses. The results also suggest Ammix butter is behaving as might be expected, ie., sectility hardness is dependent on solid fat content.

9B.4. CONCLUSION

The sum of compliances and viscosity terms found for the initial creep curves are well correlated with sectility hardness and solid fat content. Solid fat content has a much greater influence on the creep behaviour of Ammix butter, while it is likely the behaviour of Fritz butter is more influenced by other factors, especially in the case of viscous flow.

As sectility hardness has previously been shown to be dependent on milkfat composition and thus time of season (Part A) it can be said the initial creep compliance response of butter is dependent on season. The sum of compliances seen during recovery and subsequent creep also show a dependence on sectility hardness. The difficulties in ascertaining the very small effects of the very large viscosities found during recovery and subsequent creep may be obscuring any seasonal trends present in these parameters.

CHAPTER TEN

GENERAL DISCUSSION

This work was undertaken to study the rheological properties of butter and related fat products using a creep compliance method. Through this study it was hoped a clearer understanding of the relationship between rheological properties, composition and structure of butter and related products would be acheived.

10.1. DEVELOPEMENT OF THE CREEP COMPLIANCE METHOD

10.1.1. Equipment

Shama and Sherman (1968) used a parallel plate viscoelastometer to perform creep compliance tests on margarine and later, 1970, on both butter and margarine. A parallel plate viscoelastometer, such as that described was built to carry out creep compliance testing on butter and related systems. A linear displacement transducer was used to measure the very small creep responses seen in this work. The transducer was found to be very sensitive.

10.1.2. Data Collection

The signal from the transducer was recorded simultaneously by data logger, and chart recorder to provide a permanent record of the experiment.

The data logger was designed and built by Mr. A. Matheson of the Applied Mathematics Section of New Zealand Dairy Research Institute. It was specifically programmed to record data from creep compliance experiments. A reading was taken every half second for the first ten minutes of any experiment and then at

20 second intervals. On completion of an experiment data was offloaded on to a disk for storage and analysis.

10.1.3. Temperature Control

Fats such as milkfat contain a wide variety of triglycerides with a correspondingly wide range of melting points, consequently temperature control is a vital part of creep compliance experimentation. Changes in solid fat content as a result of changes in temperature would lead to changing rheological responses. This must be avoided if useful measurements are to be made.

A temperature of 10°C was chosen to conduct creep compliance testing of butter and related systems. Small fluctuations in temperature at 10°C had less effect on solid fat content than at other, higher temperatures. In addition, other tests, such as sectility hardness, were routinely carried out at 10°C.

Temperature was maintained by placing the parallel plate viscoelastometer in an Environ-Shaker which acted as a refrigerated incubator. All experiments were conducted in the incubator. Constant temperatures (10 ± 0.2°C) were maintained despite ambient temperatures ranging from 10°C - 30°C during a twentyfour hour period.

10.1.4. Accuracy

Creep compliance was found to be very sensitive to slight differences in samples (see below, Section 3.3). However, in many cases repeatability was found to be poor.

Poor repeatability was thought to be due in the main to slight differences between samples and the process of fitting parameters to observed creep curves.

Materials such as butter and related fats are often inhomogenous. Grossly inhomogenous samples were easily detected and excluded from creep compliance testing. However, samples with minor variations were not easily detected and some were inevitably used for creep compliance testing. Furthermore, samples for one test only could be cut from a 500g pat of butter. As pats are packed into cartons which contain 40 pats there is the possibility the stress and temperature history of each pat of butter in a carton may differ from it's neighbour, and give slightly different creep responses on testing. Interestingly, samples made specifically for creep testing (Chapter 2) gave the most repeatable results.

A second factor contributing to the difficulty of obtaining repeatable results was thought to involve the curve fitting process itself. Two curves which may look superficially alike, ie. show a similar overall creep, may be fitted with vastly differing parameters. The parameters fitted varied by 10 - 20% or even more in some cases.

As a result of the difficulty in obtaining repeatable data experiments were done in triplicate or quadruplicate, until two similar sets of results were obtained.

10.2. DATA ANALYSIS

10.2.1. The Viscoelastic Model

The creep behaviour of butter is usually thought of as viscoelastic. The creep compliance curve for a substance exhibiting classical viscoelastic behaviour can be said to consist of three regions; a) a region of instantaneous elastic response, b) a region of retarded elastic response and c) a region of pure viscous flow. Viscoelastic behaviour has been modelled by the generalised Kelvin model (Chapter 1, Section A.6.1.1.2).

The equation for creep behaviour based on this model is

$$J(t) = J_o + \Sigma J_i(1-\exp(-t/\tau_i)) + t/\eta_N \qquad (10.1)$$

where J(t) = the overall creep compliance, J_o = the instantaneous elastic response, J_i = the retarded elasticities, τ_i = the retardation times associated with the retarded elasticities, η_N = the viscous flow term and t = time.

This model was used to analyse creep responses.

10.2.2 Data Analysis

Sherman (1968) carried out analysis of data using a graphical method. One disadvantage of this approach is the uncertainty involved in establishing when the curve has become linear and thus ascertaining and subtracting the viscous term. This would affect the first set of parameters found. A second problem associated with graphical analysis occurs in some cases, with the retardation times ceasing to be distinguishable, as the effect of one retardation mechanism would not have died out completely before the next commenced. In addition, manual graphical analysis is tedious and, at short times, is prone to large errors.

The problem of deciding when a creep curve has become linear was avoided with the use of a Marquadt non-linear least squares curve algorithm (Marquadt, 1963). The viscosity value found by the program is the value which best fits the data and model used.

While both methods were found to give similar indications of J_o, overall retarded compliance responses and viscosities, the retardation times found are different. Computerized curve fitting has more advantages, compared with the method of graphical analysis. Consequently computerised curve fitting using the non-linear least squares curve fitting progarm, NONLIN, was used throughout this work.

10.2.3. Retardation Spectra

The retardation spectrum is the continuous spectrum of retardation times, usually found by plotting L(τ) (see Equation 10.2) against ln time. Retardation spectra offer an alternative way to view raw data from creep compliance experiments.

Continuous retardation spectra can be calculated from data obtained from creep compliance experiments using the second order approximation of the inverse Laplace transform,

$$L(\tau) = (d/d\ln t)\ [J(t)-J(t)/d\ln t]_{t=2\tau} \qquad (10.2)$$

An ideal viscoelastic material, whose creep behaviour can be described by the classic equation (Equation (10.1)), and which has distinguishable retardation times would have a smooth continuous retardation spectrum with a well defined peak at each retardation time. In contrast, the retardation spectra found for raw data on plotting L(τ) against ln time gave very jagged spectra.

Plotting data which had been both smoothed and differentiated by the methods of Savitzky and Golay (1964) gave retardation spectra which were more like the ideal spectra. These spectra gave a reasonable indication of the actual retardation spectra. The complex nature of the spectra made them difficult to interpret, however, the retardation spectra found offered some evidence for the existence of three or four main groups of retardation mechanisms between the times of 0 and 10000 seconds.

10.2.3. Appropriateness of the Model

The appropriateness of the viscoelastic model can be checked by comparing ideal retardation spectra (Chapter 1, Section A.6.1.1.3) with retardation spectra found from experimental data. In general, the experimental continuous retardation spectra obtained after smoothing and differentiation by the methods of Savitzky and Golay seemed to be similar to the ideal continuous retardation spectra obtained using parameters fitted by the program NONLIN which had also been smoothed and differentiated. Given the parameters used to calculate the ideal continuous spectra were obtained using a model based on Equation (10.1), with all the implied limitations of a model, the similarity of the two sets of continuous spectra suggested the viscoelastic model was appropriate to model creep compliance behaviour.

The similarity of the spectra also suggested that fitting a model with three retardation times was not too inappropriate. Three retardation times have been used consistently throughout this work to analyse initial creep responses. Other workers have used from one to four exponentials to analyse creep curves (Chapter 1, Table 1).

10.3. PRELIMINARY EXPERIMENTS

10.3.1. Linearity

With non-linear viscoelastic materials a curvilinear relationship exists between stress and strain. Most viscoelastic materials exhibit linear stress/strain behaviour at very low stresses. If the stress selected does not exceed the value beyond which non-linearity develops it is possible to analyse the creep compliance data obtained.

A series of experiments were performed to establish if linear viscoelastic behaviour was exhibited by butter at low stresses. Two butters were subjected to a range of stresses varying from 784 - 3920 Pa for five minutes. Linear creep compliance responses were seen for both butters.

The response of butter to a creep compliance test of five minutes duration is essentially elastic in nature. The contribution of the viscous term would be negligible in the first five minutes. However, the contribution of viscosity to the total compliance should be independent of the stress used.

In order to determine the response of the viscous term to varying stresses a single butter was exposed to varying stresses for 15.5 hours. The results showed viscosity to be independent of the applied stress, remaining approximately the same as stress increased. The instantaneous compliance and sum of the compliances also increased linearly as stress increased indicating a linear elastic response was observed over long time creep experiments as well as experiments lasting only five minutes.

All creep compliance work was carried out using a stress of 3136 Pa at 10^{o}C.

10.3.2. Duration of Experiment

To determine the effect of varying the duration of creep compliance experiments, two butters were subjected to creep compliance testing of varying duration and allowed to recover after creep compliance testing. A typical creep and recovery curve is shown in Figure 10.1.

The sum of compliances found for the initial creep curves did not vary much as experimental length changed. In contrast, the sum of the compliance values recovered showed a tendency to change as duration of the experiment changed.

In all cases the viscosity term obtained from creep was larger than the viscosity term found from the recovery curve. The viscosity terms calculated for the creep curves showed little variation with changing experimental length. However, the viscosity terms found from the recovery curve showed some tendency to increase as the duration of the experiment increased.

The variation seen in some creep compliance results as experimental length changes demonstrated the need for creep compliance experiments to be carried out over a constant

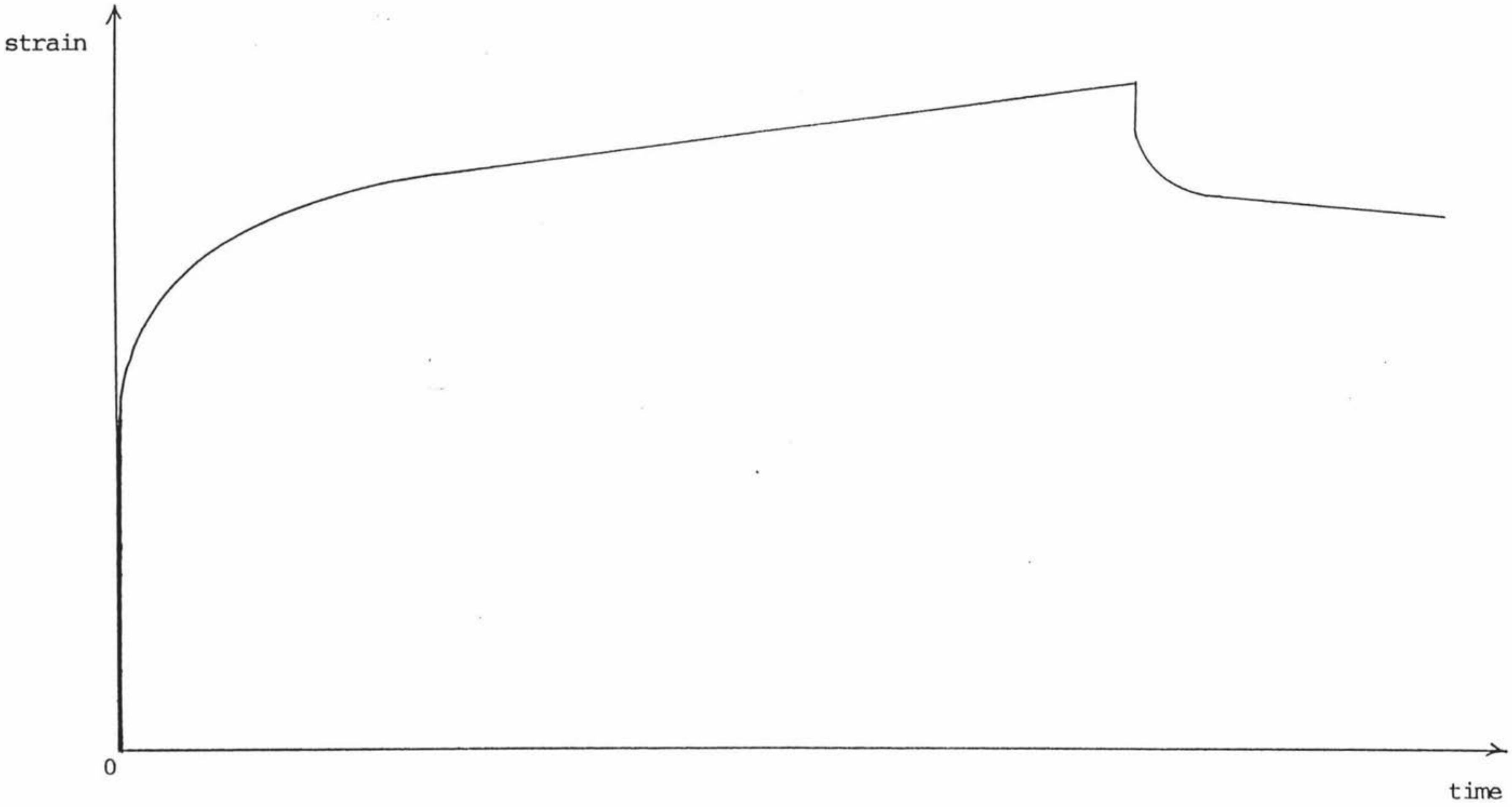


Figure 10.1: A creep and recovery curve.

length of time. This must be done to enable meaningful comparisons of data obtained from different experiments.

The length of time taken by one stress/recovery cycle is theoretically unlimited. However, the data logger can only record 15.5 hours of data, and, if any number of experiments were to be performed the cycles could not be too long. In practice, a cycle of 17 hours creep and 7 hours recovery was found to give meaningful data. All subsequent creep/recovery experiments followed this pattern.

10.3.3. Orientation of Sample

A sample cut from a pat of butter can be sheared in three directions. If the fold face of a pat of butter is designated the top face, a set of three-dimensional axes can then be imposed on the butter such that the top and bottom faces lie in the xy plane, side faces in the xz plane and end faces in the yz plane and shear in the x, y or z directions is possible.

In order to evaluate any possible effect of direction of shear, two patted Fritz butters and two patted Ammix butters were sheared in all three directions.

The creep compliance results for the Ammix butters indicated the direction in which shear occured did not affect the creep compliance response greatly. In contrast, a difference in the magnitude of creep compliance response was observed for patted Fritz butters, shear in the x direction gave the smallest response, followed by shear in the y direction, with shear in the z direction giving the greatest response. The sum of the compliances increased and the viscous terms decreased as shear direction changed from x to y to z.

A possible explanation for the difference in behaviour observed for shear in the three directions, x, y, and z, exists. Both pumping through pipes and the process of patting exposes butter to shear stresses. It is possible some order is imposed on fat crystals during pumping and patting, thus leading to a larger creep compliance response in some directions. Additionally, the shear forces involved may cause 'bonds' or weak van-der-Waals forces to break which are not later reformed (ie. a form of reworking).

The direction of butter flow through pipes is manifested in the z axis of the finished pat. Butter is then exposed to further stresses during the process of patting and wrapping. Both the Fritz and Ammix samples were packed using a pump fed SIG FD140 patter. The major stress during patting seems to be caused by the removal of the block of butter from the piston. As this happens the butter is sheared in what will be the y direction in the finished pat.

The explanation implies increasing shear will lead to an increase in creep compliance response. If it is assumed that pumping produces more shear than the patting process, the trends in creep compliance results may be explained.

In the manufacture of Fritz butter the milkfat is completely crystallized before churning. Any rearrangement of the fat crystals which occurs after churning and working would be permanent. In contrast, in the manufacture of butter by the Ammix process, crystallization is not completed until after processing. Presumably any rearrangement or imposed order resulting from pumping or patting would be obscured by subsequent crystallization.

The above explanation is supported by the creep responses of two samples of Fritz butter which were collected as the butter left the butter making machine (ie. before being pumped through pipes). Samples sheared in the direction of flow from the buttermaking machine gave similar results to samples sheared at right angles to the flow.

These orientation results suggest creep compliance testing is very sensitive and capable of picking up the effect of stresses applied to butter during pumping and patting operations.

For consistent results it is important that samples are always cut and placed in the parallel plate viscoelastometer in the same way. All patted butters were prepared by cutting samples from the top face of the pat, with shear occurring in the x direction.

10.4. LOAD CYCLING

On removal of stress after creep compliance testing, a partial recovery of strain was observed. The application of stress and its recovery was referred to as a creep/recovery cycle, or a load cycle. After allowing a sample to recover for some time stress could be applied again, followed by a further recovery.

Three samples of Fritz butter and three samples of Ammix butter collected throughout the dairying season which were chosen to give a range of sectility hardnesses and solid fat contents were subjected to two 17 hour creep/7 hour recovery cycles.

All samples gave the same general response curve illustrated in Figure 10.2. On the first application of stress the usual creep compliance response was seen. On the removal of stress some recovery takes place. On a second application of stress a creep response of approximately the same magnitude as the first recovery was observed (softer samples crept a little further). If the stress was then removed, a second recovery, very similar to the first, was observed. From the general shapes of the observed curves it seemed butter was be behaving in a viscoelastic manner after the initial creep response.

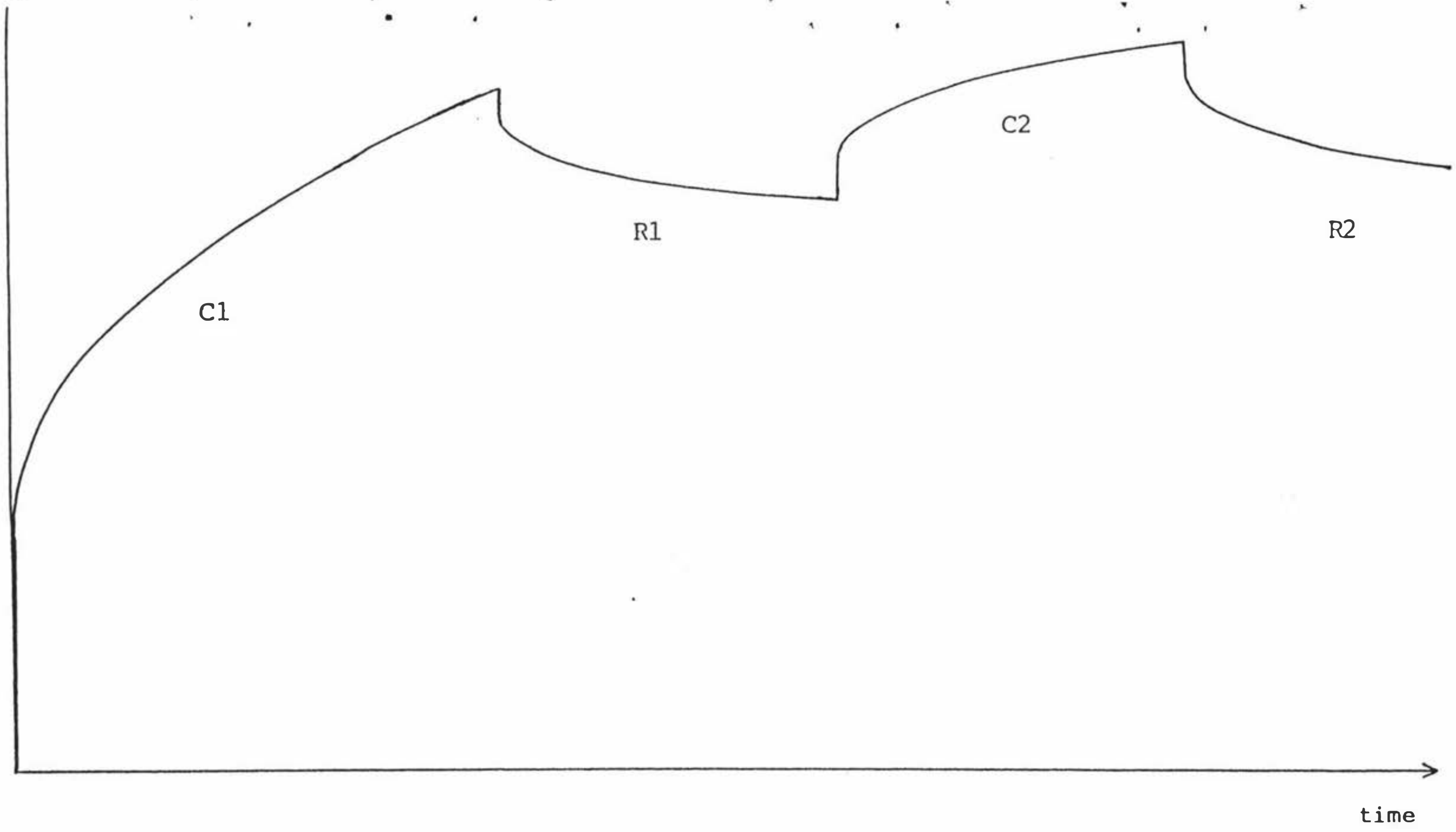


Figure 10.2: Typical creep compliance curve seen on repeatedly applying and removing stress.

A comparison of the retardation spectra found for the first and second creep curves showed the spectra were not alike. The retardation spectrum for the second creep curve was much reduced in magnitude. The first curve had a far greater contribution to overall response from retardation mechanisms between ln time 3.5 and 8.5, while retardation mechanisms contributed very little to the second curve until long times.

The necessity of fitting a reduced number of retardation mechanisms to second creep curves became obvious (two, as opposed to three), given the much reduced contribution of such retardation mechanisms at short and medium times. The time constants fitted tended to be in the regions of approximately ln time 6.5 and 8.5. These constants also indicate a loss of retardation mechanisms at short times.

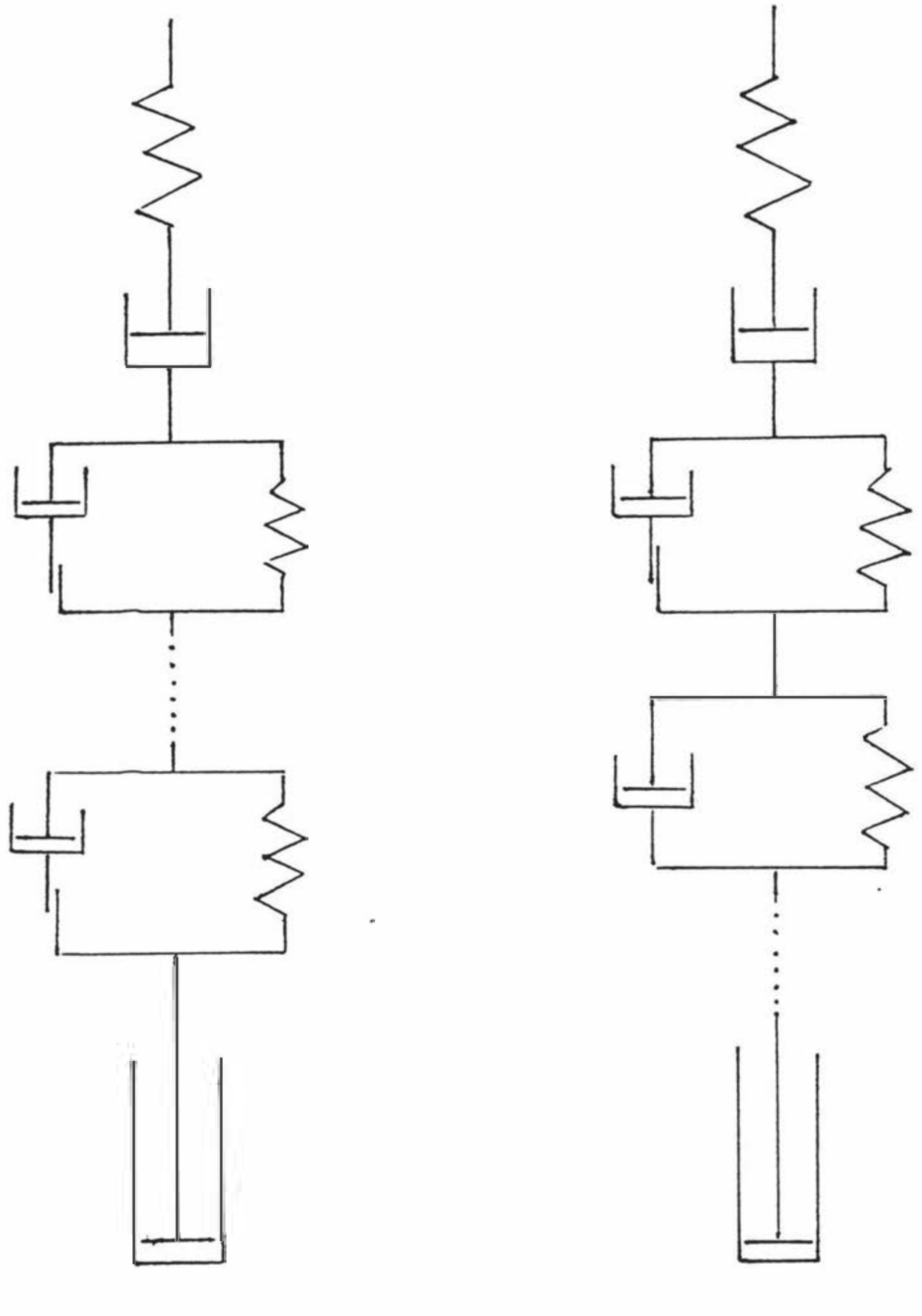
All samples subjected to repeated creep/recovery cycling showed the same general response as illustrated in Figure 10.2 (including butter both original and reworked, and anhydrous fat products, both original and reworked). It became obvious the creep compliance and recovery behaviour of the fat products being investigated could not be described as viscoelastic.

It was suggested that on the application of a shear stress, the crystal network may be behaving in a fashion similar to polymers under stress (Mandelkern, 1964). The network was thought to be deforming along the axis of applied stress. As this happens elements of the crystal network would be distorted from their most probable configurations. In polymers this results in a decrease in configurational entropy and this may also be happening here. As deformation is maintained, crystal, or structural units would become increasingly orientated along the axis of shear. This would lead to opportunities for the formation of a range of bonds. Weak bonds and/or van-der-Waals attractive forces would break and reform and, as duration of the experiment increases, increasingly strong 'bonds' would break and reform. Additional strong 'bonds', or crystal-crystal linkages may also be formed during this process.

The net result of forming new linkages and the continuous breaking and reforming of van-der-Waals bonds as the network becomes increasingly deformed was thought to gradually 'lock' the network into a deformed state. Not only would the deformation of the network be permanent, the deformed state will be more ordered and therefore have reduced entropy. As a result little recovery will be seen on the removal of stress. If the structure becomes locked into a more ordered state subsequent application of stress may be expected to cause little further deformation.

The generalized Kelvin model (outlined in Section 2) satisfactorily describes the initial and subsequent creep curves. However, it fails to describe the overall response observed during creep/recovery load cycling. Consequently, an alternative rheological model becomes necessary. In the first creep and recovery cycle the model should account for the initial instantaneous response and the declining recovery of this response as experimental length increases. Similarly, it must account for the retarded elastic response and the decline in retarded elastic recovery. The model should also account for the viscous flow seen. Finally, it should also be able to model the second creep and recovery cycle (which does seem to be viscoelastic).

A possible model is presented in Figure 10.3a. The proposed model features an initial spring and a dashpot with very low viscosity to represent the instantaneous response. When stress is removed only the spring recovers. The retarded compliances are represented by Kelvin units with weak springs and a yield element. As the length of the experiment increases the yield elements fail. When stress is removed only those units whose yield elements have not failed are able to recover. Long term



(a) (b)

Figure 10.3: Propsed rheological models to represent the creep compliance behaviour of butter.

viscous flow is represnted by a large final dashpot with high viscosity. Eventually, when all the Kelvin units with yield elements have failed the model is reduced to a Maxwell unit.

An alternative (Fig. 10.3b) would be to include ordinary Kelvin units (spring and dashpot in parallel) in series with units with yield elements. Thus, when all yield elements have failed the model will revert to the generalized Kelvin model represent viscoelastic behaviour.

10.5. PRODUCTS MADE FROM THE SAME FAT

A plasticized milkfat, a milkfat/oil blend and a butter were prepared from the same milkfat source in order to investigate the effect of the presence of water and the influence of solid fat content on creep compliance behaviour.

The shortenings and butter were subjected to two 17 hour creep/ 7 hour recovery cycles. All samples exhibited the same behaviour as mentioned above (Fig. 10.2).

It was noted that even though the plasticized milkfat and the butter had approximately the same sectility hardness and elastic compliances, their viscosities differed, with that of the butter being much greater than that found for the plasticized milkfat. This difference was thought to be due to the presence of water droplets in the butter somehow increasing viscosity.

The addition of oil to milkfat to decrease solid fat content had the expected effect of lowering sectility hardness, and increasing elastic responses. The viscous flow term was not affected. This was unexpected, as other results indicated decreasing amounts of solid fat had the effect of decreasing viscosity.

10.6 REWORKED PRODUCTS

A number of samples were reworked, a Fritz butter and an Ammix butter, and the anhydrous and butter samples prepared from the same milkfat. Reworking produced a marked reduction in the hardness of all samples but had virtually no effect on solid fat content.

Reworking results in a major disruption of any crystalline structures present. Crystals, or small clumps of crystals, will be disturbed and relocated throughout the sample. When the process of reworking is complete, crystal networks will reform. However, owing to the breaking of bonds and the disruption of structural units, these units will no longer be in their most probable configuration. This process is also thought to break strong 'bonds' or linkages between structural elements. It is thought that once these bonds are broken a large proportion either do not reform, or only partially reform over a long period of time (Haighton, 1965).

On being subjected to two creep/recovery cycles all samples exhibited the behaviour mentioned above (Fig. 10.2). However, reworked samples showed a much greater creep response than corresponding original samples.

The instantaneous response seen for reworked samples was 2.5-3 times the instantaneous response seen for original samples. In general there was an inverse relationship between increase in instantaneous response and reduction in hardness, for example, the reworked Fritz butter had a third of the hardness of the original butter, and showed an instantaneous response three times greater than the unworked butter.

Retarded compliances of reworked samples were four to five times larger than those seen for the originals. These increases were larger than would be predicted by sectility hardness alone. This suggests reworking affects elastic compliances in ways other than just breaking strong 'bonds'.

The less favourable configurations of elements of the crystal lattice may make deformation easier and explain the increases seen.

The decrease in viscosity seen for reworked butter was expected. With strong 'bonds' being broken during reworking fewer bonds would need to break for particles or crystals to be able to flow. Interestingly, the percentage decrease in viscosity was close to the percentage decrease in sectility hardness.

The retardation spectra of reworked samples differed from those seen for the original samples in several ways. Spectra were larger and smoother than those seen for the original samples. It appeares some 'bonds' that break at medium to long times are lost on reworking. This may happen as structural units are forced from their most probable positions. On reformation of crystal networks these 'bonds' may not reform or reform very slowly. The bulk of the spectra also moves to shorter times as retardation times decrease. It seems that as deformation becomes easier, it becomes faster.

The second creep response of reworked samples also increased, compared to the original samples. This increase was approximately the same order as that seen for the initial creep response.

10.7. SEASONAL SURVEY

Samples of Fritz and Ammix butters were collected over two and one half dairying seasons. Traditional sectility hardness and solid fat content by NMR were determined for all samples. Differential scanning calorimetry melting thermograms, fatty acid and triglyceride compositions were determined for samples collected during the 1985-1986 season.

The sectility hardness results showed a steep rise in hardness in the spring, reaching a peak around November/December, followed by a decrease in the autumn. Autumn hardnesses do not fall as low as spring hardnesses. The seasonal variation in the solid fat content at 10°C shows a similar trend to that seen for hardness, with a rapid increase in solid fat content through spring to summer, followed by a decline in autumn. The correlation between sectility hardness at 10°C and solid fat content at the same temperature for samples of Fritz and Ammix butters collected throughout the season was high ($r = 0.81$ for all samples).

Solid fat content was directly linked to fatty acid composition, especially to levels of unsaturated fatty acids. These were observed to be high in spring, fall to a minimum in summer and rise again in autumn.

Butters manufactured by the Ammix method during the sampling period were consistently softer than corresponding butters manufactured using the Fritz process. Milkfat extracted from butter made by the Ammix method had consistently lower solid fat levels than that made by the Fritz process. These differences can also be related to fatty acid composition. The Ammix samples consistently had a smaller proportion of $C_{16:0}$ and a greater proportion of $C_{18:1}$ leading to lower solid fat contents. Differences in cream source were thought to be the principle factor behind the different fatty acid compositions of Fritz and Ammix butters.

Creep compliances testing was carried out on selected samples. Fritz and Ammix butters from the months of October, January and April were chosen to give samples with a wide range of sectility hardness and solid fat contents.

In general, the initial sum of the compliance values decreased as sectility hardness and solid fat content increasd. Initial viscosity values tended to increase as hardness and solid fat content increased. The sum of the compliance values for all samples was found to correlate well with sectility hardness (r = -0.77) and solid fat content (r = -0.80). Viscosity correlated well with sectility hardness (r = 0.81), and less well with solid fat content (r = 0.56).

When samples are subjected to creep/recovery cycling the compliances observed for recovery and creep after the initial creep response tend to decrease as sectility hardness and solid fat increase. No trends were discernible for the viscosities, this may be due to the difficulties in ascertaining the very small effects of the very large viscosities found during recovery and subsequent creep.

As sectility hardness and solid fat content have been shown to be dependent on milkfat composition and thus time of season it can be said the initial creep compliance response of butter is dependent on season. The sum of compliances seen during recovery and subsequent creep also showed a dependence on sectility hardness.

10.8. CONCLUSION AND FUTURE WORK

The work undertaken has lead to the building up of a substantial knowledge base about the rheological and physical properties of butter.

Creep compliance has been a useful method for examining the rheological response of fat products. A heretofore unreported response of butter and similar fat products to creep/recovery cycling has been observed. After the initial creep response samples failed to recover a large proportion of the elastic compliance. A further application of stress resulted in a creep response similar to the first recovery. The second recovery also seemed to be of the same order as the first recovery and the second creep. This is shown in Figure 10.2.

The observed response was not viscoelastic in the classical sense. An explanation for the observed response, based on the behavior of polymers, has been put forward. The crystal network is thought to align in the direction in which stress is applied. The formation of new 'bonds' is then thought to lock the network in its' new position. A rheological model has been proposed to represent this behaviour.

A problem existed in getting reproducible results, possibly because of the very complex nature of butter itself. An attempt to overcome this problem was made by manufacturing anhydrous products and butter, controlling both manufacturing conditions and composition. The results obtained showed an improvement in repeatability. The creep responses of these 'model' systems showed the same pattern of behaviour as the results discussed above. This work could be taken further by manufacturing a wider range of products to further test the proposed model.

From this point attempts could be made to modify the structure of fat products. This could be approached in the following two ways:

a) Limiting the formation of the network.

This could possibly be acheived by the adsorption of an appropriate hydrophobic polymer or surfactant onto the surface of fat crystals.

b) Modifying the overall structure of the network.

The crystal network could be modified by the incorporation of filler particles, resulting in the formation of a structure similar to a composite gel. A number of experimental approaches are possible.

i) Adding a soft, inert filler which could create weak points throughout the network.

ii) Adding a non-inert filler which could break up the crystal lattice, for example, a modified starch granule with attached fatty acid chains.

iii) Using extra fat globules as a filler. Increasing the number of intact fat globues would result in more solid fat being contained in globules and unable to participate in formation of crystal networks. The globules would also be expected to act as mechanical blocks to the formation of the network. The globules may also act as soft filler particles.

The number of fat globules may be increased by making an artificial or recombined cream to which a surfactant has been added. In this way globules may be created with sufficiently strong surface layers to survive churning. The recombined cream could then be blended with natural cream and churned conventionally or blended with anhydrous milkfat and put through a margarine type process.

APPENDIX 1

COMPUTER PROGRAMS

1) Uart

2) Fileedit

3) Nonlin

4) Model

5) Retard

6) SandD

1) Uart

A program in Pascal which transfers data from a data logger to disk.

```
program uart;  { Ver 6.1 }

var
   arrayofdata : array [1..4000] of string[7];
   finish      : boolean;
   divisor     : byte;
   inputchar   : char;
   i,datacount : integer;
   inputstring : string[7];
   filename    : string[20];
   opf         : text;

{============================================================}

procedure setportmode;
begin {proc}
   divisor:=$30;                      {2400 baud}
   port[$3FB]:=port[$3FB] or $80;     {DLAB:=1}
   port[$3F8]:=divisor;               {DLL:=divisor}
   port[$3F9]:=0;                     {DLM:=0}
   port[$3FB]:=port[$3FB] and $80;    {DLAB:=0}
   port[$3fb]:=3;                     {set mode n,8,1}
end; {proc}

{============================================================}

procedure initialise;
begin {proc}
   clrscr;
   gotoxy(5,3);  lowvideo;
   writeln('This program transfers data from a remote computer/lunchbox');
   gotoxy(5,4);  writeln('to the Redstone');
   gotoxy(5,7);  write('Filename for data storage ( <21 chars )...');
   normvideo; write('B:');
   buflen:=20;
   readln(filename);
   for i:=1 to length(filename) do filename[i]:=upcase(filename[i]);
   filename:='B:' + filename;
   assign(opf,filename);
   rewrite(opf);
   clrscr;  gotoxy(5,2);
   lowvideo;  write('Writing to: ');
   normvideo;  writeln(filename);
   writeln;  writeln;
   window(1,5,80,25);
   gotoxy(5,1);
   writeln('Please initiate data transfer from remote computer');
end; {proc}
```

```
{==============================================================}

begin {program}
   setportmode;
   initialise;
   inputstring := '';
   finish:=false;
   datacount := 0;
   repeat
      while(port[$3FD] and 1) = 0 do;
      inputchar:=chr(port[$3F8]);
      if inputchar=':' then begin
         writeln(inputstring);
         datacount := datacount + 1;
         arrayofdata[datacount] := inputstring;
         if (pos('65535',inputstring)<>0) or (datacount>4000) then
finish:=true;
         inputstring:='';
      end
      else inputstring:=inputstring+inputchar;
   until finish;
   for i := 1 to datacount do writeln(opf,arrayofdata[i]);
   flush(opf);  close(opf);
   writeln;  writeln;
   lowvideo;  write('Data saved on file ');
   normvideo;  writeln(filename);
end. {program}
```

2) Fileedit

A program written in Pascal to edit creep compliance data. The program selects points at ln time intervals of 0.055.

```
program FileEdit;

(* This program edits data files created by saving creep compliance data *)
(* from the data logger. *)

var
   dst                           : string [10];
   dst7                          : string [7];
   gal,arraylength, basel        :integer;
   i,j                           :integer;
   k                             :real;
   filename                      :string[20];
   IPF,OPF                       :text;
   baddy                         :array[1..4000] of integer;
   btime                         :array[1..4000] of real;
   goody                         :array[1..250] of integer;
   gtime                         :array[1..250] of real;
   dfactor,tfactor               :integer;

procedure startIPF;
(* Assigns a filename to an input file. *)
   begin
   clrscr;
   write('enter drive:filename  ');  readln(filename);
   assign(IPF,filename);
   end;

procedure readdata;
(* Reads data from disk into the input file. *)
   begin
     i:=0;
     reset(IPF);
     while not EOF(IPF) do
     begin
        i := i + 1;
        readln(IPF, baddy[i]);
        end;
    close (IPF);
    arraylength:=i;
    writeln (arraylength);

(* Creating a baseline of zero. *)

    write('Enter number of data points to be deleted   ');
    readln(dfactor);
    write ('Enter time to be subtracted    ');
    readln (tfactor);
    btime[dfactor] :=1;
    dfactor:=dfactor +1;
```

```
(* Assigning the appropriate time to each data point. For the first 10 *)
(* minutes data is recorded at the rate of sec/2, and then at 20s
intervals. *)

    for i:=dfactor to 1200 do
       begin
          k:=i/2;
          btime[i]:=k - tfactor;
          btime[i]:=ln(btime[i]);
          end;
    k:=600;
    for i:=1201 to arraylength do
       begin
          k:=k+20;
          btime[i]:=k-tfactor;
          btime[i]:=ln(btime[i]);
          end;
          writeln('Stopping criteria is ',ln(k));
    end;

procedure selectbyln;
(* 200 data points out of 4000 are chosen for final analysis at regular ln
time intervals of 0.055. *)

var
   r,g                    :integer;
   stopfactor,l,s         :real;
   final                  :boolean;

begin
   write('Enter baseline value    ');
   readln(basel);
   write('enter criteria for stopping    ');
   readln(stopfactor);
   l:=btime[dfactor];
   i:=dfactor;
   g:=dfactor;
   r:=1;
   final:=false;
   gtime[1]:=btime[dfactor];
   goody[1]:=(baddy[dfactor]-basel);
   repeat
      repeat
         i:=i+1;
         s:= btime[i] -l;
         g:=g+1;
         until s>0.01;
      r:=r+1;
      gtime[r]:=btime[g];
      goody[r]:=(baddy[g]-basel);
      l:=l+0.055;
      writeln(goody[r]);
      if i=arraylength then final :=true;
      if l>=stopfactor then final :=true;
      until final;
```

```
   gal:=r;
   end;

procedure antilogtime;
(* Log time is converted into seconds. *)
begin
   for i:=1 to gal do
   begin
      gtime[i]:=exp(gtime[i]);
      end;
   end;

procedure discsave;
(* Saving the selected data points as a disk file in the correct layout for
further analysis. *)
begin
   write('enter drive : filename ');
   readln(filename);
   assign(OPF,filename);
   rewrite(OPF);
   for i:=1 to gal do begin
   write(OPF,'           ');
   str(goody[i]:7,dst7);
   dst:=dst7 + '.00';
   write(OPF,dst);
   str(gtime[i]:10:2,dst);
   writeln(OPF,dst);
   end;
   writeln(OPF,'                       10000000');
   close (OPF);
   end;

begin {main program}
   startIPF;
   readdata;
   selectbyln;
   antilogtime;
   discsave;
   end.
```

3) Nonlin

A non-linear least squares curve fitting program based on the Marquadt method (Marquadt, 1963) (in Fortran).

```
$DO66
      PROGRAM NONLIN
C     NON-LINEAR LEAST SQUARES FITTING PROGRAM BASED ON MARQUART METHOD
C     USER INPUT - MEANING OF VARIABLES AS IN B6700 VERSION
C     USER'S OWN SUBROUTINE MUST BE SUPPLIED & LINKED IN
      INTEGER SIZEX,SIZEY
C  SIZEX IS BIGGER OF NUMBER OF COEFFICIENTS
C  OR NUMBER OF INDEPENDENT VARIABLES
C  SIZEY IS MAXIMUM NUMBER OF OBSERVATIONS OF DEPENDENT VARIABLE
      PARAMETER (SIZEX=8,SIZEY=200)
      REAL Y(SIZEY),X(SIZEX,SIZEY),F(SIZEY),R(SIZEY),DELZ(SIZEY,SIZEX),
     1  B(SIZEX),DIFZ(SIZEX),E(SIZEX),P(SIZEX),PHI(SIZEX),Q(SIZEX),
     2  TB(SIZEX),SIGNS(SIZEX),A(SIZEX,SIZEX),D(SIZEX,SIZEX),
     3  U(SIZEX,SIZEX)
      CHARACTER*5 FIDENT(SIZEY)
      CHARACTER*8 BI(10)
      CHARACTER*12 FILNAM
      CHARACTER*20 FMT,TITLE
      COMMON /WWWW/ BI
      LOGICAL RDFLAG
      DATA FMT/' A5, 6X, 6F10.2'/
      RDFLAG=.FALSE.
C     RESET WHEN INPUT FILE NAME SPECIFIED LATER
1     N=0
C  NVARX IS MAXIMUM NUMBER OF PARAMETERS, NOT MAXIMUM NUMBER OF X'S.
      NVARX=SIZEX
      NOBMAX=SIZEY
      LUN=1
C     DATA INPUT FROM TERMINAL, MEMORY, OR LAST RUN ?
  699 CONTINUE
      WRITE(*,2)
2     FORMAT(' DATA FROM DISK FILE (ENTER -1), TERMINAL (JUST RETURN)'
     1 /' OR PREVIOUS SET (ENTER +1) ',//'TO QUIT ENTER 9')
      READ(*,3) ISAME
    3 FORMAT(I4)
      IF(ISAME.EQ.1) THEN
         GO TO 220
       ELSE IF (ISAME.EQ.0) THEN
         GO TO 5
       ELSE IF (ISAME.EQ.-1) THEN
C SET-UP ROUTINE FOR READING DATA FROM DISK
         IF(RDFLAG) THEN
            LUN = 7
            GO TO 5
         ENDIF
         WRITE(*,701)
  701    FORMAT(' ENTER NAME OF DISK FILE TO BE READ')
         READ(*,704) FILNAM
  704    FORMAT(A12)
```

```
         CALL OPEN(7,FILNAM,2)
         RDFLAG=.TRUE.
         LUN = 7
       ELSE IF (ISAME.EQ.9) THEN
         GO TO 9999
       ELSE
         GO TO 699
      ENDIF
5     IF (LUN.EQ.1) WRITE(*,6)
6     FORMAT(' ENTER TITLE FOR THIS RUN ')
      IF (LUN.EQ.7) THEN
         READ(7,8) TITLE
        ELSE
          READ(*,8) TITLE
      ENDIF
8     FORMAT(A20)
      WRITE(*,9)TITLE
9     FORMAT(1X,A20)
      WRITE(*,11)
11    FORMAT(' NO OF INDEPENDENT VARIABLES (X) = ')
      READ(*,NOIND)
      WRITE(*,12)FMT
12    FORMAT(' TO CHANGE INPUT FORMAT FROM ',A20,' ENTER 1,'/
     1       ' OTHERWISE RETURN:')
      READ(*,3) I
      IF (I.EQ.1) THEN
           WRITE(*,33)
33        FORMAT(' ENTER DATA INPUT FORMAT, EG (A4,6X,3F10.2) ')
          READ(*,44) FMT
44        FORMAT(A20)
      ENDIF
      IF (LUN.EQ.1) WRITE(*,55)
55    FORMAT(' 1234567890',6(9X,'0')/)
C     READ IN DATA IN FORMAT SPECIFIED EARLIER
14    N=N+1
      IF(LUN.EQ.1) THEN
        READ(*,*)Y(N),(X(I,N),I=1,NOIND)
      ELSE
        READ(LUN,80)FIDENT(N),Y(N),(X(I,N),I=1,NOIND)
      ENDIF
80    FORMAT(A5,6X,6F10.2)
      IF (X(1,N).LT.1.0E05) GO TO 14
      NOB=N-1
      IF (NOB.GT.NOBMAX) THEN
          WRITE(*,555) NOBMAX,NOB
555   FORMAT(/' PROGRAM DIMENSIONED FOR ',I4,' OBSERVATIONS. ',I4,
     1 ' READ IN '/' TRY AGAIN')
          GO TO 1
        ELSE
          GO TO 15
      ENDIF
220   WRITE(*,222)
222   FORMAT(/'  OBSERVATIONS THE SAME AS PREVIOUS PROBLEM')
C     READ IN CONTROL PARAMS ETC 1 AT A TIME, DEFAULTS AVAILABLE
15    WRITE(*,16)
16    FORMAT(' NO OF COEFFICIENTS (PARAMETERS) = ')
```

```
      READ(*,3) NC
      IF (NC.LE.0) GO TO 15
      WRITE(*,17)
17    FORMAT(’ STARTING VALUE OF LAMBDA - HIT RETURN FOR DEFAULT ’)
      READ(*,18) FLAM
18    FORMAT(F10.2)
      IF (FLAM.LE.0.0) FLAM=0.1
      WRITE(*,19)
19    FORMAT(’ STARTING VALUE OF NU - HIT RETURN FOR DEFAULT  ’)
      READ(*,18) FNU
      IF (FNU.LE.0.0) FNU=10.
      WRITE(*,20)
20    FORMAT(’ MAX NO OF ITERATIONS - HIT RETURN FOR DEFAULT  ’)
      READ(*,3)MIT
      IF (MIT.EQ.0) MIT=20
      WRITE(*,21)
21    FORMAT(’ MULTIPLIER "DIFF" - HIT RETURN FOR DEFAULT  ’)
      READ(*,18) DIFF
      IF(DIFF.LE.0.0) DIFF=.01
      WRITE(*,22)
22    FORMAT(’ SUM SQUARES CRITERION FOR STOPPING ITERATION = ’)
      READ(*,18) STOPSS
      IF(STOPSS.LE.0) STOPSS=0.001
      WRITE(*,24)
24    FORMAT(’ RATIO OF COEFFS CRITERION FOR STOPPING ITERATION = ’)
      READ(*,18) STOPCR
      IF(STOPCR.LE.0) STOPCR=0.001
      DO 32 I=1,NC
      SIGNS(I)=1.0
C     SIGNS OF COEFFS ARE +VE
32    DIFZ(I)=DIFF
C     ENTER STARTING GUESSES OF COEFFICIENTS, 1 AT A TIME
      DO 38 I=1,NC
      WRITE(*,39)I
39    FORMAT(’ STARTING GUESS FOR COEFF B(’,I1,’)  ’)
38    READ(*,18)  B(I)
      DO 40 I=1,NC
C     ENTER NAMES OF COEFFICIENTS FOR PRINTOUT IF DESIRED
      WRITE(*,41) I
41    FORMAT(’ NAME FOR COEFF. B(’,I1,’) UPTO 8 LETTERS (OR BLANK) ’)
      READ(*,106)BI(I)
106   FORMAT(A8)
   40 CONTINUE
      WRITE(*,107) NC,FLAM,FNU,MIT
107   FORMAT(’ NUMBER OF COEFFICIENTS’,I5/’ STARTING LAMBDA’,F12.4/
     1’ STARTING NU’,F12.4/’ MAX NO OF ITERATIONS’,I6/)
      CALL GAUSHS(FIDENT,Y,F,R,DELZ,B,DIFZ,E,P,PHI,Q,
     1 SIGNS,TB,A,D,U,X,TITLE,STOPSS,STOPCR,FLAM,FNU,MIT,
     2 NC,NOB,NOIND,NVARX,NOBMAX)
      GO TO 1
 9999 CONTINUE
      STOP
      END
```

4) Model

A user supplied model for use with the least squares curve fiting program Nonlin (in Fortran). This example fits two retardation mechanisms. The model is easily extended by adding more exponential terms.

```
      SUBROUTINE MODEL(TITLE, B, F, NOB, NP, X, NVARX, NOBMAX)
      REAL B(NVARX), F(NOBMAX),X(NVARX,*)
      CHARACTER*20 TITLE
      I=1
      DO 10, J=1,NOB
        F(J)=B(1) + B(2)*(1.0 - EXP( -X(I,J)/B(3)))
     1            + B(4)*(1.0 - EXP( -X(I,J)/B(5)))
     2          +X(I,J)/B(6)
10    CONTINUE
      RETURN
      END
```

5) SandD

A program (in Pascal) differentiating and (optionally) smoothing according to the procedures of Savitzky and Golay, 196. The number of points used in differentiation and the degree of polynomial are chosen by the user.

```
program SandD;
(* A program to calculate retardation spectra from creep compliance curves
ie. .dat files using the least squares method Golay and Savitsky with
optional smoothing. *)

var
  OPF,IPF              :text;
  filename             :string[12];
  jvalue               :array[1..250] of real;
  time                 :array[1..250] of real;
  lntime               :array[1..250] of real;
  laplace              :array[1..250] of real;
  arraylength,i,j      :integer;
  firstd, second       :real;
  deltat               :real;

procedure startIPF;
   begin
      write('enter drive:filename ·  ');
      readln(filename);
      assign(IPF,filename);
      end;

procedure readdata;
   begin
      i:=0;
      reset(IPF);
      while not EOF(IPF) do
      begin
         i:=i+1;
         readln(IPF, jvalue[i], time[i]);
         end;
      arraylength:=i;
      for i:=1 to arraylength do
      lntime[i]:=ln(time[i]);
      end;

procedure smooth; (* 17 point convoluting smooth*)
var m,j,k,ka                :integer;
nsum,cnsum                  :real;
np                          :array[1..25] of real;

   begin
      m:=arraylength -8;
      for i:= 2 to 17 do
      begin
```

```
          j:=i-1;
          np[i] := jvalue[j];
          end;
       for i:= 9 to m do
       begin
          j:= i + 8;
          for k:=1 to 16 do
          begin
             ka:=k+1;
             np[k]:=np[ka];
             end;
          np[17]:=jvalue[j];
          nsum:=(-21*(np[1]+np[17]))+(-
16*(np[2]+np[16]))+(7*(np[3]+np[15]))+(18*(np[4]+np[14]))+(27*(np[5]+np[13]
));

cnsum:=nsum+(34*(np[6]+np[12]))+(39*(np[7]+np[11]))+(42*(np[8]+np[10]))+(43
*np[9]);
          jvalue[i]:=cnsum/323;
{          writeln(jvalue[i]);}
          end;
       if i>=m then arraylength:=m;
       end;

procedure differentiate;
var
   m,k,ka,pts     : integer;
   nsum,c1,c2     :real;
   np             : array[1..19] of real;
   mdata,ndata    : array[1..250] of real;

begin
write('enter the number of points to differentiate  ');
readln(pts);
   m:=arraylength - 3;
   for i:=2 to pts do
   begin
      j := i-1;
      np[i]:=jvalue[j];
      end;
   for i:= 4 to m do
   begin
      j:=i+3;
      for k:=1 to (pts-1) do
      begin
         ka := k+1;
         np[k]:=np[ka];
         end;
      np[pts]:=jvalue[j];
{(* 5 point,  1st derivative, cubic, quartic *)
      nsum:=np[1]-np[5]-(8*(np[2]-np[4]));
      mdata[i]:=nsum/12;}

{(* 9 point, 1st derivative, cubic and quartic *)
     nsum:=(86*(np[1]-np[9]))+(142*(-np[2]+np[8]))+(193*(np[3]+np[7]))
+(129*(-np[4]+np[6]));
```

```
     mdata[i]:=nsum/1188;}

(* 7 point, 1st derivative, cubic and quartic *)
      nsum:= (22*(np[1] -np[7]))+(67*(-np[2]+np[6]))+(58*(-np[3]+np[5]));
      mdata[i]:=nsum/252.0;

{(* 13 point cubic, 1st derivative *)
      c1:=(1133*(np[1]-np[13]))+(660*(-np[2]+np[12]))+(1578*(-np[3]+np[11]
))+(1796*(-np[4]+np[10]));
      nsum:= c1+(1489*(-np[5]+np[9]))+(832*(-np[6]+np[8]));
      mdata[i]:=nsum/24024;}

{(* 7 point, 1st derivative, quintic, sexic *)
     nsum:=(-np[1]+np[7])+(9*(np[2]-np[6]))+(45*(-np[3]+np[5]));
     mdata[i]:=nsum/60;}

{           j:=i+(pts-1);
          for k:= 1 to (pts-1) do
          begin
             ka:=k+1;
             np[k]:=np[ka];
             end;
 }
{(* 5 point, 2nd derivative cubic *)
     nsum:=(2*(np[1]-np[3]-np[5]))-(np[2]+np[4]);
     ndata[i]:=nsum/7;}

(* 7 point, 2nd derivative cubic *)
          nsum:=(5*(np[1]+np[7]))-(3*(np[3] +np[5]))-(4*np[4]);
          ndata[i]:=nsum/42;

{(* 9 point, 2nd derivative cubic *)
     nsum:=(28*(np[1]+np[9]))+(7*(np[2]+np[8]))-(8*(np[3]+np[7]))-
(17*(np[4]+np[6]))-(20*np[5]);
     ndata[i]:=nsum/462;}

{(* 7 point, 2nd derivative quartic, quintic *)
     nsum:=(-13*(np[1]+np[7]))+(67*(np[2]+np[6]))-(19*(np[3]+np[5]))-
(70*np[4]);
     ndata[i]:=nsum/132;}

{(*13 point, 2nd derivative cubic *)
     c2:=(22*(np[1]+np[13]))+(11*(np[2]+np[12]))+(2*(np[3]+np[11]))+(-
5*(np[4]+np[10]));
     nsum:=c2 +(-10*(np[5]+np[9]))+(-13*(np[6]+np[8]))+-14*np[7];
     ndata[i]:=nsum/1001;}

          end;
(* laplace transform *)
          for i:=4 to m do
          laplace[i]:= mdata[i]-ndata[i];
          end;

procedure discsave;
   begin
      write('enter drive:filename  ');
```

```
      readln(filename);
      assign (OPF, filename);
      rewrite(OPF);
      for i:=1 to arraylength do
      begin
        writeln(OPF,laplace[i],'    ',jvalue[i],'    ',lntime[i]);
        end;
     close (OPF);
     end;

begin (*Main program*)
   startIPF;
   readdata;
   smooth;
   differentiate;
{    for i:= 1 to arraylength do
   writeln(laplace[i],'     ',jvalue[i],'     ',lntime[i]);}
   discsave;
  end.
```

6) Retard

A program (in Pascal) to calculate retardation spectra from creep compliance data, differentiating using a method reported by Fox and Maynes, 1966, with an optional smoothing procedure.

```
program RetardationSpectra;
(* A program to calculate retardation spectra from creep compliance
curves*)
(* using .dat files. *)

var
  OPF,IPF              :text;
  filename             :string[10];
  jvalue               :array[1..250] of real;
  time                 :array[1..250] of real;
  lntime               :array[1..250] of real;
  laplace              :array[1..250] of real;
  arraylength,i        :integer;
  firstd, second       :real;
  deltat               :real;

procedure startIPF;
   begin
      write('enter drive:filename   ');
      readln(filename);
      assign(IPF,filename);
      end;

procedure readdata;
   begin
      i:=0;
      reset(IPF);
      while not EOF(IPF) do
      begin
         i:=i+1;
         readln(IPF, jvalue[i], time[i]);
         end;
      arraylength:=i;
      for i:=1 to arraylength do
      lntime[i]:=ln(time[i]);
      end;

{procedure quadsmooth; (*17 point convoluting smooth*)
   var
   m,j,k,ka           :integer;
   nsum,cnsum            :real;
   np                 :array[1..25] of real;

   begin
      m:=arraylength - 8;
      for i:=2 to 17 do
      begin
```

```
         j:=i-1;
         np[i]:=jvalue[j]
         end;
      for i:=9 to m do
      begin
         j:=i+8;
         for k:= 1 to 16 do
         begin
            ka:=k+1;
            np[k]:=np[ka];
            end;
         np[17]:=jvalue[j];
         nsum:=(-21*(np[1]+np[17]))+(-
6*(np[2]+np[16]))+(7*(np[3]+np[15]))+(18*(np[4]+np[14]))+(27*(np[5]+np[13])
);
         cnsum:=nsum
+(34*(np[6]+np[12]))+(39*(np[7]+np[11]))+(42*(np[8]+np[10]))+(43*np[9]);
         jvalue[i]:= cnsum/323;
         writeln(jvalue[i]);
         end;
      if i>=m then arraylength :=m;
      end;}

procedure fancyderivation;
   begin
      write('enter delta t value  ');
      readln(deltat);
      for i:=3 to arraylength do
      begin
         firstd:=(1/(12*deltat))*(jvalue[i-2]-(8*jvalue[i-1])+
(8*jvalue[i+1])-jvalue[i+2]);
         second:=(1/(12*(sqr(deltat))))*(-jvalue[i-2]+(16* jvalue[i-1])-
(30*jvalue[i])+(16*jvalue[i+1])-jvalue[i+2]);
         laplace[i]:=firstd-second;
         end;
      i:=arraylength;
      end;

procedure discsave;
   begin
      write('enter drive:filename  ');
      readln(filename);
      assign (OPF, filename);
      rewrite(OPF);
      for i:=1 to arraylength do
      begin
         writeln(OPF,laplace[i],'    ',jvalue[i],'    ',lntime[i]);
         end;
      close (OPF);
      end;

begin (*Main program*)
   startIPF;
   readdata;
{   quadsmooth;
   fancyderivation;
```

```
for i:= 1 to arraylength do
writeln(laplace[i],'     ',jvalue[i],'     ',lntime[i]);
discsave;
end.
```

APPENDIX 2

NON-LINEAR LEAST SQUARES FITTING RESULTS

Conversion of non-linear least square fitting results to SI units.

a) J_0, J_1, J_2 and J_3.

$J = \quad /\sigma$

$=$ answer in datalogger units (dlu)/(10 x 776 x 30)

where 10 converts dlu to mV, 776mm/mV is the reported sensitivity of the data logger and 30mm is the height of the sample.

$\sigma = 3136$ pa.

Therefore, to convert results, divide answer in dlu by (10 x 776 x 30 x 3136), or 7.3×10^{8}.

eg. $33.45/7.3\text{x}10^8 = 4.6 \times 10^{-8}$ Pa^{-1}.

b) τ_1, τ_2 and τ_3.

Multiply by the appropriate J value, ie. $J_i \times \tau_i$.

eg. 43.54 x 0.47 = 20.5s.

c) η_N. Viscosity (Pa.s) = dlu (10 x 776 x 30 x 3136), or multiply answer in dlu by 7.3×10^8,

eg. $850 \times 7.3 \times 10^8 = 6.2 \times 10^{11}$ Pa.s.

1 = $\mathbf{J_0}$, instantaneous compliance.

2 = $\mathbf{J_1}$, first retarded compliance.

3 = τ_1, first retardation time.

4 = $\mathbf{J_2}$, second retarded compliance.

5 = τ_2, second retardation time.

6 = $\mathbf{J_3}$, third retarded compliance.

7 = τ_3, third retardation time.

8 = η_N, Newtonian viscosity.

```
                                                                       95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)     S. E. COEF.    T-VALUE     LOWER          UPPER
     1                   3. 34151E+01     9. 94E-01       33. 6     3. 15E+01      3. 54E+01
     2                   4. 35450E+01     2. 81E+00       15. 5     3. 80E+01      4. 90E+01
     3                   4. 74223E-01     2. 89E-02       16. 4     4. 18E-01      5. 31E-01
     4                   1. 13704E+02     3. 92E+00       29. 0     1. 06E+02      1. 21E+02
     5                   1. 55243E+00     9. 65E-02       16. 1     1. 36E+00      1. 74E+00
     6                   8. 34553E+01     4. 76E+00       17. 5     7. 41E+01      9. 28E+01
     7                   1. 26092E+01     1. 47E+00        8. 6     9. 73E+00      1. 55E+01
     8                   8. 49873E+02     1. 94E+01       43. 9     8. 12E+02      8. 88E+02
NO.  OF OBSERVATIONS                211
NO.  OF COEFFICIENTS                  8
RESIDUAL DEGREES OF FREEDOM         203
RESIDUAL ROOT MEAN SQUARE             2. 44513416
RESIDUAL MEAN SQUARE                  5. 97868156
RESIDUAL SUM OF SQUARES            1213. 67236328
```

X TUI October, 1985, Run 1.

```
                                                                       95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)     S. E. COEF.    T-VALUE     LOWER          UPPER
     1                   4. 07819E+01     1. 02E+00       40. 0     3. 88E+01      4. 28E+01
     2                   5. 17400E+01     2. 86E+00       18. 1     4. 61E+01      5. 73E+01
     3                   4. 66105E-01     2. 51E-02       18. 6     4. 17E-01      5. 15E-01
     4                   1. 25517E+02     3. 49E+00       36. 0     1. 19E+02      1. 32E+02
     5                   1. 74588E+00     1. 03E-01       16. 9     1. 54E+00      1. 95E+00
     6                   8. 88712E+01     3. 95E+00       22. 5     8. 11E+01      9. 66E+01
     7                   1. 76797E+01     1. 77E+00       10. 0     1. 42E+01      2. 12E+01
     8                   4. 10125E+02     5. 64E+00       72. 8     3. 99E+02      4. 21E+02
NO.  OF OBSERVATIONS                211
NO.  OF COEFFICIENTS                  8
RESIDUAL DEGREES OF FREEDOM         203
RESIDUAL ROOT MEAN SQUARE             2. 74559546
RESIDUAL MEAN SQUARE                  7. 53829575
RESIDUAL SUM OF SQUARES            1530. 27416992
```

Y TUI October, 1985, Run 2.

```
                                                                       95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)     S. E. COEF.    T-VALUE     LOWER          UPPER
     1                   4. 00365E+01     1. 03E+00       38. 8     3. 80E+01      4. 21E+01
     2                   8. 24401E+01     3. 22E+00       25. 6     7. 61E+01      8. 87E+01
     3                   4. 13909E-01     1. 50E-02       27. 6     3. 84E-01      4. 43E-01
     4                   1. 29065E+02     3. 14E+00       41. 1     1. 23E+02      1. 35E+02
     5                   2. 20654E+00     1. 37E-01       16. 2     1. 94E+00      2. 47E+00
     6                   1. 44690E+02     2. 32E+01        6. 2     9. 92E+01      1. 90E+02
     7                   1. 27308E+02     3. 98E+00       32. 0     1. 20E+02      1. 35E+02
     8                   3. 04798E+04     2. 80E+05        0. 1    -5. 18E+05      5. 79E+05
NO.  OF OBSERVATIONS                211
NO.  OF COEFFICIENTS                  8
RESIDUAL DEGREES OF FREEDOM         203
RESIDUAL ROOT MEAN SQUARE             3. 26843357
RESIDUAL MEAN SQUARE                 10. 68265915
RESIDUAL SUM OF SQUARES            2168. 58007812
```

X TUI January, 1986, Run 3.

```
                                                                       95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)     S. E. COEF.    T-VALUE     LOWER          UPPER
     1                   3. 95811E+01     7. 01E-01       56. 5     3. 82E+01      4. 10E+01
     2                   7. 70358E+01     2. 92E+00       26. 4     7. 13E+01      8. 27E+01
     3                   4. 08351E-01     1. 04E-02       39. 4     3. 88E-01      4. 29E-01
     4                   1. 36725E+02     2. 84E+00       48. 1     1. 31E+02      1. 42E+02
     5                   1. 70428E+00     8. 74E-02       19. 5     1. 53E+00      1. 88E+00
     6                   8. 79159E+01     3. 07E+00       28. 7     8. 19E+01      9. 39E+01
     7                   1. 92786E+01     1. 53E+00       12. 6     1. 63E+01      2. 23E+01
     8                   6. 24001E+02     1. 03E+01       60. 7     6. 04E+02      6. 44E+02
NO.  OF OBSERVATIONS                211
NO.  OF COEFFICIENTS                  8
RESIDUAL DEGREES OF FREEDOM         203
RESIDUAL ROOT MEAN SQUARE             2. 10631943
RESIDUAL MEAN SQUARE                  4. 43659161
RESIDUAL SUM OF SQUARES             900. 62609863
```

Z TUI January, 1986, Run 5.

```
                                                                          95%CONFIDENCE LIMITS
 IND.VAR(I) NAME            COEF.B(I)        S.E.COEF.       T-VALUE    LOWER              UPPER
       1                  1.71585E+01        9.55E-01         18.0       1.53E+01          1.90E+01
       2                  3.62594E+01        2.10E+00         17.3       3.22E+01          4.04E+01
       3                  6.34448E-01        4.59E-02         13.8       5.45E-01          7.24E-01
       4                  6.85416E+01        2.08E+00         32.9       6.45E+01          7.26E+01
       5                  3.42623E+00        2.85E-01         12.0       2.87E+00          3.98E+00
       6                  4.15435E+01        1.62E+00         25.6       3.84E+01          4.47E+01
       7                  8.26866E+01        9.41E+00          8.8       6.42E+01          1.01E+02
       8                  8.64505E+02        3.16E+01         27.4       8.03E+02          9.26E+02
 NO. OF OBSERVATIONS                    211
 NO. OF COEFFICIENTS                      8
 RESIDUAL DEGREES OF FREEDOM            203
 RESIDUAL ROOT MEAN SQUARE                 2.53828335
 RESIDUAL MEAN SQUARE                      6.44288349
 RESIDUAL SUM OF SQUARES                1307.90551758
```

X TUI April, 1986, Run 1.

```
                                                                          95%CONFIDENCE LIMITS
 IND.VAR(I) NAME            COEF.B(I)        S.E.COEF.       T-VALUE    LOWER              UPPER
       1                  2.63289E+01        9.26E-01         28.4       2.45E+01          2.81E+01
       2                  2.70967E+01        2.52E+00         10.8       2.22E+01          3.20E+01
       3                  9.14331E-01        8.58E-02         10.7       7.46E-01          1.08E+00
       4                  7.80680E+01        3.08E+00         25.3       7.20E+01          8.41E+01
       5                  2.98240E+00        2.52E-01         11.8       2.49E+00          3.48E+00
       6                  8.41144E+01        3.42E+00         24.6       7.74E+01          9.08E+01
       7                  2.06055E+01        1.94E+00         10.6       1.68E+01          2.44E+01
       8                  1.16616E+03        4.34E+01         26.9       1.08E+03          1.25E+03
 NO. OF OBSERVATIONS                    211
 NO. OF COEFFICIENTS                      8
 RESIDUAL DEGREES OF FREEDOM            203
 RESIDUAL ROOT MEAN SQUARE                 2.53380013
 RESIDUAL MEAN SQUARE                      6.42014313
 RESIDUAL SUM OF SQUARES                1303.28906250
```

X TUI April, 1986, Run 4.

```
                                                                          95%CONFIDENCE LIMITS
 IND.VAR(I) NAME            COEF.B(I)        S.E.COEF.       T-VALUE    LOWER              UPPER
       1                  3.99825E+01        1.30E+00         30.6       3.74E+01          4.25E+01
       2                  7.82805E+01        3.25E+00         24.1       7.19E+01          8.47E+01
       3                  3.79969E-01        1.79E-02         21.2       3.45E-01          4.15E-01
       4                  1.22792E+02        3.13E+00         39.2       1.17E+02          1.29E+02
       5                  2.45057E+00        1.74E-01         14.1       2.11E+00          2.79E+00
       6                  5.60917E+01        2.87E+00         19.5       5.05E+01          6.17E+01
       7                  9.97637E+01        1.23E+01          8.1       7.56E+01          1.24E+02
       8                  7.51954E+02        5.28E+01         14.2       6.48E+02          8.56E+02
 NO. OF OBSERVATIONS                    211
 NO. OF COEFFICIENTS                      8
 RESIDUAL DEGREES OF FREEDOM            203
 RESIDUAL ROOT MEAN SQUARE                 3.90821648
 RESIDUAL MEAN SQUARE                     15.27415657
 RESIDUAL SUM OF SQUARES                3100.65380859
```

Y TUI April, 1986, Run 3.

```
                                                                          95%CONFIDENCE LIMITS
 IND.VAR(I) NAME            COEF.B(I)        S.E.COEF.       T-VALUE    LOWER              UPPER
       1                  3.14670E+01        1.18E+00         26.7       2.92E+01          3.38E+01
       2                  4.10602E+01        2.63E+00         15.6       3.59E+01          4.62E+01
       3                  4.78371E-01        3.69E-02         13.0       4.06E-01          5.51E-01
       4                  1.10754E+02        2.62E+00         42.3       1.06E+02          1.16E+02
       5                  1.54278E+00        9.58E-02         16.1       1.35E+00          1.73E+00
       6                  7.39985E+01        1.78E+00         41.6       7.05E+01          7.75E+01
       7                  6.58426E+01        3.53E+00         18.6       5.89E+01          7.28E+01
       8                  5.84911E+02        2.01E+01         29.0       5.45E+02          6.24E+02
 NO. OF OBSERVATIONS                    211
 NO. OF COEFFICIENTS                      8
 RESIDUAL DEGREES OF FREEDOM            203
 RESIDUAL ROOT MEAN SQUARE                 2.85823298
 RESIDUAL MEAN SQUARE                      8.16949844
 RESIDUAL SUM OF SQUARES                1658.40820312
```

Y TUI April, 1986, Run 6.

```
                                                                      95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)       S. E. COEF.     T-VALUE   LOWER             UPPER
      1                  4. 78845E+01      6. 40E-01        74. 8     4. 66E+01        4. 91E+01
      2                  6. 14831E+01      2. 41E+00        25. 5     5. 68E+01        6. 62E+01
      3                  5. 26225E-01      1. 55E-02        34. 0     4. 96E-01        5. 57E-01
      4                  1. 26638E+02      2. 26E+00        56. 1     1. 22E+02        1. 31E+02
      5                  2. 00142E+00      9. 38E-02        21. 3     1. 82E+00        2. 19E+00
      6                  8. 28293E+01      2. 07E+00        40. 0     7. 88E+01        8. 69E+01
      7                  2. 76903E+01      1. 75E+00        15. 8     2. 43E+01        3. 11E+01
      8                  8. 48880E+02      1. 97E+01        43. 2     8. 10E+02        8. 87E+02
NO. OF OBSERVATIONS                     211
NO. OF COEFFICIENTS                       8
RESIDUAL DEGREES OF FREEDOM             203
RESIDUAL ROOT MEAN SQUARE                 1. 95815754
RESIDUAL MEAN SQUARE                      3. 83438158
RESIDUAL SUM OF SQUARES                 778. 37951660
```

Z TUI April, 1986, Run 8.

```
                                                                     95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)       S. E. COEF.     T-VALUE   LOWER             UPPER
      1                  4. 42832E+01      9. 38E-01        47. 2     4. 24E+01        4. 61E+01
      2                  8. 53631E+01      2. 43E+00        35. 1     8. 06E+01        9. 01E+01
      3                  3. 67078E-01      1. 16E-02        31. 6     3. 44E-01        3. 90E-01
      4                  1. 31805E+02      2. 76E+00        47. 7     1. 26E+02        1. 37E+02
      5                  2. 51722E+00      1. 26E-01        20. 0     2. 27E+00        2. 76E+00
      6                  8. 89968E+01      2. 67E+00        33. 3     8. 38E+01        9. 42E+01
      7                  3. 62507E+01      2. 97E+00        12. 2     3. 04E+01        4. 21E+01
      8                  3. 95263E+02      7. 41E+00        53. 3     3. 81E+02        4. 10E+02
NO. OF OBSERVATIONS                     211
NO. OF COEFFICIENTS                       8
RESIDUAL DEGREES OF FREEDOM             203
RESIDUAL ROOT MEAN SQUARE                 2. 88457870
RESIDUAL MEAN SQUARE                      8. 32079697
RESIDUAL SUM OF SQUARES                1689. 12207031
```

Z TUI April, 1986, Run 9.

```
                                                                     95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)       S. E. COEF.     T-VALUE   LOWER             UPPER
      1                  4. 70360E+01      1. 01E+00        46. 7     4. 51E+01        4. 90E+01
      2                  8. 49047E+01      2. 62E+00        32. 4     7. 98E+01        9. 00E+01
      3                  3. 97411E-01      1. 38E-02        28. 8     3. 70E-01        4. 24E-01
      4                  1. 35788E+02      2. 55E+00        53. 3     1. 31E+02        1. 41E+02
      5                  2. 43929E+00      1. 23E-01        19. 9     2. 20E+00        2. 68E+00
      6                  1. 95156E+02      7. 59E+01         2. 6     4. 64E+01        3. 44E+02
      7                  1. 51276E+02      1. 54E+01         9. 8     1. 21E+02        1. 82E+02
      8                  7. 69777E+03      5. 15E+04         0. 2    -9. 30E+04        1. 09E+05
NO. OF OBSERVATIONS                     211
NO. OF COEFFICIENTS                       8
RESIDUAL DEGREES OF FREEDOM             203
RESIDUAL ROOT MEAN SQUARE                 3. 20339060
RESIDUAL MEAN SQUARE                     10. 26171303
RESIDUAL SUM OF SQUARES                2083. 12792969
```

X TUI April, 1987, Run 1.

```
                                                                     95%CONFIDENCE LIMITS
IND VAR(I) NAME           COEF. B(I)       S. E. COEF      T-VALUE   LOWER             UPPER
      1                  4. 18201E+01      6. 20E-01        67. 4     4. 06E+01        4. 30E+01
      2                  9. 92607E+01      3. 01E+00        33. 0     9. 34E+01        1. 05E+02
      3                  3. 75574E-01      6. 80E-03        55. 3     3. 63E-01        3. 89E-01
      4                  1. 56701E+02      2. 61E+00        60. 0     1. 52E+02        1. 62E+02
      5                  1. 58934E+00      7. 14E-02        22. 3     1. 45E+00        1. 73E+00
      6                  6. 09988E+01      1. 75E+00        35. 0     5. 76E+01        6. 44E+01
      7                  4. 41822E+01      3. 44E+00        12. 9     3. 74E+01        5. 09E+01
      8                  6. 20738E+02      1. 15E+01        54. 1     5. 98E+02        6. 43E+02
NO. OF OBSERVATIONS                     211
NO. OF COEFFICIENTS                       8
RESIDUAL DEGREES OF FREEDOM             203
RESIDUAL ROOT MEAN SQUARE                 1. 99626279
RESIDUAL MEAN SQUARE                      3. 98506546
RESIDUAL SUM OF SQUARES                 808. 96838379
```

X TUI April, 1987, Run 4.

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                                                                    95%CONFIDENCE LIMITS
IND. VAR(I) NAME              COEF. B(I)       S. E. COEF.   T-VALUE    LOWER          UPPER
      1                     5. 64859E+01       8. 50E-01       66. 5     5. 48E+01      5. 82E+01
      2                     1. 09942E+02       1. 92E+00       57. 4     1. 06E+02      1. 14E+02
      3                     2. 68698E-01       5. 93E-03       45. 3     2. 57E-01      2. 80E-01
      4                     2. 04061E+02       1. 88E+00      108. 7     2. 00E+02      2. 08E+02
      5                     1. 61593E+00       4. 16E-02       38. 8     1. 53E+00      1. 70E+00
      6                     6. 13007E+01       2. 42E+00       25. 3     5. 66E+01      6. 60E+01
      7                     1. 12949E+02       8. 19E+00       13. 8     9. 69E+01      1. 29E+02
      8                     4. 95636E+02       1. 87E+01       26. 5     4. 59E+02      5. 32E+02
NO. OF OBSERVATIONS                      211
NO. OF COEFFICIENTS                        8
RESIDUAL DEGREES OF FREEDOM              203
RESIDUAL ROOT MEAN SQUARE                  2. 56556416
RESIDUAL MEAN SQUARE                       6. 58211994
RESIDUAL SUM OF SQUARES                 1336. 17041016
```

Y TUI April, 1987, Run 2.

```
                                                                    95%CONFIDENCE LIMITS
IND VAR(I) NAME               COEF. B(I)       S. E. COEF.   T-VALUE    LOWER          UPPER
      1                     1. 47690E+01       6. 64E-01       22. 2     1. 35E+01      1. 61E+01
      2                     1. 10282E+02       2. 03E+00       54. 4     1. 06E+02      1. 14E+02
      3                     3. 67364E-01       6. 76E-03       54. 3     3. 54E-01      3. 81E-01
      4                     1. 83416E+02       2. 07E+00       88. 4     1. 79E+02      1. 87E+02
      5                     2. 17288E+00       6. 39E-02       34. 0     2. 05E+00      2. 30E+00
      6                     1. 11685E+02       1. 84E+00       60. 6     1. 08E+02      1. 15E+02
      7                     4. 03071E+01       1. 97E+00       20. 5     3. 65E+01      4. 42E+01
      8                     5. 26969E+02       1. 30E+01       40. 6     5. 02E+02      5. 52E+02
NO. OF OBSERVATIONS                      211
NO. OF COEFFICIENTS                        8
RESIDUAL DEGREES OF FREEDOM              203
RESIDUAL ROOT MEAN SQUARE                  2. 26189[illegible]
RESIDUAL MEAN SQUARE                       5. 11618[illegible]
RESIDUAL SUM OF SQUARES                 1038. 58496094
```

Y TUI April, 1987, Run 5.

```
                                                                    95%CONFIDENCE LIMITS
IND. VAR(I) NAME              COEF. B(I)       S. E. COEF.   T-VALUE    LOWER          UPPER
      1                     7. 04458E+01       1. 09E+00       64. 7     6. 83E+01      7. 26E+01
      2                     1. 04873E+02       2. 69E+00       39. 0     9. 96E+01      1. 10E+02
      3                     3. 08653E-01       9. 30E-03       33. 2     2. 90E-01      3. 27E-01
      4                     1. 78798E+02       3. 12E+00       57. 3     1. 73E+02      1. 85E+02
      5                     2. 02540E+00       8. 39E-02       24. 1     1. 86E+00      2. 19E+00
      6                     1. 60308E+02       2. 97E+00       54. 0     1. 54E+02      1. 66E+02
      7                     2. 30643E+01       1. 22E+00       18. 9     2. 07E+01      2. 55E+01
      8                     2. 83161E+02       4. 91E+00       57. 7     2. 74E+02      2. 93E+02
NO. OF OBSERVATIONS                      211
NO. OF COEFFICIENTS                        8
RESIDUAL DEGREES OF FREEDOM              203
RESIDUAL ROOT MEAN SQUARE                  3. 40665245
RESIDUAL MEAN SQUARE                      11. 60528183
RESIDUAL SUM OF SQUARES                 2355. 87255859
```

Z TUI April, 1987, Run 3.

```
                                                                    95%CONFIDENCE LIMITS
IND. VAR(I) NAME              COEF. B(I)       S. E. COEF.   T-VALUE    LOWER          UPPER
      1                     4. 04886E+01       2. 91E+00       13. 9     3. 48E+01      4. 62E+01
      2                     5. 58984E+01       6. 42E+00        8. 7     4. 33E+01      6. 85E+01
      3                     2. 60639E-01       3. 53E-02        7. 4     1. 91E-01      3. 30E-01
      4                     1. 16964E+02       6. 81E+00       17. 2     1. 04E+02      1. 30E+02
      5                     1. 00396E+00       1. 46E-01        6. 9     7. 18E-01      1. 29E+00
      6                     1. 24349E+02       7. 40E+00       16. 8     1. 10E+02      1. 39E+02
      7                     7. 48318E+00       1. 00E+00        7. 5     5. 52E+00      9. 45E+00
      8                     2. 21828E+02       3. 05E+00       72. 7     2. 16E+02      2. 28E+02
NO. OF OBSERVATIONS                      211
NO. OF COEFFICIENTS                        8
RESIDUAL DEGREES OF FREEDOM              203
RESIDUAL ROOT MEAN SQUARE                  5. 88755035
RESIDUAL MEAN SQUARE                      34. 66325378
RESIDUAL SUM OF SQUARES                 7036. 64160156
```

Z TUI April, 1987, Run 6.

```
                                                                        95%CONFIDENCE LIMITS
IND.VAR(I) NAME             COEF.B(I)       S.E.COEF.     T-VALUE     LOWER              UPPER
     1                    3.92801E+01      1.24E+00        31.7      3.69E+01          4.17E+01
     2                    5.61469E+01      3.26E+00        17.2      4.98E+01          6.25E+01
     3                    2.88600E-01      1.66E-02        17.4      2.56E-01          3.21E-01
     4                    1.15810E+02      3.61E+00        32.1      1.09E+02          1.23E+02
     5                    1.07304E+00      7.68E-02        14.0      9.22E-01          1.22E+00
     6                    1.37386E+02      4.24E+00        32.4      1.29E+02          1.46E+02
     7                    6.10966E+00      3.98E-01        15.4      5.33E+00          6.89E+00
     8                    2.38502E+02      1.56E+00       153.4      2.35E+02          2.42E+02
NO. OF OBSERVATIONS                    211
NO. OF COEFFICIENTS                      8
RESIDUAL DEGREES OF FREEDOM            203
RESIDUAL ROOT MEAN SQUARE                2.63916731
RESIDUAL MEAN SQUARE                     6.96520424
RESIDUAL SUM OF SQUARES               1413.93652344
```

TUI April, 1987, Run 1, first creep.

```
                                                                        95%CONFIDENCE LIMITS
IND.VAR(I) NAME             COEF.B(I)       S.E.COEF.     T-VALUE     LOWER              UPPER
     1                    1.67427E+01      9.09E-01        18.4      1.50E+01          1.85E+01
     2                    5.26701E+00      8.79E-01         6.0      3.54E+00          6.99E+00
     3                    2.64136E+00      1.11E+00         2.4      4.68E-01          4.81E+00
     4                    1.12825E+01      6.50E-01        17.3      1.00E+01          1.26E+01
     5                    1.66279E+02      2.38E+01         7.0      1.20E+02          2.13E+02
     6                    4.27560E+02      4.47E+00        95.6      4.19E+02          4.36E+02
NO. OF OBSERVATIONS                    211
NO. OF COEFFICIENTS                      6
RESIDUAL DEGREES OF FREEDOM            205
RESIDUAL ROOT MEAN SQUARE                2.02844381
RESIDUAL MEAN SQUARE                     4.11458568
RESIDUAL SUM OF SQUARES                843.49011230
```

TUI April, 1987, Run 1,second creep.

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                                                                        95%CONFIDENCE LIMITS
IND.VAR(I) NAME             COEF.B(I)       S.E.COEF.     T-VALUE     LOWER              UPPER
     1                    4.14129E+01      6.76E-01        61.3      4.01E+01          4.27E+01
     2                    8.31602E+01      2.44E+00        34.1      7.84E+01          8.79E+01
     3                    3.87592E-01      8.92E-03        43.4      3.70E-01          4.05E-01
     4                    1.42241E+02      2.30E+00        62.0      1.38E+02          1.47E+02
     5                    1.82713E+00      7.82E-02        23.4      1.67E+00          1.98E+00
     6                    9.05417E+01      2.06E+00        43.9      8.65E+01          9.46E+01
     7                    2.71292E+01      1.61E+00        16.9      2.40E+01          3.03E+01
     8                    4.30592E+02      5.51E+00        78.2      4.20E+02          4.41E+02
NO. OF OBSERVATIONS                    211
NO. OF COEFFICIENTS                      8
RESIDUAL DEGREES OF FREEDOM            203
RESIDUAL ROOT MEAN SQUARE                2.07069016
RESIDUAL MEAN SQUARE                     4.28775787
RESIDUAL SUM OF SQUARES                870.41503906
```

TUI April, 1987, Run 2, first creep.

```
                                                                          95%CONFIDENCE LIMITS
 IND VAR(I) NAME          COEF B(I)        S.E. COEF.       T-VALUE       LOWER             UPPER
        1              [illegible]       [illegible]      [illegible]   2.78E+01          2.94E+01
        2              5.675[illegible]  [illegible]      [illegible]   5.44E-01          5.90E-01
        3              4.5744[illegible] [illegible]      [illegible]   4.39E-01          4.76E-01
        4              1.08954E+02       1.47E+00         73.9          1.06E+02          1.12E+02
        5              2.3620[illegible] [illegible]      [illegible]   2.24E+00          2.49E+00
        6              5.2195[illegible] 1.65E+00         31.6          4.90E+01          5.54E+01
        7              3.53[illegible]   2.58E+00         13.7          3.03E+01          4.04E+01
        8              7.95683E+02       9.66E+00         82.2          7.77E+02          8.14E+02
 NO. OF OBSERVATIONS                 211
 NO. OF COEFFICIENTS                   8
 RESIDUAL DEGREES OF FREEDOM         203
 RESIDUAL ROOT MEAN SQUARE             1.16874242
 RESIDUAL MEAN SQUARE                  1.36555[illegible]
 RESIDUAL SUM OF SQUARES             277.28[illegible]7285
```

TUI January 1987, Run 2, first creep.

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                                                                          95%CONFIDENCE LIMITS
 IND VAR(I) NAME          COEF B(I)        S.E. COEF.       T-VALUE       LOWER             UPPER
        1              [illegible]       [illegible]      [illegible]   [illegible]       [illegible]
        2              [illegible]       [illegible]      [illegible]   [illegible]       [illegible]
        3              [illegible]       [illegible]      [illegible]   [illegible]       [illegible]
        4              [illegible]       [illegible]      [illegible]   -7.16E+04         [illegible]
        5              [illegible]       [illegible]      [illegible]   [illegible]       [illegible]
        6              [illegible]       [illegible]      [illegible]   -1.62E+03         [illegible]
 NO. OF OBSERVATIONS                 211
 NO. OF COEFFICIENTS                   6
 RESIDUAL DEGREES OF FREEDOM         205
 RESIDUAL ROOT MEAN SQUARE           [illegible]
 RESIDUAL MEAN SQUARE                [illegible]
 RESIDUAL SUM OF SQUARES             [illegible]
```

TUI January 1987 , Run 2, second creep.

```
                                                                          95%CONFIDENCE LIMITS
 IND VAR(I) NAME          COEF B(I)        S.E. COEF.       T-VALUE       LOWER             UPPER
        1              [illegible]       [illegible]      [illegible]   [illegible]       [illegible]
        2              [illegible]       [illegible]      [illegible]   [illegible]       [illegible]
        3              [illegible]       [illegible]      [illegible]   4.02E-01          [illegible]
        4              6.4063[illegible] [illegible]      [illegible]   2.36E+01          1.05E+02
        5              3.0205[illegible] [illegible]      [illegible]   2.21E+00          3.83E+00
        6              [illegible]       [illegible]      [illegible]   1.14E+00          [illegible]
        7              1.3482[illegible] [illegible]      1.8           -8.94E+00         [illegible]
        8              2.79697E+02       [illegible]      107.[illegible] 2.75E+02        2.85E+02
 NO. OF OBSERVATIONS                 211
 NO. OF COEFFICIENTS                   8
 RESIDUAL DEGREES OF FREEDOM         203
 RESIDUAL ROOT MEAN SQUARE             3.270[illegible]
 RESIDUAL MEAN SQUARE                 10.6974[illegible]
 RESIDUAL SUM OF SQUARES            2171.5874[illegible]
```

TUI January 1987, Run 4, first creep.

```
                                                                          95%CONFIDENCE LIMITS
 IND VAR(I) NAME          COEF B(I)        S.E. COEF.       T-VALUE       LOWER             UPPER
        1              1.13[illegible]   1.79E+00         6.[illegible] 7.[illegible]E+00 1.49E+01
        2              2.13[illegible]   [illegible]      [illegible]   -1.[illegible]E+00 5.43E+00
        3              [illegible]       [illegible]      [illegible]   [illegible]       [illegible]
        4              2.02[illegible]   [illegible]E-01  [illegible]   [illegible]       7.49E+00
        5              1.32542E+01       [illegible]      [illegible]   3.33E+00          2.32E+01
        6              7.45245E+02       [illegible]      94.8          7.30E+02          7.61E+02
 NO. OF OBSERVATIONS                 211
 NO. OF COEFFICIENTS                   6
 RESIDUAL DEGREES OF FREEDOM         205
 RESIDUAL ROOT MEAN SQUARE             1.79[illegible]
 RESIDUAL MEAN SQUARE                [illegible]
 RESIDUAL SUM OF SQUARES             661.00014844
```

TUI January 1987, Run 4, second creep.

```
                                                                  95%CONFIDENCE LIMITS
IND VAR(I) NAME          COEF B(I)       S.E COEF.     T-VALUE    LOWER           UPPER
     1                 2.70494E+01       6.25E-01        43.3     2.58E+01        2.83E+01
     2                 7.15278E+01       1.41E+00        50.9     6.88E+01        7.43E+01
     3                 3.32311E-01       7.99E-03        41.6     3.17E-01        3.48E-01
     4                 1.43999E+02       1.40E+00       103.0     1.41E+02        1.47E+02
     5                 1.58438E+00       4.06E-02        39.0     1.50E+00        1.66E+00
     6                 3.45343E+01       3.62E+00         9.5     2.74E+01        4.16E+01
     7                 3.14777E+02       2.00E+01        15.7     2.76E+02        3.54E+02
     8                 1.64950E+03       2.33E+02         7.1     1.19E+03        2.11E+03
NO. OF OBSERVATIONS                  211
NO. OF COEFFICIENTS                    8
RESIDUAL DEGREES OF FREEDOM          203
RESIDUAL ROOT MEAN SQUARE              1.69289565
RESIDUAL MEAN SQUARE                   2.86589622
RESIDUAL SUM OF SQUARES              581.77697754
```

TUI October 1987, Run 1, first creep.

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                                                                  95%CONFIDENCE LIMITS
IND.VAR(I) NAME          COEF.B(I)       S.E.COEF.     T-VALUE    LOWER           UPPER
     1                 1.08152E+01       1.25E+00         8.7     8.37E+00        1.33E+01
     2                 2.99800E+00       1.21E+00         2.5     6.25E-01        5.37E+00
     3                 1.86629E+00       1.79E+00         1.1    -1.62E+00        5.40E+00
     4                 6.13905E+00       4.12E-01        14.9     5.33E+00        6.95E+00
     5                 1.96974E+02       3.49E+01         5.6     1.29E+02        2.65E+02
     6                 1.11667E+03       2.09E+01        53.4     1.08E+03        1.16E+03
NO. OF OBSERVATIONS                  211
NO. OF COEFFICIENTS                    6
RESIDUAL DEGREES OF FREEDOM          205
RESIDUAL ROOT MEAN SQUARE              1.57347894
RESIDUAL MEAN SQUARE                   2.47583628
RESIDUAL SUM OF SQUARES              507.54644775
```

TUI October 1987, Run 1, second creep.

```
                                                                  95%CONFIDENCE LIMITS
IND.VAR(I) NAME          COEF.B(I)       S.E.COEF.     T-VALUE    LOWER           UPPER
     1                 2.99844E+01       6.98E-01        43.0     2.86E+01        3.14E+01
     2                 7.07561E+01       1.30E+00        54.3     6.82E+01        7.33E+01
     3                 3.55065E-01       9.77E-03        36.3     3.36E-01        3.74E-01
     4                 1.19453E+02       1.32E+00        90.6     1.17E+02        1.22E+02
     5                 2.67071E+00       8.23E-02        32.5     2.51E+00        2.83E+00
     6                 8.48220E+01       1.79E+00        47.3     8.13E+01        8.83E+01
     7                 7.96248E+01       3.14E+00        25.3     7.35E+01        8.58E+01
     8                 1.64869E+03       1.54E+02        10.7     1.35E+03        1.95E+03
NO. OF OBSERVATIONS                  211
NO. OF COEFFICIENTS                    8
RESIDUAL DEGREES OF FREEDOM          203
RESIDUAL ROOT MEAN SQUARE              1.97089458
RESIDUAL MEAN SQUARE                   3.88442612
RESIDUAL SUM OF SQUARES              788.53857422
```

TUI October 1987, Run 3, first creep.

```
                                                                  95%CONFIDENCE LIMITS
IND.VAR(I) NAME          COEF.B(I)       S.E.COEF.     T-VALUE    LOWER           UPPER
     1                 1.09997E+01       1.85E+00         6.0     7.38E+00        1.46E+01
     2                 4.43220E+00       1.82E+00         2.4     8.72E-01        7.99E+00
     3                 9.63254E-01       8.63E-01         1.1    -7.28E-01        2.65E+00
     4                 1.01258E+01       8.62E-01        11.7     8.44E+00        1.18E+01
     5                 3.53509E+02       4.38E+01         8.1     2.68E+02        4.39E+02
     6                 1.27790E+03       4.84E+01        26.4     1.18E+03        1.37E+03
NO. OF OBSERVATIONS                  211
NO. OF COEFFICIENTS                    6
RESIDUAL DEGREES OF FREEDOM          205
RESIDUAL ROOT MEAN SQUARE              1.87159586
RESIDUAL MEAN SQUARE                   3.50287151
RESIDUAL SUM OF SQUARES              718.08874512
```

TUI October 1987, Run 3, second creep.

```
IND VAR(I) NAME        COEF B(I)      S.E. COEF.    T-VALUE   95% CONFIDENCE LIMITS
                                                               LOWER        UPPER
     1                 [illegible]    [illegible]   [illegible] [illegible] 3.[illegible]E+01
     2                 [illegible]    [illegible]   [illegible] [illegible] [illegible]
     3                 [illegible]    [illegible]   [illegible] [illegible] [illegible]4E-01
     4                 [illegible]    [illegible]   [illegible] [illegible] 1.27E+02
     5                 [illegible]    [illegible]   [illegible] [illegible] [illegible]E+00
     6                 [illegible]    [illegible]   [illegible] [illegible] [illegible]E+01
     7                 [illegible]    [illegible]   [illegible] [illegible] [illegible]E+01
     8                 [illegible]    [illegible]   [illegible] [illegible] [illegible]E+02
NO. OF OBSERVATIONS                 [illegible]
NO. OF COEFFICIENTS                   [illegible]
RESIDUAL DEGREES OF FREEDOM         183
RESIDUAL ROOT MEAN SQUARE             [illegible]
RESIDUAL MEAN SQUARE                  [illegible]
RESIDUAL SUM OF SQUARES           1304.[illegible]
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TUI March 1987, 5 hours.

```
IND. VAR(I) NAME       COEF B(I)      S.E. COEF.    T-VALUE   95% CONFIDENCE LIMITS
                                                               LOWER        UPPER
     1                 [illegible]    [illegible]   [illegible] [illegible] [illegible]E+01
     2                 [illegible]    [illegible]   [illegible] [illegible] [illegible]E+01
     3                 [illegible]    [illegible]   [illegible] [illegible] [illegible]E+01
     4                 [illegible]    [illegible]   [illegible] [illegible] [illegible]E+02
     5                 [illegible]    [illegible]   [illegible] [illegible] [illegible]E+00
     6                 [illegible]    [illegible]   [illegible] [illegible] [illegible]E+01
     7                 [illegible]    [illegible]   [illegible] [illegible] [illegible]E+01
     8                 [illegible]    [illegible]   [illegible] [illegible] [illegible]E+02
NO. OF OBSERVATIONS                 [illegible]
NO. OF COEFFICIENTS                   [illegible]
RESIDUAL DEGREES OF FREEDOM         [illegible]
RESIDUAL ROOT MEAN SQUARE             [illegible]
```

TUI March 1987, 8 hours.

```
IND. VAR(I) NAME       COEF B(I)      S.E. COEF.    T-VALUE   95% CONFIDENCE LIMITS
                                                               LOWER        UPPER
     1                 [illegible]    [illegible]   [illegible] [illegible]E+00 [illegible]E+01
     2                 [illegible]    [illegible]   [illegible] [illegible]E+01 [illegible]E+02
     3                 [illegible]    [illegible]   [illegible] [illegible]E-01 [illegible]E-01
     4                 [illegible]    [illegible]   [illegible] [illegible]E+01 [illegible]E+02
     5                 [illegible]    [illegible]   [illegible] [illegible]E+01 [illegible]E+02
     6                 [illegible]    [illegible]   [illegible] [illegible]E+00 1.83E+02
     7                 [illegible]    [illegible]   [illegible] [illegible]E+01 [illegible]E+02
     8                 [illegible]    [illegible]   [illegible] [illegible]E+02 1.[illegible]E+02
NO. OF OBSERVATIONS                 211
NO. OF COEFFICIENTS                   8
RESIDUAL DEGREES OF FREEDOM         [illegible]
RESIDUAL ROOT MEAN SQUARE            [illegible].472[illegible]
RESIDUAL MEAN SQUARE               [illegible]
RESIDUAL SUM OF SQUARES          [illegible]
```

TUI March 1987, 19 hours.

```
                                                                      95%CONFIDENCE LIMITS
 IND. VAR(I) NAME            COEF B(I)       S. E. COEF.    T-VALUE    LOWER               UPPER
      1                     3. 95927E+01      6. 97E-01      56. 8     3. 82E+01       4. 10E+01
      2                     8. 56329E+01      1. 67E+00      51. 1     8. 24E+01       8. 89E+01
      3                     3. 29556E-01      7. 59E-03      43. 4     3. 15E-01       3. 44E-01
      4                     1. 05191E+02      2. 75E+00      38. 3     9. 98E+01       1. 11E+02
      5                     3. 05425E+00      1. 31E-01      23. 2     2. 80E+00       3. 31E+00
      6                     8. 32066E+01      3. 04E+00      27. 4     7. 73E+01       8. 92E+01
      7                     2. 65337E+01      2. 25E+00      11. 8     2. 21E+01       3. 09E+01
      8                     4. 81692E+02      6. 64E+00      72. 6     4. 69E+02       4. 95E+02
 NO.  OF OBSERVATIONS                      211
 NO.  OF COEFFICIENTS                        8
 RESIDUAL DEGREES OF FREEDOM               203
 RESIDUAL ROOT MEAN SQUARE                   2. 05271339
 RESIDUAL MEAN SQUARE                        4. 21363258
 RESIDUAL SUM OF SQUARES                   855. 36755371
```

TUI Febuary 1987, Run 1, first creep.

```
                                                                      95%CONFIDENCE LIMITS
 IND. VAR(I) NAME            COEF. B(I)      S. E. COEF.    T-VALUE    LOWER               UPPER
      1                     1. 04409E+01      3. 08E-01      33. 9     9. 84E+00       1. 10E+01
      2                     4. 53621E+00      3. 40E-01      13. 4     3. 87E+00       5. 20E+00
      3                     7. 56840E+00      1. 47E+00       5. 2     4. 69E+00       1. 04E+01
      4                     1. 50795E+01      4. 57E-01      33. 0     1. 42E+01       1. 60E+01
      5                     2. 21693E+02      1. 35E+01      16. 4     1. 95E+02       2. 48E+02
      6                     7. 99212E+02      1. 02E+01      78. 1     7. 79E+02       8. 19E+02
 NO.  OF OBSERVATIONS                      211
 NO.  OF COEFFICIENTS                        6
 RESIDUAL DEGREES OF FREEDOM               205
 RESIDUAL ROOT MEAN SQUARE                   1. 04119229
 RESIDUAL MEAN SQUARE                        1. 08408165
 RESIDUAL SUM OF SQUARES                   222. 23675537
```

TUI Febuary 1987, Run 1, second creep.

```
                                                                      95%CONFIDENCE LIMITS
 IND. VAR(I) NAME            COEF B(I)       S. E. COEF.    T-VALUE    LOWER               UPPER
      1                     4. 56273E+01      7. 89E-01      57. 8     4. 41E+01       4. 72E+01
      2                     1. 03157E+02      1. 66E+00      62. 0     9. 99E+01       1. 06E+02
      3                     2. 81073E-01      6. 13E-03      45. 9     2. 69E-01       2. 93E-01
      4                     1. 65443E+02      1. 63E+00     101. 8     1. 62E+02       1. 69E+02
      5                     2. 05082E+00      5. 68E-02      36. 1     1. 94E+00       2. 16E+00
      6                     9. 18059E+01      5. 08E+00      18. 1     8. 18E+01       1. 02E+02
      7                     1. 17479E+02      4. 66E+00      25. 2     1. 08E+02       1. 27E+02
      8                     2. 60080E+02      8. 34E+00      31. 2     2. 44E+02       2. 76E+02
 NO.  OF OBSERVATIONS                      211
 NO.  OF COEFFICIENTS                        8
 RESIDUAL DEGREES OF FREEDOM               203
 RESIDUAL ROOT MEAN SQUARE                   2. 36986780
 RESIDUAL MEAN SQUARE                        5. 61627388
 RESIDUAL SUM OF SQUARES                  1140. 10375977
```

TUI Febuary 1987, Run 2, first creep.

```
                                                                95%CONFIDENCE LIMITS
IND VAR(I) NAME          COEF B(I)      S.E.COEF.    T-VALUE    LOWER           UPPER
     1                 1.50115E+02     3.36E+00       44.7      1.44E+02       1.57E+02
     2                 3.67818E+02     8.59E+00       42.8      3.51E+02       3.85E+02
     3                 6.68239E-02     1.68E-03       39.8      6.35E-02       7.01E-02
     4                 6.40193E+02     9.29E+00       68.9      6.22E+02       6.58E+02
     5                 3.69139E-01     1.32E-02       27.9      3.43E-01       3.95E-01
     6                 2.63628E+02     9.17E+00       28.7      2.46E+02       2.82E+02
     7                 8.28329E+00     7.39E-01       11.2      6.83E+00       9.73E+00
     8                 9.08844E+01     1.03E+00       88.0      8.89E+01       9.29E+01
NO. OF OBSERVATIONS                211
NO. OF COEFFICIENTS                  8
RESIDUAL DEGREES OF FREEDOM        203
RESIDUAL ROOT MEAN SQUARE            9.17903519
RESIDUAL MEAN SQUARE                84.25469971
RESIDUAL SUM OF SQUARES          17103.70703125
```

Reworked TUI Febuary 1987, Run 1, first creep.

```
                                                                95%CONFIDENCE LIMITS
IND.VAR(I) NAME          COEF.B(I)      S.E.COEF.    T-VALUE    LOWER           UPPER
     1                 6.17946E+01     1.04E+00       59.5      5.98E+01       6.38E+01
     2                 4.67126E+01     2.41E+00       19.4      4.20E+01       5.14E+01
     3                 6.82152E+00     8.18E-01        8.3      5.22E+00       8.43E+00
     4                 6.93975E+02     8.35E+02        0.8     -9.43E+02       2.33E+03
     5                 7.44890E+01     3.36E+01        2.2      8.58E+00       1.40E+02
     6                 1.97051E+03     2.36E+04        0.1     -4.43E+04       4.82E+04
NO. OF OBSERVATIONS                211
NO. OF COEFFICIENTS                  6
RESIDUAL DEGREES OF FREEDOM        205
RESIDUAL ROOT MEAN SQUARE            7.98600578
RESIDUAL MEAN SQUARE                63.77629089
RESIDUAL SUM OF SQUARES          13074.14062500
```

Reworked TUI Febuary 1987, Run 1, second creep.

```
                                                                95%CONFIDENCE LIMITS
IND.VAR(I) NAME          COEF.B(I)      S.E.COEF.    T-VALUE    LOWER           UPPER
     1                 1.26308E+02     1.62E+01        7.8      9.46E+01       1.58E+02
     2                 2.23819E+02     3.68E+01        6.1      1.52E+02       2.96E+02
     3                 7.38555E-02     1.41E-02        5.2      4.63E-02       1.01E-01
     4                 5.13066E+02     3.84E+01       13.3      4.38E+02       5.88E+02
     5                 2.71530E-01     5.19E-02        5.2      1.70E-01       3.73E-01
     6                 4.59492E+02     3.94E+01       11.7      3.82E+02       5.37E+02
     7                 2.61653E+00     5.28E-01        5.0      1.58E+00       3.65E+00
     8                 8.03423E+01     2.54E+00       31.6      7.54E+01       8.53E+01
NO. OF OBSERVATIONS                211
NO. OF COEFFICIENTS                  8
RESIDUAL DEGREES OF FREEDOM        203
RESIDUAL ROOT MEAN SQUARE           35.25579834
RESIDUAL MEAN SQUARE              1242.97143555
RESIDUAL SUM OF SQUARES         252323.21875000
```

Reworked TUI Febuary 1987, Run 3, first creep.

```
                                                                95%CONFIDENCE LIMITS
IND.VAR(I) NAME          COEF.B(I)      S.E.COEF.    T-VALUE    LOWER           UPPER
     1                 5.67057E+01     4.69E-01      120.8      5.58E+01       5.76E+01
     2                 3.17245E+01     7.63E-01       41.6      3.02E+01       3.32E+01
     3                 3.06080E+00     1.87E-01       16.3      2.69E+00       3.43E+00
     4                 9.04362E+01     1.17E+00       77.1      8.81E+01       9.27E+01
     5                 4.17312E+01     1.22E+00       34.1      3.93E+01       4.41E+01
     6                 2.36006E+02     2.23E+00      105.7      2.32E+02       2.40E+02
NO. OF OBSERVATIONS                211
NO. OF COEFFICIENTS                  6
RESIDUAL DEGREES OF FREEDOM        205
RESIDUAL ROOT MEAN SQUARE            2.37807369
RESIDUAL MEAN SQUARE                 5.65523529
RESIDUAL SUM OF SQUARES           1159.32324219
```

Reworked TUI Febuary 1987, Run 3, second creep.

```
                                                                        95%CONFIDENCE LIMITS
   IND. VAR(I) NAME            COEF. B(I)       S.E. COEF.      T-VALUE    LOWER              UPPER
        1                    6.01376E+01       2.59E+00         23.2       5.51E+01        6.52E+01
        2                    1.10280E+02       5.94E+00         18.6       9.86E+01        1.22E+02
        3                    2.08442E-01       1.34E-02         15.5       1.82E-01        2.35E-01
        4                    1.72972E+02       6.18E+00         28.0       1.61E+02        1.85E+02
        5                    1.33503E+00       1.25E-01         10.7       1.09E+00        1.58E+00
        6                    1.51908E+02       5.50E+00         27.6       1.41E+02        1.63E+02
        7                    1.69402E+01       1.69E+00         10.0       1.36E+01        2.03E+01
        8                    2.59611E+02       6.72E+00         38.6       2.46E+02        2.73E+02
   NO. OF OBSERVATIONS                   211
   NO. OF COEFFICIENTS                     8
   RESIDUAL DEGREES OF FREEDOM           203
   RESIDUAL ROOT MEAN SQUARE               6.87765980
   RESIDUAL MEAN SQUARE                   47.30220795
   RESIDUAL SUM OF SQUARES              9602.34960937
```

TT October 1985, Run 3.

```
                                                                        95%CONFIDENCE LIMITS
   IND. VAR(I) NAME            COEF. B(I)       S.E. COEF.      T-VALUE    LOWER              UPPER
        1                    6.52552E+01       1.14E+00         57.1       6.30E+01        6.75E+01
        2                    8.85861E+01       2.50E+00         35.5       8.37E+01        9.35E+01
        3                    2.00961E-01       6.92E-03         29.1       1.87E-01        2.15E-01
        4                    1.76538E+02       2.52E+00         70.2       1.72E+02        1.81E+02
        5                    9.01781E-01       3.45E-02         26.2       8.34E-01        9.69E-01
        6                    1.54889E+02       2.21E+00         70.1       1.51E+02        1.59E+02
        7                    1.10584E+01       4.12E-01         26.9       1.03E+01        1.19E+01
        8                    2.96563E+02       2.83E+00        104.6       2.91E+02        3.02E+02
   NO. OF OBSERVATIONS                   211
   NO. OF COEFFICIENTS                     8
   RESIDUAL DEGREES OF FREEDOM           203
   RESIDUAL ROOT MEAN SQUARE               2.61723757
   RESIDUAL MEAN SQUARE                    6.84993362
   RESIDUAL SUM OF SQUARES              1390.53662109
```

TT October 1985, Run 4.

```
                                                                        95%CONFIDENCE LIMITS
   IND. VAR(I) NAME            COEF. B(I)       S.E. COEF.      T-VALUE    LOWER              UPPER
        1                    1.03189E+02       2.22E+00         46.5       9.88E+01        1.08E+02
        2                    5.19720E+01       8.09E+00          6.4       3.61E+01        6.78E+01
        3                    3.74772E-01       4.13E-02          9.1       2.94E-01        4.56E-01
        4                    1.45536E+02       1.07E+01         13.7       1.25E+02        1.66E+02
        5                    9.46600E-01       1.22E-01          7.8       7.08E-01        1.19E+00
        6                    1.31466E+02       1.38E+01          9.5       1.04E+02        1.58E+02
        7                    5.34103E+00       1.06E+00          5.1       3.27E+00        7.41E+00
        8                    3.98989E+02       8.33E+00         47.9       3.83E+02        4.15E+02
   NO. OF OBSERVATIONS                   211
   NO. OF COEFFICIENTS                     8
   RESIDUAL DEGREES OF FREEDOM           203
   RESIDUAL ROOT MEAN SQUARE               5.17679405
   RESIDUAL MEAN SQUARE                   26.79920578
   RESIDUAL SUM OF SQUARES              5440.23925781
```

X TT January 1986, Run 3.

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                                                                        95%CONFIDENCE LIMITS
   IND. VAR(I) NAME            COEF. B(I)       S.E. COEF.      T-VALUE    LOWER              UPPER
        1                    4.14027E+01       4.87E+00          8.5       3.19E+01        5.09E+01
        2                    4.73174E+01       7.26E+00          6.5       3.31E+01        6.15E+01
        3                    3.36683E-01       9.27E-02          3.6       1.55E-01        5.18E-01
        4                    1.43751E+02       7.37E+00         19.5       1.29E+02        1.58E+02
        5                    1.28253E+00       1.84E-01          7.0       9.21E-01        1.64E+00
        6                    1.93627E+ 2       5.96E+00         32.5       1.82E+02        2.05E+02
        7                    1.96044E+01       1.67E+00         11.7       1.63E+01        2.29E+01
        8                    5.69015E+02       6.05E+01          9.4       4.50E+02        6.88E+02
   NO. OF OBSERVATIONS                   211
   NO. OF COEFFICIENTS                     8
   RESIDUAL DEGREES OF FREEDOM           203
   RESIDUAL ROOT MEAN SQUARE              10.73168182
   RESIDUAL MEAN SQUARE                  115.16900635
   RESIDUAL SUM OF SQUARES             23379.30859375
```

X TT January 1986, Run 4.

```
                                                                      95%CONFIDENCE LIMITS
IND VAR(I) NAME           COEF B(I)      S.E.COEF     T-VALUE    LOWER           UPPER
     1                 2.86031E+00       1.15E+01       0.2      -1.97E+01      2.54E+01
     2                 1.20116E+02       1.13E+01      10.6       9.80E+01      1.42E+02
     3                 1.10456E-02       1.98E-03       5.6       7.16E-03      1.49E-02
     4                 9.20515E+01       2.04E+00      45.1       8.81E+01      9.61E+01
     5                 8.73858E-01       2.90E-02      30.1       8.17E-01      9.31E-01
     6                 1.07871E+02       2.12E+00      50.9       1.04E+02      1.12E+02
     7                 8.19581E+00       4.21E-01      19.5       7.37E+00      9.02E+00
     8                 2.46359E+02       1.89E+00     131.1       2.45E+02      2.52E+02
NO. OF OBSERVATIONS                  215
NO. OF COEFFICIENTS                    8
RESIDUAL DEGREES OF FREEDOM          207
RESIDUAL ROOT MEAN SQUARE              2.99101162
RESIDUAL MEAN SQUARE                   8.94615173
RESIDUAL SUM OF SQUARES             1851.85351562
```

Y TT January 1986, Run 1.

```
                                                                      95%CONFIDENCE LIMITS
IND.VAR(I) NAME           COEF B(I)      S.E.COEF     T-VALUE    LOWER           UPPER
     1                 4.17273E+01       1.78E+00      23.5       3.82E+01      4.52E+01
     2                 7.02899E+01       5.63E+00      12.5       5.92E+01      8.13E+01
     3                 3.09934E-01       2.09E-02      14.9       2.69E-01      3.51E-01
     4                 8.96657E+01       2.58E+01       3.5       3.91E+01      1.40E+02
     5                 2.18419E+00       2.88E-01       7.6       1.62E+00      2.75E+00
     6                 6.64667E+01       2.92E+01       2.3       9.24E+00      1.24E+02
     7                 9.94326E+00       7.62E+00       1.3      -4.99E+00      2.49E+01
     8                 4.68233E+02       1.01E+01      46.4       4.48E+02      4.88E+02
NO. OF OBSERVATIONS                  211
NO. OF COEFFICIENTS                    8
RESIDUAL DEGREES OF FREEDOM          203
RESIDUAL ROOT MEAN SQUARE              4.51478833
RESIDUAL MEAN SQUARE                  20.38331664
RESIDUAL SUM OF SQUARES             4137.81347656
```

Y TT January 1986, Run 2.

```
                                                                      95%CONFIDENCE LIMITS
IND.VAR(I) NAME           COEF.B(I)      S.E.COEF     T-VALUE    LOWER           UPPER
     1                 4.60238E+01       9.28E+00       5.0       2.78E+01      6.42E+01
     2                 7.04903E+01       9.37E+00       7.5       5.21E+01      8.89E+01
     3                 1.69801E-01       5.75E-02       3.0       5.72E-02      2.82E-01
     4                 1.50810E+02       9.03E+00      16.7       1.33E+02      1.69E+02
     5                 1.48944E+00       2.41E-01       6.2       1.02E+00      1.96E+00
     6                 9.96333E+01       1.19E+01       8.4       7.63E+01      1.23E+02
     7                 5.25363E+01       1.40E+01       3.8       2.52E+01      7.99E+01
     8                 3.34572E+02       4.38E+01       7.6       2.49E+02      4.20E+02
NO. OF OBSERVATIONS                  211
NO. OF COEFFICIENTS                    8
RESIDUAL DEGREES OF FREEDOM          203
RESIDUAL ROOT MEAN SQUARE             17.80863190
RESIDUAL MEAN SQUARE                 317.14746094
RESIDUAL SUM OF SQUARES            64380.94531250
```

Z TT January 1986, Run 5.

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                                                                      95%CONFIDENCE LIMITS
IND.VAR(I) NAME           COEF.B(I)      S.E.COEF.    T-VALUE    LOWER           UPPER
     1                 5.32113E+01       9.89E-01      53.8       5.13E+01      5.52E+01
     2                 7.07836E+01       2.63E+00      26.9       6.56E+01      7.59E+01
     3                 3.05983E-01       1.16E-02      26.5       2.83E-01      3.29E-01
     4                 1.53233E+02       6.30E+00      24.3       1.41E+02      1.66E+02
     5                 1.36374E+00       5.66E-02      24.1       1.25E+00      1.47E+00
     6                 5.14381E+01       7.46E+00       6.9       3.68E+01      6.61E+01
     7                 1.89908E+01       5.14E+00       3.7       8.91E+00      2.91E+01
     8                 3.18109E+02       2.77E+00     114.7       3.13E+02      3.24E+02
NO. OF OBSERVATIONS                  211
NO. OF COEFFICIENTS                    8
RESIDUAL DEGREES OF FREEDOM          203
RESIDUAL ROOT MEAN SQUARE              2.51403332
RESIDUAL MEAN SQUARE                   6.32036400
RESIDUAL SUM OF SQUARES             1283.03393555
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Z TT January 1986, Run 6.

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                                                                       95%CONFIDENCE LIMITS
IND VAR(I) NAME              COEF. B(I)       S. E. COEF.     T-VALUE    LOWER              UPPER
     1                     5. 89165E+01       8. 13E-01        72. 5      5. 73E+01        6. 05E+01
     2                     7. 47377E+01       2. 00E+00        37. 4      7. 08E+01        7. 87E+01
     3                     4. 57624E-01       1. 47E-02        31. 2      4. 29E-01        4. 86E-01
     4                     1. 33421E+02       1. 94E+00        68. 7      1. 30E+02        1. 37E+02
     5                     2. 79173E+00       1. 14E-01        24. 5      2. 57E+00        3. 02E+00
     6                     8. 16180E+01       2. 95E+00        27. 7      7. 58E+01        8. 74E+01
     7                     9. 50848E+01       5. 47E+00        17. 4      8. 44E+01        1. 06E+02
     8                     6. 81591E+02       4. 14E+01        16. 5      6. 00E+02        7. 63E+02
NO. OF OBSERVATIONS                     211
NO. OF COEFFICIENTS                       8
RESIDUAL DEGREES OF FREEDOM             203
RESIDUAL ROOT MEAN SQUARE                  2. 60691738
RESIDUAL MEAN SQUARE                       6. 79601860
RESIDUAL SUM OF SQUARES                1379. 59179687
```

X TT April 1986, Run 1.

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                                                                       95%CONFIDENCE LIMITS
IND. VAR(I) NAME             COEF. B(I)       S. E. COEF.     T-VALUE    LOWER              UPPER
     1                     5. 50476E+01       1. 03E+00        53. 6      5. 30E+01        5. 71E+01
     2                     7. 00044E+01       2. 72E+00        25. 8      6. 47E+01        7. 53E+01
     3                     3. 57360E-01       1. 44E-02        24. 8      3. 29E-01        3. 86E-01
     4                     1. 24111E+02       2. 76E+00        45. 0      1. 19E+02        1. 30E+02
     5                     1. 87483E+00       1. 09E-01        17. 3      1. 66E+00        2. 09E+00
     6                     9. 36871E+01       2. 50E+00        37. 4      8. 88E+01        9. 86E+01
     7                     2. 54779E+01       1. 82E+00        14. 0      2. 19E+01        2. 90E+01
     8                     6. 54548E+02       1. 71E+01        38. 4      6. 21E+02        6. 88E+02
NO. OF OBSERVATIONS                     211
NO. OF COEFFICIENTS                       8
RESIDUAL DEGREES OF FREEDOM             203
RESIDUAL ROOT MEAN SQUARE                  2. 82856989
RESIDUAL MEAN SQUARE                       8. 00080872
RESIDUAL SUM OF SQUARES                1624. 16455078
```

X TT April 1986, Run 4.

```
                                                                       95%CONFIDENCE LIMITS
IND VAR(I) NAME              COEF. B(I)       S. E. COEF.     T-VALUE    LOWER              UPPER
     1                     5. 21560E+01       1. 45E+00        35. 9      4. 93E+01        5. 50E+01
     2                     5. 41768E+01       2. 83E+00        19. 1      4. 86E+01        5. 97E+01
     3                     3. 08496E-01       2. 20E-02        14. 0      2. 65E-01        3. 52E-01
     4                     1. 36108E+02       2. 92E+00        46. 6      1. 30E+02        1. 42E+02
     5                     1. 15601E+00       6. 64E-02        17. 4      1. 03E+00        1. 29E+00
     6                     1. 26465E+02       2. 56E+00        49. 5      1. 21E+02        1. 31E+02
     7                     1. 40656E+01       7. 57E-01        18. 6      1. 26E+01        1. 55E+01
     8                     4. 02270E+02       6. 50E+00        61. 9      3. 90E+02        4. 15E+02
NO. OF OBSERVATIONS                     211
NO. OF COEFFICIENTS                       8
RESIDUAL DEGREES OF FREEDOM             203
RESIDUAL ROOT MEAN SQUARE                  3. 22405338
RESIDUAL MEAN SQUARE                      10. 39451981
RESIDUAL SUM OF SQUARES                2110. 08789062
```

Y TT April 1986, Run 2.

```
                                                                       95%CONFIDENCE LIMITS
IND. VAR(I) NAME             COEF. B(I)       S. E. COEF.     T-VALUE    LOWER              UPPER
     1                     6. 03104E+01       1. 15E+00        52. 5      5. 81E+01        6. 26E+01
     2                     9. 50926E+01       2. 80E+00        33. 9      8. 96E+01        1. 01E+02
     3                     3. 66869E-01       1. 31E-02        28. 0      3. 41E-01        3. 93E-01
     4                     1. 42096E+02       2. 71E+00        52. 4      1. 37E+02        1. 47E+02
     5                     2. 68408E+00       1. 44E-01        18. 7      2. 40E+00        2. 97E+00
     6                     6. 49172E+01       6. 96E+00         9. 3      5. 13E+01        7. 86E+01
     7                     1. 55211E+02       1. 50E+01        10. 4      1. 26E+02        1. 85E+02
     8                     8. 68380E+02       1. 34E+02         6. 5      6. 05E+02        1. 13E+03
NO  OF OBSERVATIONS                     211
NO. OF COEFFICIENTS                       8
RESIDUAL DEGREES OF FREEDOM             203
RESIDUAL ROOT MEAN SQUARE                  3. 71556139
RESIDUAL MEAN SQUARE                      13. 80539703
RESIDUAL SUM OF SQUARES                2802. 49560547
```

Y TT April 1986, Run 5.

```
                                                                       95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)      S. E. COEF.    T-VALUE    LOWER             UPPER
      1                  4. 71640E+01      1. 99E+00       23. 7     4. 33E+01       5. 11E+01
      2                  6. 47242E+01      3. 59E+00       18. 0     5. 77E+01       7. 18E+01
      3                  2. 05898E-01      1. 65E-02       12. 5     1. 74E-01       2. 38E-01
      4                  1. 34218E+02      5. 11E+00       26. 3     1. 24E+02       1. 44E+02
      5                  9. 15058E-01      6. 66E-02       13. 7     7. 85E-01       1. 05E+00
      6                  7. 22374E+01      6. 10E+00       11. 8     6. 03E+01       8. 42E+01
      7                  1. 13327E+01      2. 03E+00        5. 6     7. 36E+00       1. 53E+01
      8                  5. 30579E+02      1. 12E+01       47. 5     5. 09E+02       5. 52E+02
NO.  OF OBSERVATIONS                    211
NO.  OF COEFFICIENTS                      8
RESIDUAL DEGREES OF FREEDOM             203
RESIDUAL ROOT MEAN SQUARE                 3. 85669756
RESIDUAL MEAN SQUARE                     14. 87411690
RESIDUAL SUM OF SQUARES                3019. 44580078
```

Z TT April 1986, Run 3.

```
                                                                       95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)      S. E. COEF.    T-VALUE    LOWER             UPPER
      1                  5. 85127E+01      1. 03E+00       56. 9     5. 65E+01       6. 05E+01
      2                  9. 12529E+01      2. 37E+00       38. 4     8. 66E+01       9. 59E+01
      3                  2. 39959E-01      7. 36E-03       32. 6     2. 26E-01       2. 54E-01
      4                  1. 35047E+02      2. 35E+00       57. 6     1. 30E+02       1. 40E+02
      5                  1. 54773E+00      7. 34E-02       21. 1     1. 40E+00       1. 69E+00
      6                  8. 78426E+01      1. 83E+00       48. 0     8. 43E+01       9. 14E+01
      7                  3. 11543E+01      1. 86E+00       16. 7     2. 75E+01       3. 48E+01
      8                  8. 57001E+02      2. 89E+01       29. 7     8. 00E+02       9. 14E+02
NO.  OF OBSERVATIONS                    211
NO.  OF COEFFICIENTS                      8
RESIDUAL DEGREES OF FREEDOM             203
RESIDUAL ROOT MEAN SQUARE                 2. 65562773
RESIDUAL MEAN SQUARE                      7. 05235863
RESIDUAL SUM OF SQUARES                1431. 62890625
```

Z TT April 1986, Run 6.

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                                                                      95%CONFIDENCE LIMITS
IND.VAR(I) NAME          COEF.B(I)       S.E.COEF.      T-VALUE      LOWER              UPPER
     1                 2.43672E+01       6.06E-01        40.3       2.32E+01          2.56E+01
     2                 4.84712E+01       1.25E+00        38.7       4.60E+01          5.09E+01
     3                 4.89548E-01       1.69E-02        29.0       4.56E-01          5.23E-01
     4                 8.81483E+01       1.24E+00        71.3       8.57E+01          9.06E+01
     5                 2.93487E+00       1.15E-01        25.6       2.71E+00          3.16E+00
     6                 2.75722E+01       1.10E+00        25.1       2.54E+01          2.97E+01
     7                 1.82816E+02       1.83E+01        10.0       1.47E+02          2.19E+02
     8                 8.80248E+02       2.77E+01        31.8       8.26E+02          9.34E+02
NO.  OF  OBSERVATIONS                211.
NO.  OF  COEFFICIENTS                  8
RESIDUAL  DEGREES  OF  FREEDOM       203
RESIDUAL  ROOT  MEAN  SQUARE           1.64789295
RESIDUAL  MEAN  SQUARE                 2.71555138
RESIDUAL  SUM  OF  SQUARES           551.25695801
```

TT January 1987, Run 1, first creep.

```
                                                                      95%CONFIDENCE LIMITS
IND.VAR(I) NAME          COEF.B(I)       S.E.COEF       T-VALUE      LOWER              UPPER
     1                 3.29167E+01       2.88E+00        11.4       2.73E+01          3.86E+01
     2                 5.23756E+01       6.87E+00         7.6       3.89E+01          6.58E+01
     3                 6.06926E-01       9.66E-02         6.3       4.17E-01          7.97E-01
     4                 9.67209E+01       6.69E+00        14.4       8.36E+01          1.10E+02
     5                 3.58595E+00       6.94E-01         5.2       2.23E+00          4.95E+00
     6                 7.94097E+01       8.83E+00         9.0       6.21E+01          9.67E+01
     7                 8.96333E+01       1.79E+01         5.0       5.45E+01          1.25E+02
     8                 1.95288E+03       1.05E+03         1.9      -1.09E+02          4.01E+03
NO.  OF  OBSERVATIONS                211
NO.  OF  COEFFICIENTS                  8
RESIDUAL  DEGREES  OF  FREEDOM       203
RESIDUAL  ROOT  MEAN  SQUARE           8.97160748
RESIDUAL  MEAN  SQUARE                80.49334717
RESIDUAL  SUM  OF  SQUARES         16340.15039022
```

TT January 1987, Run 2, first creep.

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                                                                      95%CONFIDENCE LIMITS
IND.VAR(I) NAME          COEF.B(I)       S.E.COEF.      T-VALUE      LOWER              UPPER
     1                 1.86776E+01       2.21E-01        84.7       1.82E+01          1.91E+01
     2                 1.29809E+01       1.08E+00        12.0       1.09E+01          1.51E+01
     3                 3.74934E+01       3.70E+00        10.1       3.02E+01          4.47E+01
     4                 9.94048E+00       2.52E+00         3.9       5.00E+00          1.49E+01
     5                 8.67968E+02       3.01E+02         2.9       2.77E+02          1.46E+03
     6                 1.30478E+03       1.24E+02        10.6       1.06E+03          1.55E+03
NO.  OF  OBSERVATIONS                211
NO.  OF  COEFFICIENTS                  6
RESIDUAL  DEGREES  OF  FREEDOM       205
RESIDUAL  ROOT  MEAN  SQUARE           1.83546972
RESIDUAL  MEAN  SQUARE                 3.36894941
RESIDUAL  SUM  OF  SQUARES           690.63464355
```

TT January 1987, Run 2, second creep.

```
                                                                  95% CONFIDENCE LIMITS
IND VAR(I) NAME      COEF B(I)        S.E. COEF     T-VALUE     LOWER          UPPER
      1              [illegible]      [illegible]   [illegible] [illegible]    3.79E+01
      2              [illegible]      [illegible]   [illegible] [illegible]    3.94E+01
      3              1.01544E+01      [illegible]   [illegible] 9.09E-01       1.10E+00
      4              9.88360E+01      [illegible]   [illegible] 9.65E+01       1.01E+02
      5              5.21830E+00      1.59E-01      [illegible] 4.91E+00       5.53E+00
      6              6.12700E+01      1.80E+00      [illegible] 5.77E+01       6.49E+01
      7              9.46?26E+01      [illegible]   [illegible] 9.64E+01       1.03E+02
      8              9.06??0E+02      [illegible]   [illegible] [illegible]    1.00E+03
NO. OF OBSERVATIONS                211
NO. OF COEFFICIENTS                  8
RESIDUAL DEGREES OF FREEDOM        203
RESIDUAL ROOT MEAN SQUARE            1.[illegible]
RESIDUAL MEAN SQUARE                 2.[illegible]
RESIDUAL SUM OF SQUARES            549.[illegible]
```

TT April 1987, Run 1, first creep.

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                                                                  95% CONFIDENCE LIMITS
IND VAR(I) NAME      COEF B(I)        S.E. COEF     T-VALUE     LOWER          UPPER
      1              [illegible]      [illegible]   [illegible] [illegible]    [illegible]
      2              [illegible]      [illegible]   [illegible] [illegible]    [illegible]
      3              [illegible]      [illegible]   [illegible] [illegible]    [illegible]
      4              [illegible]      [illegible]   [illegible] [illegible]    7.38E+01
      5              [illegible]      [illegible]   [illegible] [illegible]    [illegible]
      6              [illegible]      [illegible]   [illegible] 7.7?E+01       8.30E+01
      7              [illegible]      [illegible]   [illegible] [illegible]    4.10E+01
      8              4.06959E+02      [illegible]   [illegible] [illegible]    4.16E+02
NO  OF OBSERVATIONS                211
NO. OF COEFFICIENTS                  8
RESIDUAL DEGREES OF FREEDOM        [illegible]
RESIDUAL ROOT MEAN SQUARE            [illegible]
RESIDUAL MEAN SQUARE                 [illegible]
RESIDUAL SUM OF SQUARES            [illegible]
```

TT April 1987, Run 4, first creep.

```
                                                                  95% CONFIDENCE LIMITS
IND VAR(I) NAME      COEF B(I)        S.E. COEF     T-VALUE     LOWER          UPPER
      1              2.46467E+01      [illegible]   [illegible] 2.43E+01       2.54E+01
      2              1.25531E+01      [illegible]   [illegible] [illegible]    1.78E+01
      3              2.12751E+01      [illegible]   [illegible] 1.64E+01       2.62E+01
      4              2.49835E+01      [illegible]   [illegible] 2.00E+01       2.99E+01
      5              7.21071E+01      [illegible]   [illegible] [illegible]    [illegible]
      6              6.91002E+02      1.21E+01      57.1        6.67E+02       7.15E+02
NO  OF OBSERVATIONS                211
NO. OF COEFFICIENTS                  6
RESIDUAL DEGREES OF FREEDOM        205
RESIDUAL ROOT MEAN SQUARE            1.[illegible]
RESIDUAL MEAN SQUARE                 3.[illegible]
RESIDUAL SUM OF SQUARES            [illegible]
```

TT April 1987, Run 4, second creep.

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                                                                   95%CONFIDENCE LIMITS
IND. VAR(I) NAME        COEF. B(I)      S. E. COEF.    T-VALUE     LOWER          UPPER
     1                  [illegible]     [illegible]    [illegible] [illegible]    [illegible]E+01
     2                  [illegible]     [illegible]    [illegible] [illegible]    [illegible]E+01
     3                  [illegible]     [illegible]    [illegible] [illegible]    [illegible]E-01
     4                  [illegible]     [illegible]    [illegible] 7.43E+01       [illegible]E+01
     5                  [illegible]     [illegible]    [illegible] 1.69E+00       [illegible]E+00
     6                  [illegible]     [illegible]    [illegible] 3.08E+01       4.12E+01
     7                  [illegible]     [illegible]    [illegible] 2.15E+01       4.13E+01
     8                  1.08[illegible]E+03 [illegible]E+01 [illegible] 1.04E+03  1.13E+03
NO.  OF OBSERVATIONS                211
NO.  OF COEFFICIENTS                  8
RESIDUAL DEGREES OF FREEDOM         203
RESIDUAL ROOT MEAN SQUARE             [illegible]
RESIDUAL MEAN SQUARE                  [illegible]
RESIDUAL SUM OF SQUARES             [illegible]
```

TT October 1987, Run 3, first creep.

```
                                                                   95%CONFIDENCE LIMITS
IND. VAR(I) NAME        COEF. B(I)      S. E. COEF.    T-VALUE     LOWER          UPPER
     1                  [illegible]     [illegible]    [illegible] [illegible]E+01 [illegible]E+01
     2                  [illegible]     [illegible]    [illegible] [illegible]E+00 [illegible]E+00
     3                  [illegible]     [illegible]    [illegible] [illegible]E-01 [illegible]E+00
     4                  [illegible]     [illegible]    [illegible] 1.37E+01       1.60E+01
     5                  [illegible]     [illegible]    [illegible] 1.46E+01       [illegible]E+01
     6                  [illegible]     [illegible]    [illegible] [illegible]E+02 [illegible]E+02
NO.  OF OBSERVATIONS                211
NO.  OF COEFFICIENTS                  [illegible]
RESIDUAL DEGREES OF FREEDOM         [illegible]
RESIDUAL ROOT MEAN SQUARE             [illegible]
RESIDUAL MEAN SQUARE                  [illegible]
RESIDUAL SUM OF SQUARES             [illegible]
```

TT October 1987, Run3, second creep.

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                                                                   95%CONFIDENCE LIMITS
IND. VAR(I) NAME        COEF. B(I)      S. E. COEF.    T-VALUE     LOWER          UPPER
     1                  3.59241E+01     7.92E-01       45.3        3.44E+01       3.75E+01
     2                  4.49459E+01     3.70E+00       12.2        3.77E+01       5.22E+01
     3                  5.38191E-01     2.48E-02       21.7        4.89E-01       5.87E-01
     4                  8.99151E+01     3.92E+00       22.9        8.22E+01       9.76E+01
     5                  1.76538E+00     1.63E-01       10.8        1.45E+00       2.09E+00
     6                  6.28332E+01     5.03E+00       12.5        5.30E+01       7.27E+01
     7                  1.37383E+01     2.13E+00        6.5        9.57E+00       1.79E+01
     8                  4.71945E+02     4.85E+00       97.4        4.62E+02       4.81E+02
NO.  OF OBSERVATIONS                211
NO.  OF COEFFICIENTS                  8
RESIDUAL DEGREES OF FREEDOM         203
RESIDUAL ROOT MEAN SQUARE             2.06633615
RESIDUAL MEAN SQUARE                  4.26974678
RESIDUAL SUM OF SQUARES             866.75878906
```

TT October 1987, Run 4, first creep.

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                                                                   95%CONFIDENCE LIMITS
IND. VAR(I) NAME        COEF. B(I)      S. E. COEF.    T-VALUE     LOWER          UPPER
     1                  [illegible]     [illegible]    16.6        8.76E+00       1.20E+01
     2                  [illegible]     [illegible]     9.4        6.62E+00       1.01E+01
     3                  [illegible]     [illegible]    [illegible] 7.15E-01       [illegible]E+00
     4                  [illegible]     [illegible]    [illegible] -6.07E-02      [illegible]E+00
     5                  [illegible]     [illegible]    [illegible] -6.15E+02      3.47E+03
     6                  6.64[illegible]E+02 6.[illegible]E+00 10[illegible].8 6.52E+02  6.77E+02
NO.  OF OBSERVATIONS                211
NO.  OF COEFFICIENTS                  [illegible]
RESIDUAL DEGREES OF FREEDOM         [illegible]
RESIDUAL ROOT MEAN SQUARE             [illegible]
RESIDUAL MEAN SQUARE                  [illegible]
RESIDUAL SUM OF SQUARES             [illegible]
```

TT October 1987, Run 4, second creep.

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                                                                 95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)      S. E. COEF     T-VALUE   LOWER              UPPER
       1                 3. 06397E+01    5. 48E-01       55. 9      2. 96E+01        3. 17E+01
       2                 4. 93303E+01    1. 38E+00       35. 6      4. 66E+01        5. 20E+01
       3                 6. 17983E-01    1. 97E-02       31. 4      5. 79E-01        6. 57E-01
       4                 9. 01961E+01    1. 45E+00       62. 3      8. 74E+01        9. 30E+01
       5                 3. 55295E+00    1. 48E-01       24. 0      3. 26E+00        3. 84E+00
       6                 4. 26827E+01    1. 29E+00       33. 2      4. 02E+01        4. 52E+01
       7                 8. 75054E+01    7. 62E+00       11. 5      7. 26E+01        1. 02E+02
       8                 1. 42779E+03    6. 04E+01       23. 6      1. 31E+03        1. 55E+03
NO.  OF OBSERVATIONS                  211
NO.  OF COEFFICIENTS                    8
RESIDUAL DEGREES OF FREEDOM           203
RESIDUAL ROOT MEAN SQUARE               1. 66655445
RESIDUAL MEAN SQUARE                    2. 77740383
RESIDUAL SUM OF SQUARES               563. 81298228
```

TT Febuary 1987, Run 1, first creep.

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                                                                 95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)      S. E. COEF     T-VALUE   LOWER              UPPER
       1                 8. 22409E-06    1. 47E-02        0. 0     -2. 87E-02        2. 88E-02
       2                 5. 62097E+00    8. 74E-01        6. 4      3. 91E+00        7. 33E+00
       3                 2. 39551E-01    1. 09E-01        2. 2      2. 50E-02        4. 54E-01
       4                 1. 35650E+00    8. 64E-01        1. 6     -3. 37E-01        3. 05E+00
       5                 1. 90891E+01    2. 89E+01        0. 7     -3. 76E+01        7. 58E+01
       6                 1. 29355E+03    2. 24E+01       57. 8      1. 25E+03        1. 34E+03
NO.  OF OBSERVATIONS                  211
NO.  OF COEFFICIENTS                    6
RESIDUAL DEGREES OF FREEDOM           205
RESIDUAL ROOT MEAN SQUARE               1. 77886534
RESIDUAL MEAN SQUARE                    3. 16436241
RESIDUAL SUM OF SQUARES               648. 69433594
```

TT Febuary 1987, Run 1, second creep.

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                                                                 95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)      S. E. COEF.    T-VALUE   LOWER              UPPER
       1                 3. 78851E+01    1. 24E+00       30. 7      3. 55E+01        4. 03E+01
       2                 3. 25718E+01    2. 25E+00       14. 5      2. 82E+01        3. 70E+01
       3                 4. 51045E-01    4. 51E-02       10. 0      3. 63E-01        5. 40E-01
       4                 1. 03142E+02    3. 11E+00       33. 2      9. 71E+01        1. 09E+02
       5                 1. 37654E+00    8. 30E-02       16. 6      1. 21E+00        1. 54E+00
       6                 8. 99199E+01    3. 60E+00       25. 0      8. 29E+01        9. 70E+01
       7                 1. 12943E+01    9. 94E-01       11. 4      9. 35E+00        1. 32E+01
       8                 3. 21240E+02    2. 83E+00      113. 5      3. 16E+02        3. 27E+02
NO.  OF OBSERVATIONS                  211
NO.  OF COEFFICIENTS                    8
RESIDUAL DEGREES OF FREEDOM           203
RESIDUAL ROOT MEAN SQUARE               2. 54443455
RESIDUAL MEAN SQUARE                    6. 47414875
RESIDUAL SUM OF SQUARES              1314. 25219727
```

TT Febuary 1987, Run 2, first creep.

```
                                                                 95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)      S. E. COEF.    T-VALUE   LOWER              UPPER
       1                 2. 91706E-05    5. 56E-01        0. 0     -1. 09E+00        1. 09E+00
       2                 9. 99542E+00    3. 22E+00        3. 1      3. 68E+00        1. 63E+01
       3                 1. 99853E-01    5. 24E-01        0. 4     -8. 28E-01        1. 23E+00
       4                 4. 99679E+01    5. 17E+00        9. 7      3. 99E+01        6. 01E+01
       5                 1. 00037E+01    3. 36E+00        3. 0      3. 41E+00        1. 66E+01
       6                 1. 00042E+03    2. 28E+02        4. 4      5. 54E+02        1. 45E+03
NO.  OF OBSERVATIONS                  211
NO.  OF COEFFICIENTS                    6
RESIDUAL DEGREES OF FREEDOM           205
RESIDUAL ROOT MEAN SQUARE              24. 87269974
RESIDUAL MEAN SQUARE                  618. 65136719
RESIDUAL SUM OF SQUARES            126823. 54687500
```

TT Febuary 1987, Run 2, second creep.

```
                                                                  95%CONFIDENCE LIMITS
IND VAR(I) NAME            COEF.B(I)      S.E.COEF.    T-VALUE    LOWER              UPPER
       1                   7.98606E+01    9.92E+00        8.0     6.04E+01         9.93E+01
       2                   1.40374E+02    9.78E+00       14.4     1.21E+02         1.60E+02
       3                   5.37337E-02    9.21E-03        5.8     3.57E-02         7.18E-02
       4                   3.86855E+02    2.50E+01       15.5     3.38E+02         4.36E+02
       5                   3.32629E-01    1.82E-02       18.3     2.97E-01         3.68E-01
       6                   3.23481E+02    2.75E+01       11.8     2.70E+02         3.77E+02
       7                   2.21141E+00    3.78E-01        5.9     1.47E+00         2.95E+00
       8                   8.12719E+01    9.47E-01       85.8     7.94E+01         8.31E+01
NO. OF OBSERVATIONS                      211
NO. OF COEFFICIENTS                        8
RESIDUAL DEGREES OF FREEDOM              203
RESIDUAL ROOT MEAN SQUARE                 14.24437141
RESIDUAL MEAN SQUARE                     202.90213013
RESIDUAL SUM OF SQUARES                41189.13281250
```

Reworked TT Febuary 1987, Run 1, first creep.

```
                                                                  95%CONFIDENCE LIMITS
IND.VAR(I) NAME            COEF.B(I)      S.E.COEF.    T-VALUE    LOWER              UPPER
       1                   2.22349E+01    3.78E+00        5.9     1.48E+01         2.97E+01
       2                   1.61277E+01    3.66E+00        4.4     8.96E+00         2.33E+01
       3                   4.01689E-01    2.12E-01        1.9    -1.42E-02         8.18E-01
       4                   4.10154E+01    1.43E+00       28.6     3.82E+01         4.38E+01
       5                   3.37205E+01    2.99E+00       11.3     2.79E+01         3.96E+01
       6                   2.22237E+02    2.83E+00       78.4     2.17E+02         2.28E+02
NO. OF OBSERVATIONS                      211
NO. OF COEFFICIENTS                        6
RESIDUAL DEGREES OF FREEDOM              205
RESIDUAL ROOT MEAN SQUARE                  5.21352577
RESIDUAL MEAN SQUARE                      27.18085861
RESIDUAL SUM OF SQUARES                 5572.07617187
```

Reworked TT Febuary 1987, Run 1, second creep.

```
                                                                  95%CONFIDENCE LIMITS
IND.VAR(I) NAME            COEF.B(I)      S.E.COEF.    T-VALUE    LOWER              UPPER
       1                   5.45158E+01    9.62E+00        5.7     3.57E+01         7.34E+01
       2                   2.12695E+02    1.66E+01       12.8     1.80E+02         2.45E+02
       3                   7.20414E-02    8.47E-03        8.5     5.54E-02         8.87E-02
       4                   4.59443E+02    1.91E+01       24.1     4.22E+02         4.97E+02
       5                   3.13010E-01    3.16E-02        9.9     2.51E-01         3.75E-01
       6                   3.08338E+02    2.01E+01       15.3     2.69E+02         3.48E+02
       7                   4.06070E+00    6.27E-01        6.5     2.83E+00         5.29E+00
       8                   1.78673E+02    6.68E+00       26.7     1.66E+02         1.92E+02
NO. OF OBSERVATIONS                      210
NO. OF COEFFICIENTS                        8
RESIDUAL DEGREES OF FREEDOM              202
RESIDUAL ROOT MEAN SQUARE                 18.57210541
RESIDUAL MEAN SQUARE                     344.92315674
RESIDUAL SUM OF SQUARES                69674.48437500
```

Reworked TT Febuary 1987, Run 3, first creep.

```
                                                                  95%CONFIDENCE LIMITS
IND.VAR(I) NAME            COEF.B(I)      S.E.COEF.    T-VALUE    LOWER              UPPER
       1                   3.89295E+01    9.67E-01       40.3     3.70E+01         4.08E+01
       2                   1.78434E+01    1.04E+00       17.2     1.58E+01         1.99E+01
       3                   1.77927E+00    2.66E-01        6.7     1.26E+00         2.30E+00
       4                   5.84166E+01    1.69E+00       34.7     5.51E+01         6.17E+01
       5                   7.26868E+01    3.40E+00       21.4     6.60E+01         7.93E+01
       6                   4.25474E+02    1.02E+01       41.7     4.05E+02         4.45E+02
NO. OF OBSERVATIONS                      211
NO. OF COEFFICIENTS                        6
RESIDUAL DEGREES OF FREEDOM              205
RESIDUAL ROOT MEAN SQUARE                  3.17755795
RESIDUAL MEAN SQUARE                      10.09687614
RESIDUAL SUM OF SQUARES                 2069.85986328
```

Reworked TT Febuary 1987, Run 3, second creep.

```
                                                                    95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)       S. E. COEF.      T-VALUE    LOWER           UPPER
     1                    4. 07573E+01      1. 71E+00        23. 8      3. 74E+01      4. 41E+01
     2                    1. 12012E+02      3. 38E+00        33. 2      1. 05E+02      1. 19E+02
     3                    1. 98480E-01      8. 33E-03        23. 8      1. 82E-01      2. 15E-01
     4                    2. 12684E+02      3. 37E+00        63. 0      2. 06E+02      2. 19E+02
     5                    1. 15638E+00      5. 10E-02        22. 7      1. 06E+00      1. 26E+00
     6                    1. 44700E+02      2. 82E+00        51. 3      1. 39E+02      1. 50E+02
     7                    3. 07352E+01      1. 64E+00        18. 8      2. 75E+01      3. 39E+01
     8                    6. 54046E+02      3. 80E+01        17. 2      5. 80E+02      7. 29E+02
NO.  OF OBSERVATIONS                   211
NO.  OF COEFFICIENTS                     8
RESIDUAL DEGREES OF FREEDOM            203
RESIDUAL ROOT MEAN SQUARE                 4. 51450920
RESIDUAL MEAN SQUARE                     20. 38079834
RESIDUAL SUM OF SQUARES                4137. 30273437
```

Butter made from Alnarp treated cream, Run 1.

```
                                                                    95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)       S. E. COEF       T-VALUE    LOWER           UPPER
     1                    4. 20585E+01      7. 73E-01        54. 4      4. 05E+01      4. 36E+01
     2                    1. 13123E+02      2. 15E+00        52. 5      1. 09E+02      1. 17E+02
     3                    3. 05863E-01      6. 13E-03        49. 9      2. 94E-01      3. 18E-01
     4                    2. 41310E+02      2. 44E+00        98. 9      2. 37E+02      2. 46E+02
     5                    1. 47540E+00      3. 54E-02        41. 7      1. 41E+00      1. 54E+00
     6                    1. 17737E+02      2. 37E+00        49. 8      1. 13E+02      1. 22E+02
     7                    2. 86731E+01      1. 59E+00        18. 1      2. 56E+01      3. 18E+01
     8                    6. 28884E+02      1. 67E+01        37. 8      5. 96E+02      6. 62E+02
NO.  OF OBSERVATIONS                   211
NO.  OF COEFFICIENTS                     8
RESIDUAL DEGREES OF FREEDOM            203
RESIDUAL ROOT MEAN SQUARE                 2. 47351694
RESIDUAL MEAN SQUARE                      6. 11628709
RESIDUAL SUM OF SQUARES                1242. 01245117
```

Butter made from Alnarp treated cream, Run 5.

```
                                                                    95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)       S. E. COEF.      T-VALUE    LOWER           UPPER
     1                    4. 43581E+01      8. 16E-01        54. 4      4. 28E+01      4. 60E+01
     2                    1. 11304E+02      1. 96E+00        56. 8      1. 07E+02      1. 15E+02
     3                    3. 11319E-01      6. 75E-03        46. 1      2. 98E-01      3. 25E-01
     4                    1. 61089E+02      2. 06E+00        78. 3      1. 57E+02      1. 65E+02
     5                    2. 48203E+00      8. 38E-02        29. 6      2. 32E+00      2. 65E+00
     6                    4. 96399E+01      2. 05E+00        24. 2      4. 56E+01      5. 37E+01
     7                    1. 12725E+02      1. 27E+01         8. 9      8. 78E+01      1. 38E+02
     8                    1. 25240E+03      1. 02E+02        12. 3      1. 05E+03      1. 45E+03
NO.  OF OBSERVATIONS                   211
NO.  OF COEFFICIENTS                     8
RESIDUAL DEGREES OF FREEDOM            203
RESIDUAL ROOT MEAN SQUARE                 2. 63378239
RESIDUAL MEAN SQUARE                      6. 93681049
RESIDUAL SUM OF SQUARES                1408. 17260742
```

Butter made from slow cooled cream, Run 1.

```
                                                                    95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)       S. E. COEF.      T-VALUE    LOWER           UPPER
     1                    4. 36182E+01      8. 04E-01        54. 2      4. 20E+01      4. 52E+01
     2                    7. 63998E+01      1. 75E+00        43. 6      7. 30E+01      7. 98E+01
     3                    3. 20033E-01      9. 33E-03        34. 3      3. 02E-01      3. 38E-01
     4                    1. 80080E+02      1. 72E+00       104. 6      1. 77E+02      1. 83E+02
     5                    1. 43266E+00      3. 81E-02        37. 6      1. 36E+00      1. 51E+00
     6                    1. 30680E+02      1. 43E+00        91. 5      1. 28E+02      1. 33E+02
     7                    3. 59815E+01      1. 05E+00        34. 3      3. 39E+01      3. 80E+01
     8                    2. 85461E+03      3. 71E+02         7. 7      2. 13E+03      3. 58E+03
NO.  OF OBSERVATIONS                   211
NO.  OF COEFFICIENTS                     8
RESIDUAL DEGREES OF FREEDOM            203
RESIDUAL ROOT MEAN SQUARE                 2. 21708584
RESIDUAL MEAN SQUARE                      4. 91547012
RESIDUAL SUM OF SQUARES                 997. 84045410
```

Butter made from slow cooled cream, Run 2.

```
                                                                              95%CONFIDENCE LIMITS
 IND. VAR(I) NAME            COEF. B(I)      S. E. COEF.       T-VALUE      LOWER                UPPER
       1                  4. 02059E+01       1. 30E+00         30. 9        3. 77E+01       4. 28E+01
       2                  9. 20457E+01       3. 47E+00         26. 5        8. 52E+01       9. 89E+01
       3                  2. 28819E-01       8. 66E-03         26. 4        2. 12E-01       2. 46E-01
       4                  1. 75010E+02       3. 34E+00         52. 4        1. 68E+02       1. 82E+02
       5                  1. 00586E+00       5. 19E-02         19. 4        9. 04E-01       1. 11E+00
       6                  1. 40517E+02       2. 76E+00         50. 9        1. 35E+02       1. 46E+02
       7                  1. 35083E+01       6. 99E-01         19. 3        1. 21E+01       1. 49E+01
       8                  7. 53934E+02       2. 36E+01         31. 9        7. 08E+02       8. 00E+02
 NO.  OF OBSERVATIONS                 211
 NO.  OF COEFFICIENTS                   8
 RESIDUAL DEGREES OF FREEDOM          203
 RESIDUAL ROOT MEAN SQUARE              3. 24846125
 RESIDUAL MEAN SQUARE                  10. 55250168
 RESIDUAL SUM OF SQUARES             2142. 15820312
```

Butter made from slow cooled cream, Run 3.

```
                                                                              95%CONFIDENCE LIMITS
 IND. VAR(I) NAME            COEF. B(I)      S. E. COEF.       T-VALUE      LOWER                UPPER
       1                  3. 59328E+01       7. 83E-01         45. 9        3. 44E+01       3. 75E+01
       2                  6. 85166E+01       1. 67E+00         41. 1        6. 52E+01       7. 18E+01
       3                  3. 19788E-01       1. 00E-02         31. 9        3. 00E-01       3. 39E-01
       4                  1. 05473E+02       2. 46E+00         42. 8        1. 01E+02       1. 10E+02
       5                  2. 29552E+00       9. 97E-02         23. 0        2. 10E+00       2. 49E+00
       6                  6. 46645E+01       2. 73E+00         23. 7        5. 93E+01       7. 00E+01
       7                  2. 74608E+01       2. 69E+00         10. 2        2. 22E+01       3. 27E+01
       8                  7. 15114E+02       1. 32E+01         54. 1        6. 89E+02       7. 41E+02
 NO.  OF OBSERVATIONS                 211
 NO.  OF COEFFICIENTS                   8
 RESIDUAL DEGREES OF FREEDOM          203
 RESIDUAL ROOT MEAN SQUARE              2. 03587580
 RESIDUAL MEAN SQUARE                   4. 14479160
 RESIDUAL SUM OF SQUARES              841. 39270020
```

Butter made from rapidly cooled cream, Run 1.

```
 IND. VAR(I) NAME                                                             95%CONFIDENCE LIMITS
       1                     COEF. B(I)      S. E. COEF.       T-VALUE      LOWER                UPPER
       2                  4. 05759E+01       8. 27E-01         49. 1        3. 90E+01       4. 22E+01
       3                  7. 03305E+01       2. 48E+00         28. 4        6. 55E+01       7. 52E+01
       4                  3. 87289E-01       1. 26E-02         30. 7        3. 63E-01       4. 12E-01
       5                  1. 53916E+02       2. 47E+00         62. 3        1. 49E+02       1. 59E+02
       6                  1. 55144E+00       6. 45E-02         24. 0        1. 42E+00       1. 68E+00
       7                  8. 11576E+01       2. 30E+00         35. 3        7. 66E+01       8. 57E+01
       8                  2. 80489E+01       2. 07E+00         13. 5        2. 40E+01       3. 21E+01
 NO.  OF OBSERVATIONS     6. 43740E+02       1. 47E+01         43. 9        6. 15E+02       6. 72E+02
 NO.  OF COEFFICIENTS                 210
 RESIDUAL DEGREES OF FREEDOM            8
 RESIDUAL ROOT MEAN SQUARE            202
 RESIDUAL MEAN SQUARE                   2. 36115503
 RESIDUAL SUM OF SQUARES                5. 57505322
                                     1126. 16088867
```

Butter made from rapidly cooled cream, Run 2.

```
                                                                    95%CONFIDENCE LIMITS
IND. VAR(I) NAME        COEF. B(I)       S. E. COEF.     T-VALUE   LOWER            UPPER
      1              7. 11108E+01       1. 10E+00        64. 7      6. 90E+01        7. 33E+01
      2              1. 26818E+02       2. 80E+00        45. 3      1. 21E+02        1. 32E+02
      3              2. 68864E-01       6. 84E-03        39. 3      2. 55E-01        2. 82E-01
      4              1. 87136E+02       2. 74E+00        68. 4      1. 82E+02        1. 92E+02
      5              1. 93118E+00       7. 84E-02        24. 6      1. 78E+00        2. 08E+00
      6              1. 15930E+02       2. 92E+00        39. 7      1. 10E+02        1. 22E+02
      7              5. 38741E+01       3. 11E+00        17. 3      4. 78E+01        6. 00E+01
      8              3. 85587E+02       1. 41E+01        27. 4      3. 58E+02        4. 13E+02
NO. OF OBSERVATIONS                  211
NO. OF COEFFICIENTS                    8
RESIDUAL DEGREES OF FREEDOM          203
RESIDUAL ROOT MEAN SQUARE               3. 51221132
RESIDUAL MEAN SQUARE                   12. 33563042
RESIDUAL SUM OF SQUARES              2504. 13330078
```

MAN April 1987, Run 1.

```
                                                                    95%CONFIDENCE LIMITS
IND VAR(I) NAME         COEF B(I)        S E COEF        T-VALUE   LOWER            UPPER
      1              6. 18857E+01       3. 46E+00        17. 9      5. 51E+01        6. 87E+01
      2              1. 38013E+02       1. 25E+01        11. 1      1. 14E+02        1. 62E+02
      3              2. 29181E-01       1. 62E-02        14. 1      1. 97E-01        2. 61E-01
      4              1. 56416E+02       1. 19E+01        13. 1      1. 33E+02        1. 80E+02
      5          209 1. 62964E+00       3. 24E-01         5. 0      9. 94E-01        2. 27E+00
      6              4. 13612E+01       1. 12E+01         3. 7      1. 94E+01        6. 33E+01
      7        22544 5. 54835E+01       3. 79E+01         1. 5     -1. 88E+01        1. 30E+02
      8              2. 40684E+02       8. 49E+00        28. 3      2. 24E+02        2. 57E+02
NO. OF OBSERVATIONS                  211
NO. OF COEFFICIENTS                    8
RESIDUAL DEGREES OF FREEDOM          203
RESIDUAL ROOT MEAN SQUARE              10. 51927372
RESIDUAL MEAN SQUARE                  110. 65515137
RESIDUAL SUM OF SQUARES             22462. 99609375
```

MAN April 1987, Run 2.

```
                                                                    95%CONFIDENCE LIMITS
IND. VAR(I) NAME        COEF. B(I)       S. E. COEF.     T-VALUE   LOWER            UPPER
      1              6. 26974E+01       8. 80E-01        71. 2      6. 10E+01        6. 44E+01
      2              1. 32664E+02       2. 89E+00        46. 0      1. 27E+02        1. 38E+02
      3              2. 06982E-01       3. 78E-03        54. 7      2. 00E-01        2. 14E-01
      4              2. 53701E+02       3. 50E+00        72. 5      2. 47E+02        2. 61E+02
      5              9. 26641E-01       2. 65E-02        35. 0      8. 75E-01        9. 79E-01
      6              1. 76576E+02       3. 80E+00        46. 5      1. 69E+02        1. 84E+02
      7              9. 36932E+00       4. 91E-01        19. 1      8. 41E+00        1. 03E+01
      8              4. 07833E+02       1. 37E+01        29. 7      3. 81E+02        4. 35E+02
NO. OF OBSERVATIONS                  199
NO. OF COEFFICIENTS                    8
RESIDUAL DEGREES OF FREEDOM          191
RESIDUAL ROOT MEAN SQUARE               2. 51084709
RESIDUAL MEAN SQUARE                    6. 30435371
RESIDUAL SUM OF SQUARES              1204. 13159180
```

MAN May 1987, 8 hours.

```
                                                                    95%CONFIDENCE LIMITS
IND. VAR(I) NAME        COEF. B(I)       S. E. COEF.     T-VALUE   LOWER            UPPER
      1              5. 44556E+01       9. 33E-01        58. 4      5. 26E+01        5. 63E+01
      2              9. 53645E+01       2. 20E+00        43. 3      9. 10E+01        9. 97E+01
      3              2. 72318E-01       7. 42E-03        36. 7      2. 58E-01        2. 87E-01
      4              1. 50307E+02       2. 75E+00        54. 6      1. 45E+02        1. 56E+02
      5              1. 86324E+00       7. 46E-02        25. 0      1. 72E+00        2. 01E+00
      6              1. 51624E+02       2. 86E+00        52. 9      1. 46E+02        1. 57E+02
      7              1. 57992E+01       7. 58E-01        20. 8      1. 43E+01        1. 73E+01
      8              6. 22312E+02       1. 46E+01        42. 7      5. 94E+02        6. 51E+02
NO. OF OBSERVATIONS                  211
NO. OF COEFFICIENTS                    8
RESIDUAL DEGREES OF FREEDOM          203
RESIDUAL ROOT MEAN SQUARE               2. 63834906
RESIDUAL MEAN SQUARE                    6. 96088696
RESIDUAL SUM OF SQUARES              1413. 06005859
```

MAN May 1987, 15 hours.

```
                                                                  95%CONFIDENCE LIMITS
IND.VAR(I) NAME           COEF.B(I)       S.E.COEF.    T-VALUE    LOWER           UPPER
     1                 2.84069E+01      5.40E-01       52.6      2.73E+01       2.95E+01
     2                 5.65372E+01      1.60E+00       35.4      5.34E+01       5.97E+01
     3                 4.25655E-01      1.10E-02       38.6      4.04E-01       4.47E-01
     4                 8.19349E+01      1.51E+00       54.2      7.90E+01       8.49E+01
     5                 2.42415E+00      1.21E-01       20.0      2.19E+00       2.66E+00
     6                 3.54965E+01      1.23E+00       28.9      3.31E+01       3.79E+01
     7                 6.04633E+01      5.58E+00       10.8      4.95E+01       7.14E+01
     8                 7.18757E+02      1.00E+01       71.7      6.99E+02       7.38E+02
NO.  OF OBSERVATIONS                 211
NO.  OF COEFFICIENTS                   8
RESIDUAL DEGREES OF FREEDOM          203
RESIDUAL ROOT MEAN SQUARE              1.44668388
RESIDUAL MEAN SQUARE                   2.09289455
RESIDUAL SUM OF SQUARES              424.85766602
```

PAMF, Run 1, first creep.

```
                                                                  95%CONFIDENCE LIMITS
IND.VAR(I) NAME           COEF.B(I)       S.E.COEF.    T-VALUE    LOWER           UPPER
     1                 9.46376E+00      7.18E-01       13.2      8.06E+00       1.09E+01
     2                 3.59813E+00      7.09E-01        5.1      2.21E+00       4.99E+00
     3                 4.64098E+00      2.28E+00        2.0      1.74E-01       9.11E+00
     4                 6.13089E+00      7.85E-01        7.8      4.59E+00       7.67E+00
     5                 5.51601E+02      1.28E+02        4.3      3.01E+02       8.02E+02
     6                 1.01035E+03      2.81E+01       36.0      9.55E+02       1.07E+03
NO.  OF OBSERVATIONS                 211
NO.  OF COEFFICIENTS                   6
RESIDUAL DEGREES OF FREEDOM          205
RESIDUAL ROOT MEAN SQUARE              1.78406596
RESIDUAL MEAN SQUARE                   3.18289137
RESIDUAL SUM OF SQUARES              652.49279785
```

PAMF, Run 1, second creep.

```
                                                                  95%CONFIDENCE LIMITS
IND.VAR(I) NAME           COEF.B(I)       S.E.COEF.    T-VALUE    LOWER           UPPER
     1                 2.40224E+01      9.75E-01       24.7      2.21E+01       2.59E+01
     2                 3.97974E+01      1.66E+00       24.0      3.66E+01       4.30E+01
     3                 3.73996E-01      2.43E-02       15.4      3.26E-01       4.22E-01
     4                 6.91808E+01      2.07E+00       33.5      6.51E+01       7.32E+01
     5                 2.19620E+00      1.48E-01       14.8      1.91E+00       2.49E+00
     6                 5.55846E+01      2.24E+00       24.8      5.12E+01       6.00E+01
     7                 2.32808E+01      2.22E+00       10.5      1.89E+01       2.76E+01
     8                 3.96805E+02      3.65E+00      108.8      3.90E+02       4.04E+02
NO.  OF OBSERVATIONS                 211
NO.  OF COEFFICIENTS                   8
RESIDUAL DEGREES OF FREEDOM          203
RESIDUAL ROOT MEAN SQUARE              2.03379679
RESIDUAL MEAN SQUARE                   4.13632965
RESIDUAL SUM OF SQUARES              839.67492676
```

PAMF, Run 2, first creep.

```
                                                                  95%CONFIDENCE LIMITS
IND.VAR(I) NAME           COEF.B(I)       S.E.COEF.    T-VALUE    LOWER           UPPER
     1                 5.32857E+01      3.68E+00       14.5      4.61E+01       6.05E+01
     2                 8.20472E+01      8.89E+00        9.2      6.46E+01       9.95E+01
     3                 2.35604E-01      2.83E-02        8.3      1.80E-01       2.91E-01
     4                 1.67277E+02      9.17E+00       18.2      1.49E+02       1.85E+02
     5                 1.01545E+00      1.43E-01        7.1      7.34E-01       1.30E+00
     6                 1.56843E+02      8.90E+00       17.6      1.39E+02       1.74E+02
     7                 1.00297E+01      1.41E+00        7.1      7.28E+00       1.28E+01
     8                 4.75208E+02      2.40E+01       19.8      4.28E+02       5.22E+02
NO.  OF OBSERVATIONS                 211
NO.  OF COEFFICIENTS                   8
RESIDUAL DEGREES OF FREEDOM          203
RESIDUAL ROOT MEAN SQUARE              8.80390930
RESIDUAL MEAN SQUARE                  77.50883484
RESIDUAL SUM OF SQUARES            15734.29492187
```

MAN May 1987, 25 hours (15 hours analysed).

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                                                              95%CONFIDENCE LIMITS
IND. VAR(I) NAME         COEF. B(I)     S. E. COEF.   T-VALUE   LOWER          UPPER
      1                2. 86695E+01     1. 46E+00      19. 6    2. 58E+01     3. 15E+01
      2                4. 26310E+01     4. 12E+00      10. 3    3. 46E+01     5. 07E+01
      3                4. 51569E-01     4. 31E-02      10. 5    3. 67E-01     5. 36E-01
      4                4. 69821E+01     4. 99E+00       9. 4    3. 72E+01     5. 68E+01
      5                3. 67723E+00     7. 01E-01       5. 2    2. 30E+00     5. 05E+00
      6                4. 29723E+01     6. 13E+00       7. 0    3. 10E+01     5. 50E+01
      7                2. 03691E+01     3. 79E+00       5. 4    1. 29E+01     2. 78E+01
      8                9. 24093E+02     2. 73E+01      33. 8    8. 71E+02     9. 78E+02
NO. OF OBSERVATIONS                  211
NO. OF COEFFICIENTS                    8
RESIDUAL DEGREES OF FREEDOM          203
RESIDUAL ROOT MEAN SQUARE              3. 19296598
RESIDUAL MEAN SQUARE                  10. 19503212
RESIDUAL SUM OF SQUARES             2069. 59179667
```

Butter (from AMF), Run 1, first creep.

```
                                                           95%CONFIDENCE LIMITS
IND. VAR(I) NAME       COEF. B(I)     S. E. COEF     T-VALUE    LOWER         UPPER
      1              1. 43084E+01     3. 63E-01       37. 3    1. 36E+01     1. 51E+01
      2              4. 26590E+00     3. 68E-01       11. 6    3. 54E+00     4. 99E+00
      3              2. 53850E+00     5. 36E-01        4. 7    1. 49E+00     3. 59E+00
      4              1. 27747E+01     2. 87E-01       44. 5    1. 22E+01     1. 33E+01
      5              2. 20271E+02     9. 52E+00       23. 1    2. 02E+02     2. 39E+02
      6              3. 93576E+03     1. 61E+02       24. 4    3. 62E+03     4. 25E+03
NO. OF OBSERVATIONS                211
NO. OF COEFFICIENTS                  6
RESIDUAL DEGREES OF FREEDOM        205
RESIDUAL ROOT MEAN SQUARE            0. 74208188
RESIDUAL MEAN SQUARE                 0. 55068552
RESIDUAL SUM OF SQUARES            112. 89053345
```

Butter (from AMF), Run 1, second creep.

```
                                                           95%CONFIDENCE LIMITS
IND. VAR(I) NAME       COEF. B(I)     S. E. COEF.    T-VALUE    LOWER         UPPER
      1              3. 27509E+01     3. 89E-01       84. 3    3. 20E+01     3. 35E+01
      2              3. 82517E+01     1. 28E+00       29. 9    3. 57E+01     4. 08E+01
      3              7. 43902E-01     2. 09E-02       35. 7    7. 03E-01     7. 85E-01
      4              6. 64865E+01     1. 27E+00       52. 3    6. 40E+01     6. 90E+01
      5              3. 18514E+00     1. 47E-01       21. 7    2. 90E+00     3. 47E+00
      6              4. 02868E+01     3. 23E+00       12. 5    3. 39E+01     4. 66E+01
      7              3. 10350E+02     1. 06E+01       29. 3    2. 90E+02     3. 31E+02
      8              1. 03877E+03     7. 57E+01       13. 7    8. 90E+02     1. 19E+03
NO. OF OBSERVATIONS                211
NO. OF COEFFICIENTS                  8
RESIDUAL DEGREES OF FREEDOM        203
RESIDUAL ROOT MEAN SQUARE            1. 12821770
RESIDUAL MEAN SQUARE                 1. 27287555
RESIDUAL SUM OF SQUARES            258. 39373779
```

Butter (from AMF), Run 4, first creep.

```
                                                           95%CONFIDENCE LIMITS
IND. VAR(I) NAME       COEF. B(I)     S. E. COEF.    T-VALUE    LOWER         UPPER
      1              2. 51811E+00     3. 41E+00        0. 7   -4. 16E+00     9. 20E+00
      2              1. 64881E+01     3. 39E+00        4. 9    9. 85E+00     2. 31E+01
      3              1. 01794E-01     7. 85E-02        1. 3   -5. 21E-02     2. 56E-01
      4              7. 32842E+00     1. 84E+00        4. 0    3. 71E+00     1. 09E+01
      5              1. 01863E+03     1. 67E+02        6. 1    6. 91E+02     1. 35E+03
      6              4. 66425E+03     1. 08E+03        4. 3    2. 56E+03     6. 77E+03
NO. OF OBSERVATIONS                211
NO. OF COEFFICIENTS                  6
RESIDUAL DEGREES OF FREEDOM        205
RESIDUAL ROOT MEAN SQUARE            1. 77607608
RESIDUAL MEAN SQUARE                 3. 15444708
RESIDUAL SUM OF SQUARES            646. 66174316
```

Butter (from AMF), Run 4, second creep.

```
                                                                      95%CONFIDENCE LIMITS
 IND. VAR(I) NAME          COEF. B(I)      S. E. COEF.    T-VALUE    LOWER              UPPER
        1                4. 66330E+01      6. 09E-01       76. 6      4. 54E+01        4. 78E+01
        2                1. 06223E+02      1. 95E+00       54. 3      1. 02E+02        1. 10E+02
        3                3. 34417E-01      5. 61E-03       59. 6      3. 23E-01        3. 45E-01
        4                1. 37007E+02      1. 82E+00       75. 5      1. 33E+02        1. 41E+02
        5                2. 25843E+00      8. 26E-02       27. 3      2. 10E+00        2. 42E+00
        6                1. 03646E+02      1. 37E+00       75. 6      1. 01E+02        1. 06E+02
        7                4. 89273E+01      1. 75E+00       27. 9      4. 55E+01        5. 24E+01
        8                1. 31154E+03      7. 45E+01       17. 6      1. 17E+03        1. 46E+03
 NO.  OF OBSERVATIONS                   211
 NO.  OF COEFFICIENTS                     8
 RESIDUAL DEGREES OF FREEDOM            203
 RESIDUAL ROOT MEAN SQUARE                1. 95847583
 RESIDUAL MEAN SQUARE                     3. 83562756
 RESIDUAL SUM OF SQUARES                778. 63244629
```

AMF/oil blend, Run 1, first creep.

```
                                                                      95%CONFIDENCE LIMITS
 IND. VAR(I) NAME          COEF. B(I)      S. E. COEF.    T-VALUE    LOWER              UPPER
        1                1. 79766E+01      4. 23E-01       42. 5      1. 71E+01        1. 88E+01
        2                7. 61921E+00      7. 41E-01       10. 3      6. 17E+00        9. 07E+00
        3                2. 28929E+01      6. 28E+00        3. 6      1. 06E+01        3. 52E+01
        4                2. 61243E+01      2. 10E+01        1. 2     -1. 50E+01        6. 73E+01
        5                7. 74459E+02      1. 38E+02        5. 6      5. 04E+02        1. 04E+03
        6                1. 36428E+03      5. 77E+02        2. 4      2. 33E+02        2. 50E+03
 NO.  OF OBSERVATIONS                   211
 NO.  OF COEFFICIENTS                     6
 RESIDUAL DEGREES OF FREEDOM            205
 RESIDUAL ROOT MEAN SQUARE                2. 76003170
 RESIDUAL MEAN SQUARE                     7. 61777687
 RESIDUAL SUM OF SQUARES               1561. 64428711
```

AMF/oil blend, Run 1, second creep.

```
                                                                      95%CONFIDENCE LIMITS
 IND. VAR(I) NAME          COEF. B(I)      S. E. COEF.    T-VALUE    LOWER              UPPER
        1                2. 15168E+01      2. 33E+00        9. 2      1. 70E+01        2. 61E+01
        2                4. 16762E+01      2. 67E+00       15. 6      3. 64E+01        4. 69E+01
        3                1. 14818E-01      1. 62E-02        7. 1      8. 31E-02        1. 47E-01
        4                1. 02514E+02      3. 08E+00       33. 3      9. 65E+01        1. 09E+02
        5                4. 51013E-01      2. 93E-02       15. 4      3. 94E-01        5. 08E-01
        6                9. 41512E+01      3. 83E+00       24. 6      8. 66E+01        1. 02E+02
        7                3. 28475E+00      2. 83E-01       11. 6      2. 73E+00        3. 84E+00
        8                4. 68304E+02      4. 68E+00      100. 0      4. 59E+02        4. 77E+02
 NO.  OF OBSERVATIONS                   211
 NO.  OF COEFFICIENTS                     8
 RESIDUAL DEGREES OF FREEDOM            203
 RESIDUAL ROOT MEAN SQUARE                2. 40553904
 RESIDUAL MEAN SQUARE                     5. 78661919
 RESIDUAL SUM OF SQUARES               1174. 68383789
```

AMF/oil blend, Run 3, first creep.

```
                                                                      95%CONFIDENCE LIMITS
 IND. VAR(I) NAME          COEF. B(I)      S. E. COEF.    T-VALUE    LOWER              UPPER
        1                2. 12914E+01      8. 37E-01       25. 4      1. 97E+01        2. 29E+01
        2                6. 96228E+00      1. 18E+00        5. 9      4. 64E+00        9. 28E+00
        3                3. 02922E+00      9. 92E-01        3. 1      1. 08E+00        4. 97E+00
        4                4. 79555E+00      1. 17E+00        4. 1      2. 51E+00        7. 08E+00
        5                6. 73311E+01      4. 46E+01        1. 5     -2. 01E+01        1. 55E+02
        6                7. 26005E+02      1. 02E+01       71. 5      7. 06E+02        7. 46E+02
 NO.  OF OBSERVATIONS                   211
 NO.  OF COEFFICIENTS                     6
 RESIDUAL DEGREES OF FREEDOM            205
 RESIDUAL ROOT MEAN SQUARE                2. 19730282
 RESIDUAL MEAN SQUARE                     4. 62814121
 RESIDUAL SUM OF SQUARES                989. 76904297
```

AMF/oil blend, Run 3, second creep.

```
                                                                95%CONFIDENCE LIMITS
IND.VAR(I) NAME          COEF.B(I)      S.E.COEF.     T-VALUE    LOWER           UPPER
     1                  8.57050E+01     2.64E+00       32.5      8.05E+01       9.09E+01
     2                  2.08056E+02     5.18E+00       40.2      1.98E+02       2.18E+02
     3                  8.38815E-02     2.85E-03       29.4      7.83E-02       8.95E-02
     4                  4.30789E+02     5.77E+00       74.6      4.19E+02       4.42E+02
     5                  3.99054E-01     1.33E-02       30.0      3.73E-01       4.25E-01
     6                  2.88120E+02     5.74E+00       50.2      2.77E+02       2.99E+02
     7                  5.70843E+00     2.86E-01       19.9      5.15E+00       6.27E+00
     8                  9.86007E+01     7.14E-01      138.0      9.72E+01       1.00E+02
NO.  OF OBSERVATIONS              211
NO.  OF COEFFICIENTS                8
RESIDUAL DEGREES OF FREEDOM       203
RESIDUAL ROOT MEAN SQUARE           6.01874828
RESIDUAL MEAN SQUARE               36.22533417
RESIDUAL SUM OF SQUARES          7353.74414062
```

Reworked PAMF,   Run 2, first creep.

```
                                                                95%CONFIDENCE LIMITS
IND.VAR(I) NAME          COEF.B(I)      S.E.COEF.     T-VALUE    LOWER           UPPER
     1                  3.99113E+01     1.85E+00       21.6      3.63E+01       4.35E+01
     2                  1.60696E+01     1.89E+00        8.5      1.24E+01       1.98E+01
     3                  1.20564E+00     3.54E-01        3.4      5.12E-01       1.90E+00
     4                  5.49195E+01     1.49E+00       36.7      5.20E+01       5.78E+01
     5                  2.39434E+01     1.89E+00       12.7      2.02E+01       2.76E+01
     6                  1.46561E+02     1.14E+00      128.1      1.44E+02       1.49E+02
NO.  OF OBSERVATIONS              211
NO.  OF COEFFICIENTS                6
RESIDUAL DEGREES OF FREEDOM       205
RESIDUAL ROOT MEAN SQUARE           4.86299801
RESIDUAL MEAN SQUARE               23.64875031
RESIDUAL SUM OF SQUARES          4847.99414062
```

Reworked PAMF, Run 2, second creep.

```
                                                                95%CONFIDENCE LIMITS
IND.VAR(I) NAME          COEF.B(I)      S.E.COEF.     T-VALUE    LOWER           UPPER
     1                  8.60953E+01     4.36E+00       19.7      7.75E+01       9.46E+01
     2                  1.39453E+02     6.63E+00       21.0      1.26E+02       1.52E+02
     3                  7.61573E-02     6.05E-03       12.6      6.43E-02       8.80E-02
     4                  4.38455E+02     9.61E+00       45.6      4.20E+02       4.57E+02
     5                  2.29804E-01     9.48E-03       24.2      2.11E-01       2.48E-01
     6                  3.83363E+02     1.16E+01       33.1      3.61E+02       4.06E+02
     7                  1.76155E+00     1.13E-01       15.6      1.54E+00       1.98E+00
     8                  5.80252E+01     2.64E-01      204.3      5.75E+01       5.86E+01
NO.  OF OBSERVATIONS              209
NO.  OF COEFFICIENTS                8
RESIDUAL DEGREES OF FREEDOM       201
RESIDUAL ROOT MEAN SQUARE           7.46074104
RESIDUAL MEAN SQUARE               55.66266632
RESIDUAL SUM OF SQUARES         11188.19726563
```

Reworked PAMF, Run 1, first creep.

```
                                                                   95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)     S. E. COEF.    T-VALUE     LOWER             UPPER
      1                  9. 31576E+01    3. 54E+00       26. 4      8. 62E+01        1. 00E+02
      2                  1. 65585E+02    8. 33E+00       19. 9      1. 49E+02        1. 82E+02
      3                  1. 19854E-01    6. 88E-03       17. 4      1. 06E-01        1. 33E-01
      4                  3. 78744E+02    8. 54E+00       44. 3      3. 62E+02        3. 95E+02
      5                  4. 75573E-01    2. 80E-02       17. 0      4. 21E-01        5. 31E-01
      6                  2. 50689E+02    7. 97E+00       31. 4      2. 35E+02        2. 66E+02
      7                  7. 13170E+00    5. 80E-01       12. 3      5. 99E+00        8. 27E+00
      8                  1. 23625E+02    1. 65E+00       74. 8      1. 20E+02        1. 27E+02
NO.  OF OBSERVATIONS                211
NO.  OF COEFFICIENTS                  8
RESIDUAL DEGREES OF FREEDOM         203
RESIDUAL ROOT MEAN SQUARE              8. 61272049
RESIDUAL MEAN SQUARE                  74. 17897034
RESIDUAL SUM OF SQUARES            15058. 33203125
```

Reworked Butter (from AMF), Run 1, first creep.

```
                                                                   95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)     S. E. COEF.    T-VALUE     LOWER             UPPER
      1                  3. 12367E+01    9. 31E-01       33. 5      2. 94E+01        3. 31E+01
      2                  1. 59811E+01    1. 15E+00       13. 9      1. 37E+01        1. 82E+01
      3                  2. 67664E+00    4. 82E-01        5. 6      1. 73E+00        3. 62E+00
      4                  6. 71268E+01    1. 22E+00       54. 9      6. 47E+01        6. 95E+01
      5                  2. 97705E+01    1. 49E+00       19. 9      2. 68E+01        3. 27E+01
      6                  2. 68614E+02    3. 05E+00       88. 0      2. 63E+02        2. 75E+02
NO.  OF OBSERVATIONS                211
NO.  OF COEFFICIENTS                  6
RESIDUAL DEGREES OF FREEDOM         205
RESIDUAL ROOT MEAN SQUARE              3. 39729404
RESIDUAL MEAN SQUARE                  11. 54160690
RESIDUAL SUM OF SQUARES             2366. 02978516
```

Reworked Butter (from AMF), Run 1, second creep.

```
                                                                   95%CONFIDENCE LIMITS
IND. VAR(I) NAME          COEF. B(I)     S. E. COEF.    T-VALUE     LOWER             UPPER
      1                  7. 86724E+01    2. 49E+00       31. 6      7. 38E+01        8. 36E+01
      2                  1. 83855E+02    4. 63E+00       39. 7      1. 75E+02        1. 93E+02
      3                  1. 07363E-01    3. 96E-03       27. 1      9. 96E-02        1. 15E-01
      4                  3. 47341E+02    6. 52E+00       53. 3      3. 35E+02        3. 60E+02
      5                  6. 62922E-01    2. 50E-02       26. 5      6. 14E-01        7. 12E-01
      6                  1. 85519E+02    6. 99E+00       26. 6      1. 72E+02        1. 99E+02
      7                  1. 01781E+01    9. 35E-01       10. 9      8. 35E+00        1. 20E+01
      8                  1. 39133E+02    1. 54E+00       90. 5      1. 36E+02        1. 42E+02
NO.  OF OBSERVATIONS                211
NO.  OF COEFFICIENTS                  8
RESIDUAL DEGREES OF FREEDOM         203
RESIDUAL ROOT MEAN SQUARE              6. 15412140
RESIDUAL MEAN SQUARE                  37. 87321472
RESIDUAL SUM OF SQUARES             7688. 26367187
```

Reworked Butter (from AMF), Run 3, first creep.

```
                                                                     95%CONFIDENCE LIMITS
IND. VAR(I) NAME         COEF. B(I)      S. E. COEF.     T-VALUE    LOWER               UPPER
     1                 1. 40393E+02      1. 47E+01          9. 6      1. 12E+02         1. 69E+02
     2                 1. 99097E+02      2. 34E+01          8. 5      1. 53E+02         2. 45E+02
     3                 5. 51787E-02      1. 03E-02          5. 3      3. 49E-02         7. 54E-02
     4                 5. 18950E+02      3. 59E+01         14. 5      4. 49E+02         5. 89E+02
     5                 1. 96826E-01      2. 40E-02          8. 2      1. 50E-01         2. 44E-01
     6                 5. 18367E+02      4. 38E+01         11. 8      4. 33E+02         6. 04E+02
     7                 1. 23893E+00      2. 16E-01          5. 7      8. 16E-01         1. 66E+00
     8                 5. 84923E+01      8. 59E-01         68. 1      5. 68E+01         6. 02E+01
NO.  OF OBSERVATIONS                 211
NO.  OF COEFFICIENTS                   8
RESIDUAL DEGREES OF FREEDOM          203
RESIDUAL ROOT MEAN SQUARE             25. 49248886
RESIDUAL MEAN SQUARE                 649. 86706543
RESIDUAL SUM OF SQUARES           131923. 03125000
```

Reworked AMF/oil blend, Run 1, first creep.

```
                                                                     95%CONFIDENCE LIMITS
IND. VAR(I) NAME         COEF. B(I)      S. E. COEF.     T-VALUE    LOWER               UPPER
     1                 5. 97385E+01      8. 03E-01         74. 4      5. 82E+01         6. 13E+01
     2                 3. 62546E+01      1. 34E+00         27. 1      3. 36E+01         3. 89E+01
     3                 2. 51927E+00      2. 27E-01         11. 1      2. 07E+00         2. 96E+00
     4                 1. 01685E+02      1. 76E+00         57. 9      9. 82E+01         1. 05E+02
     5                 3. 01605E+01      1. 34E+00         22. 5      2. 75E+01         3. 28E+01
     6                 1. 69425E+02      1. 71E+00         99. 2      1. 66E+02         1. 73E+02
NO.  OF OBSERVATIONS                 211
NO.  OF COEFFICIENTS                   6
RESIDUAL DEGREES OF FREEDOM          205
RESIDUAL ROOT MEAN SQUARE              3. 95656824
RESIDUAL MEAN SQUARE                  15. 65443230
RESIDUAL SUM OF SQUARES             3209. 15869141
```

Reworked AMF/oil blend, Run 1, second creep.

```
                                                                     95%CONFIDENCE LIMITS
IND. VAR(I) NAME         COEF. B(I)      S. E. COEF.     T-VALUE    LOWER               UPPER
     1                 1. 82490E+02      3. 28E+00         55. 6      1. 76E+02         1. 89E+02
     2                 3. 27755E+02      6. 95E+00         47. 2      3. 14E+02         3. 41E+02
     3                 4. 96304E-02      1. 32E-03         37. 7      4. 70E-02         5. 22E-02
     4                 7. 23666E+02      1. 01E+01         71. 6      7. 04E+02         7. 43E+02
     5                 2. 07269E-01      5. 31E-03         39. 0      1. 97E-01         2. 18E-01
     6                 5. 27495E+02      1. 20E+01         43. 9      5. 04E+02         5. 51E+02
     7                 1. 82280E+00      8. 73E-02         20. 9      1. 65E+00         1. 99E+00
     8                 5. 30419E+01      2. 14E-01        247. 6      5. 26E+01         5. 35E+01
NO.  OF OBSERVATIONS                 211
NO.  OF COEFFICIENTS                   8
RESIDUAL DEGREES OF FREEDOM          203
RESIDUAL ROOT MEAN SQUARE              7. 12122250
RESIDUAL MEAN SQUARE                  50. 71182251
RESIDUAL SUM OF SQUARES            10294. 50000000
```

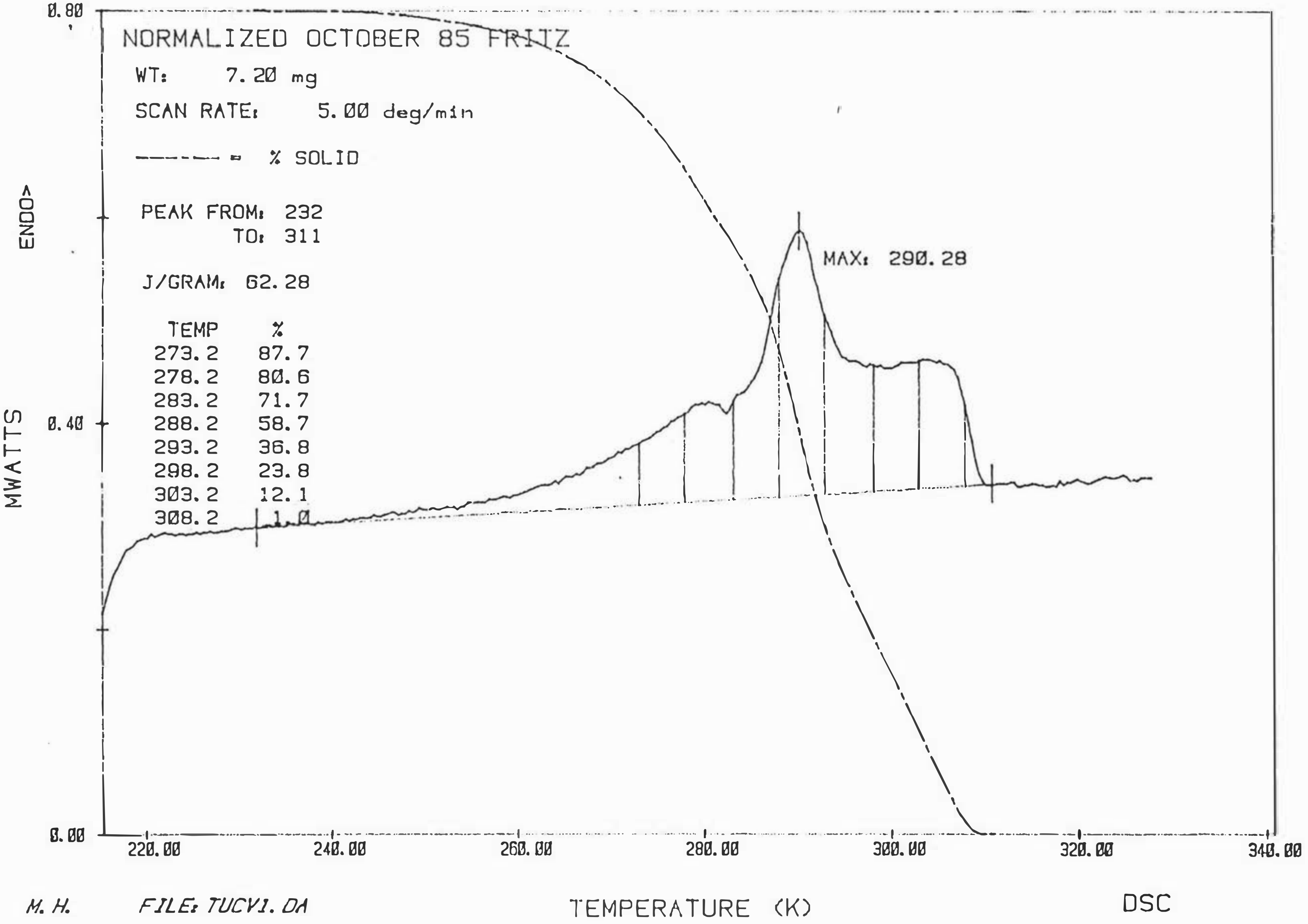
Reworked AMF/oil blend, Run 2, first creep.

```
                                                                     95%CONFIDENCE LIMITS
IND. VAR(I) NAME         COEF. B(I)      S. E. COEF.     T-VALUE    LOWER               UPPER
     1                 5. 81352E+01      2. 36E+00         24. 6      5. 35E+01         6. 28E+01
     2                 2. 45981E+01      3. 05E+00          8. 1      1. 86E+01         3. 06E+01
     3                 1. 04960E+00      2. 79E-01          3. 8      5. 04E-01         1. 60E+00
     4                 4. 63632E+01      2. 77E+00         16. 8      4. 09E+01         5. 18E+01
     5                 1. 31241E+01      2. 35E+00          5. 6      8. 51E+00         1. 77E+01
     6                 8. 75385E+01      5. 06E-01        173. 1      8. 65E+01         8. 85E+01
NO.  OF OBSERVATIONS                 211
NO.  OF COEFFICIENTS                   6
RESIDUAL DEGREES OF FREEDOM          205
RESIDUAL ROOT MEAN SQUARE              6. 95048046
RESIDUAL MEAN SQUARE                  48. 30918121
RESIDUAL SUM OF SQUARES             9903. 38281250
```

Reworked AMF/oil blend, Run 2, second creep.

APPENDIX 3

DIFFERENTIAL SCANNING CALORIMETRY MELTING THERMOGRAMS
1985 - 1986 DAIRYING SEASON



NORMALIZED OCTOBER 85 FRITZ

WT: 7.20 mg

SCAN RATE: 5.00 deg/min

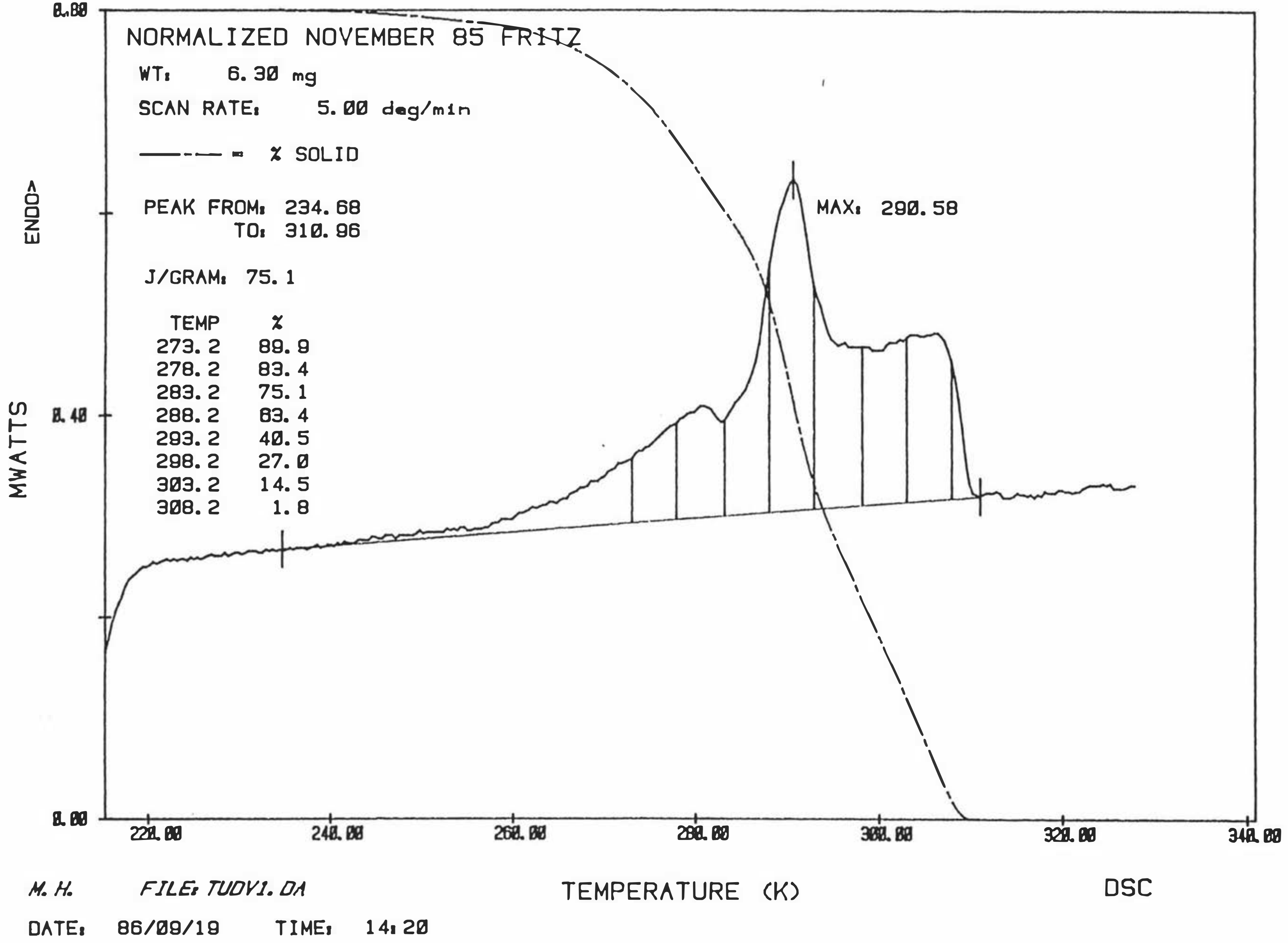
PEAK FROM: 232
TO: 311

J/GRAM: 62.28

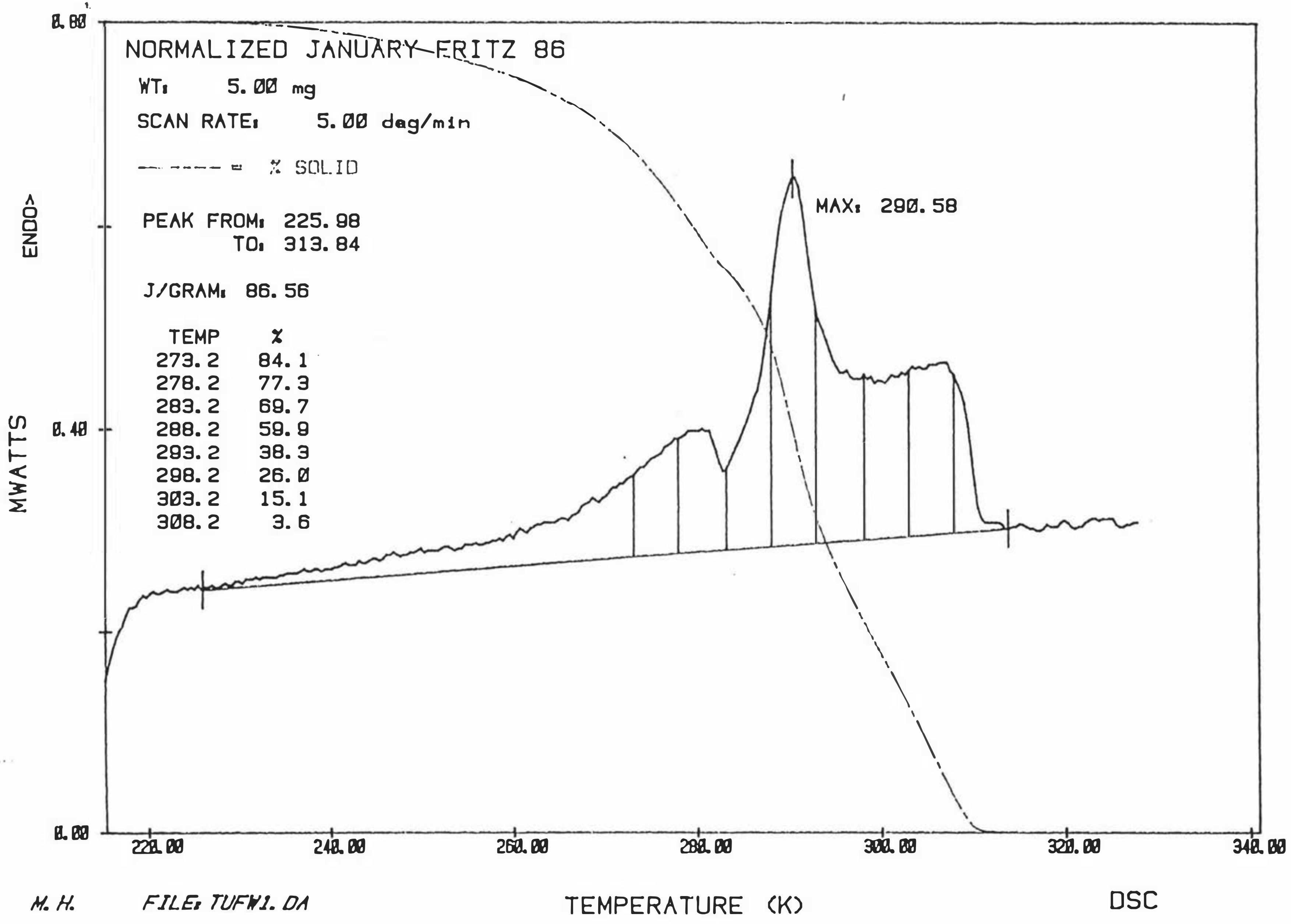
TEMP	%
273.2	87.7
278.2	80.6
283.2	71.7
288.2	58.7
293.2	36.8
298.2	23.8
303.2	12.1
308.2	1.0

M. H. *FILE: TUCVI. DA*

DATE: 86/09/19 TIME: 12:15



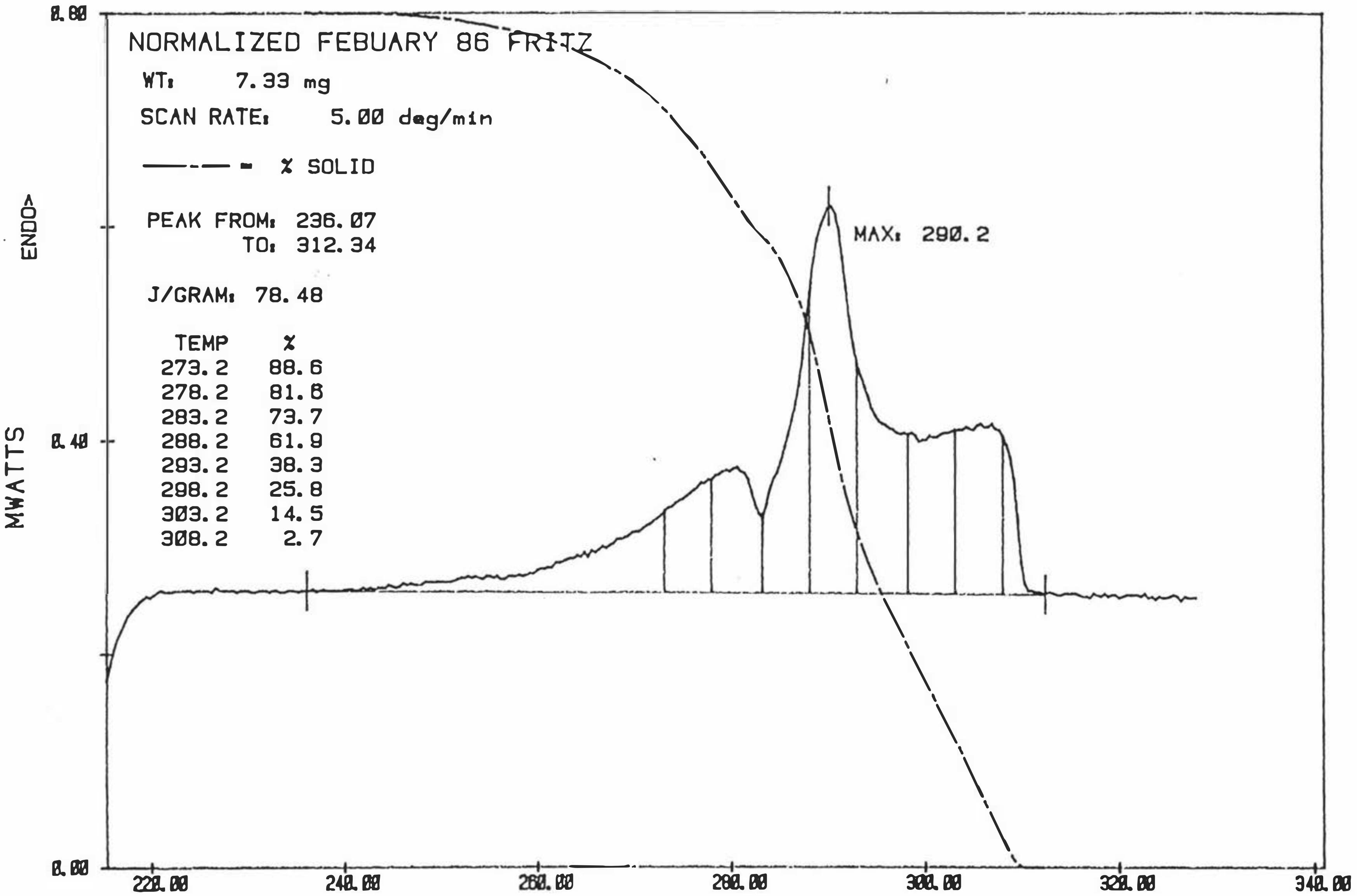
TEMP	%
273.2	89.9
278.2	83.4
283.2	75.1
288.2	63.4
293.2	40.5
298.2	27.0
303.2	14.5
308.2	1.8



TEMP	%
273.2	84.1
278.2	77.3
283.2	69.7
288.2	59.9
293.2	38.3
298.2	26.0
303.2	15.1
308.2	3.6

M. H. *FILE: TUFW1. DA*

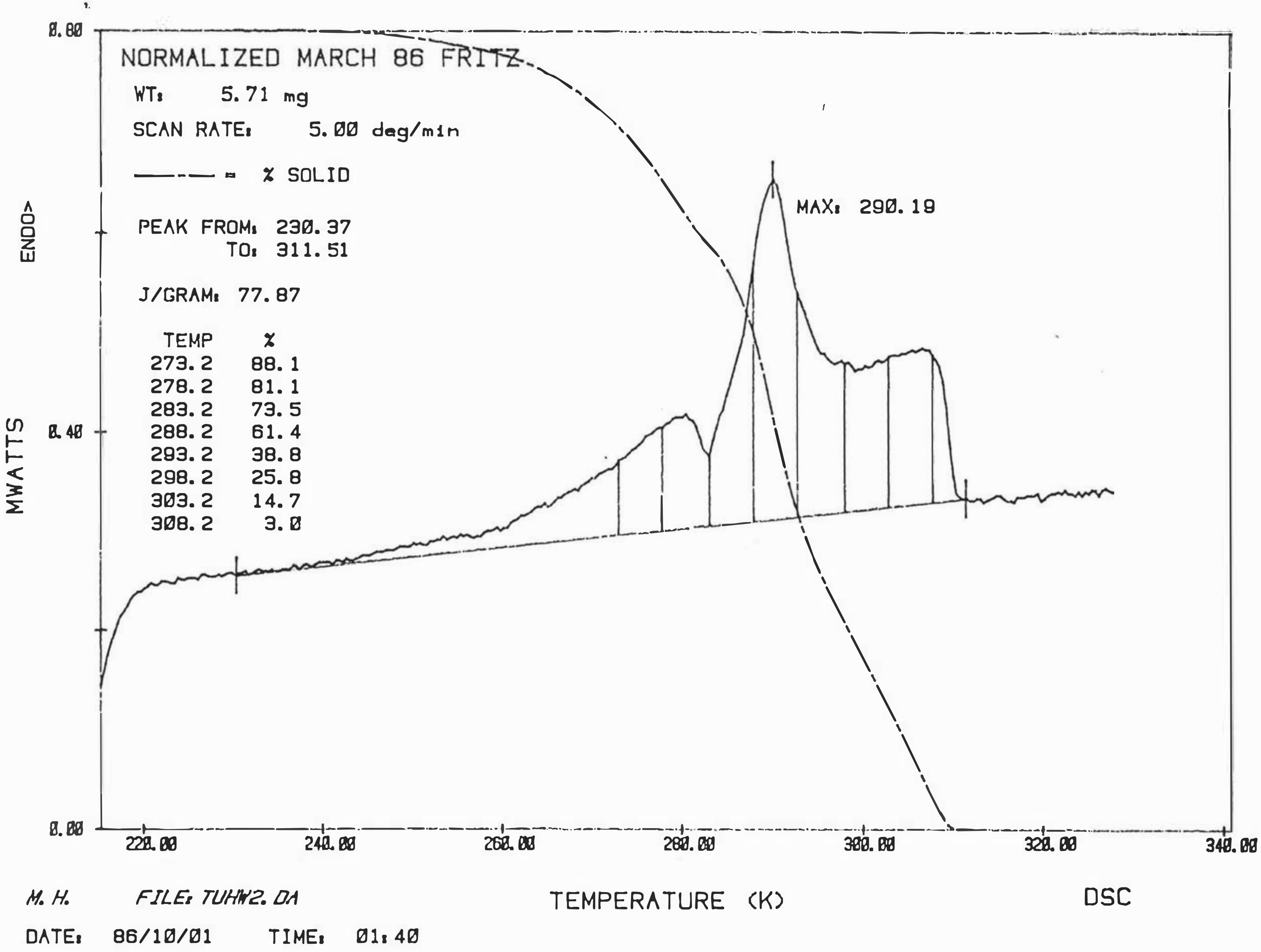
DATE: 86/09/24 TIME: 15:28



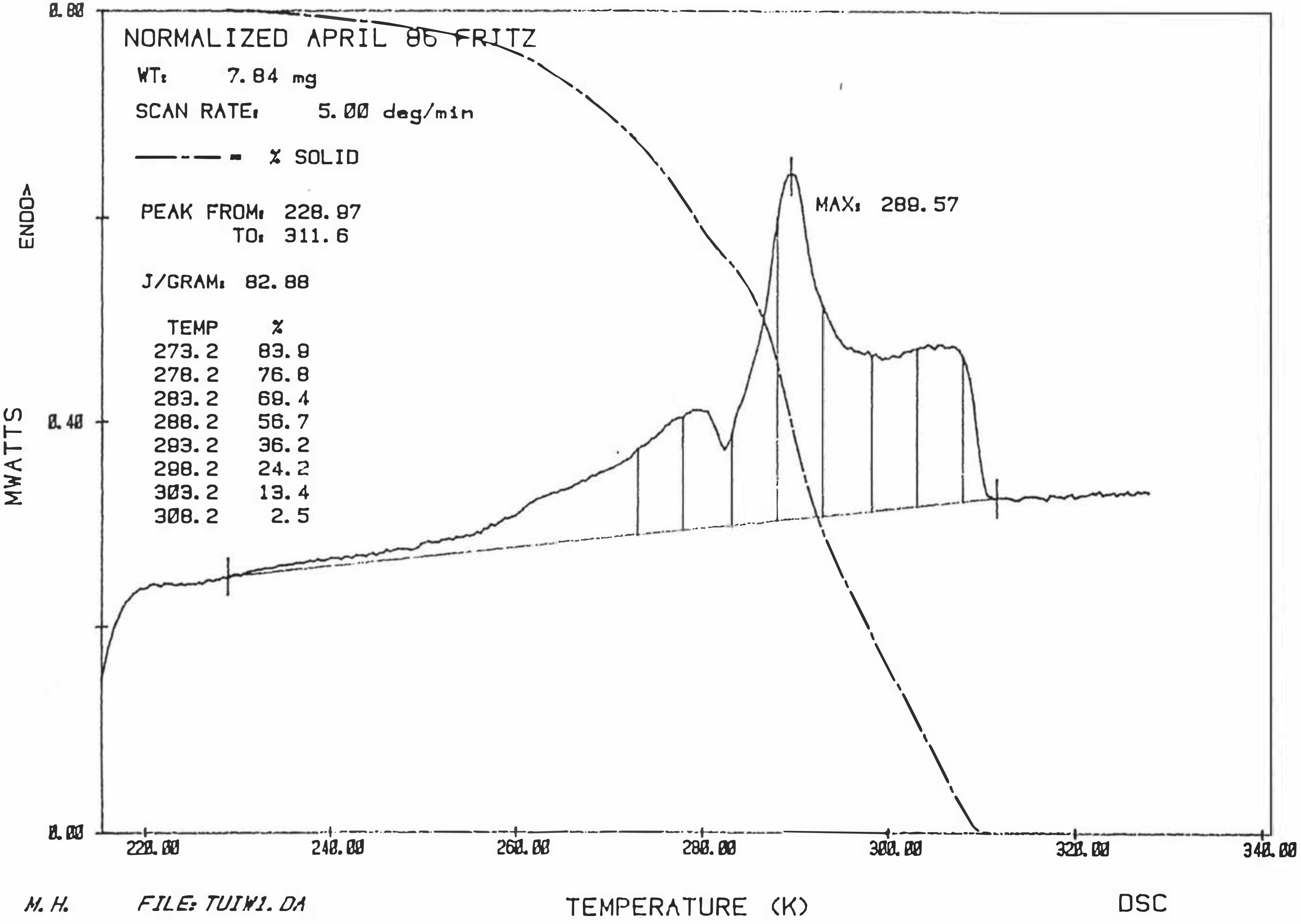
TEMP	%
273.2	88.6
278.2	81.6
283.2	73.7
288.2	61.9
293.2	38.3
298.2	25.8
303.2	14.5
308.2	2.7

M. H. *FILE: TUGW1. DA* TEMPERATURE (K) DSC

DATE: 86/09/30 TIME: 11:07



TEMP	%
273.2	88.1
278.2	81.1
283.2	73.5
288.2	61.4
293.2	38.8
298.2	25.8
303.2	14.7
308.2	3.0



NORMALIZED APRIL 86 FRITZ

WT: 7.84 mg

SCAN RATE: 5.00 deg/min

—·—·■ % SOLID

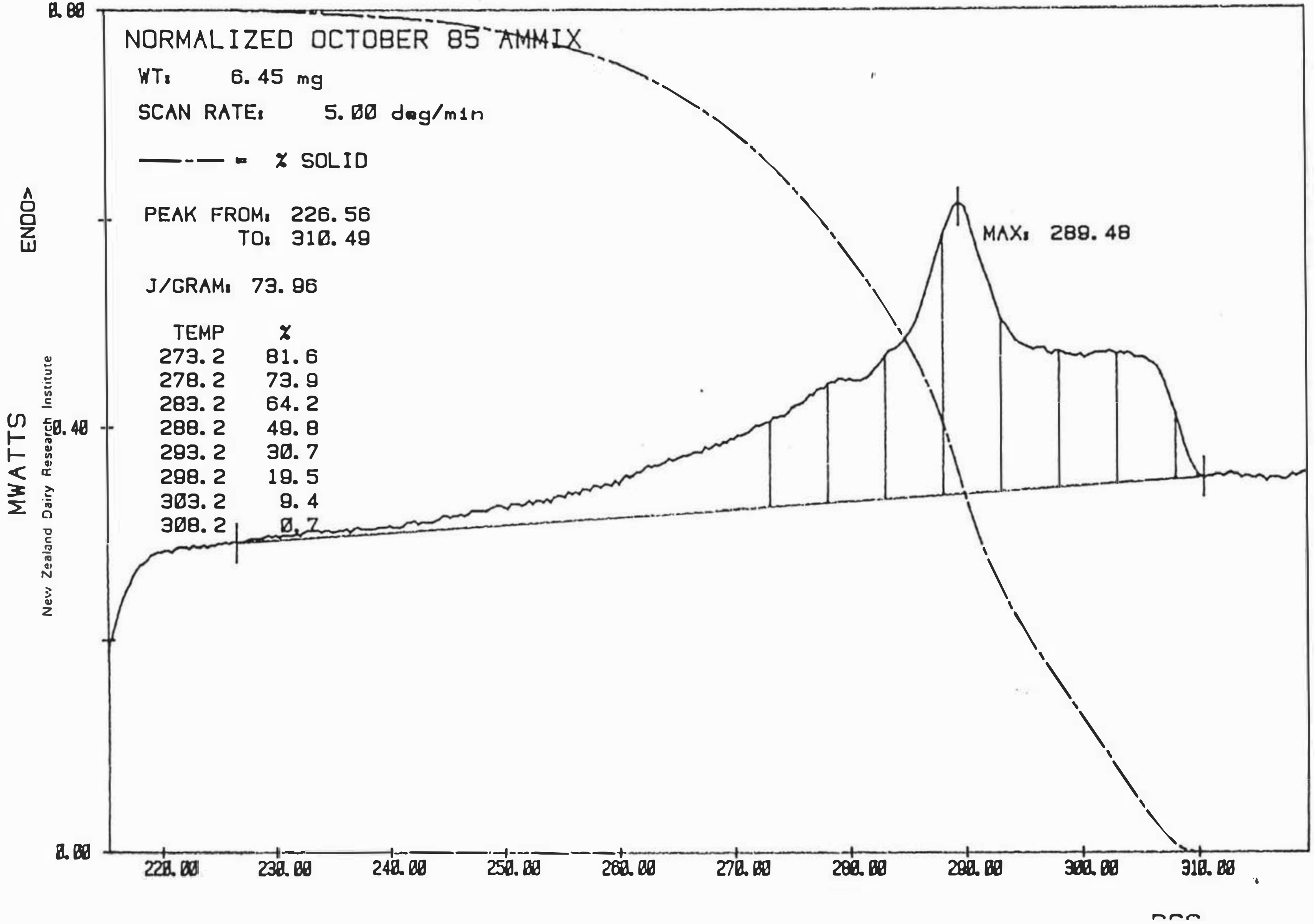
PEAK FROM: 228.87
TO: 311.6

J/GRAM: 82.88

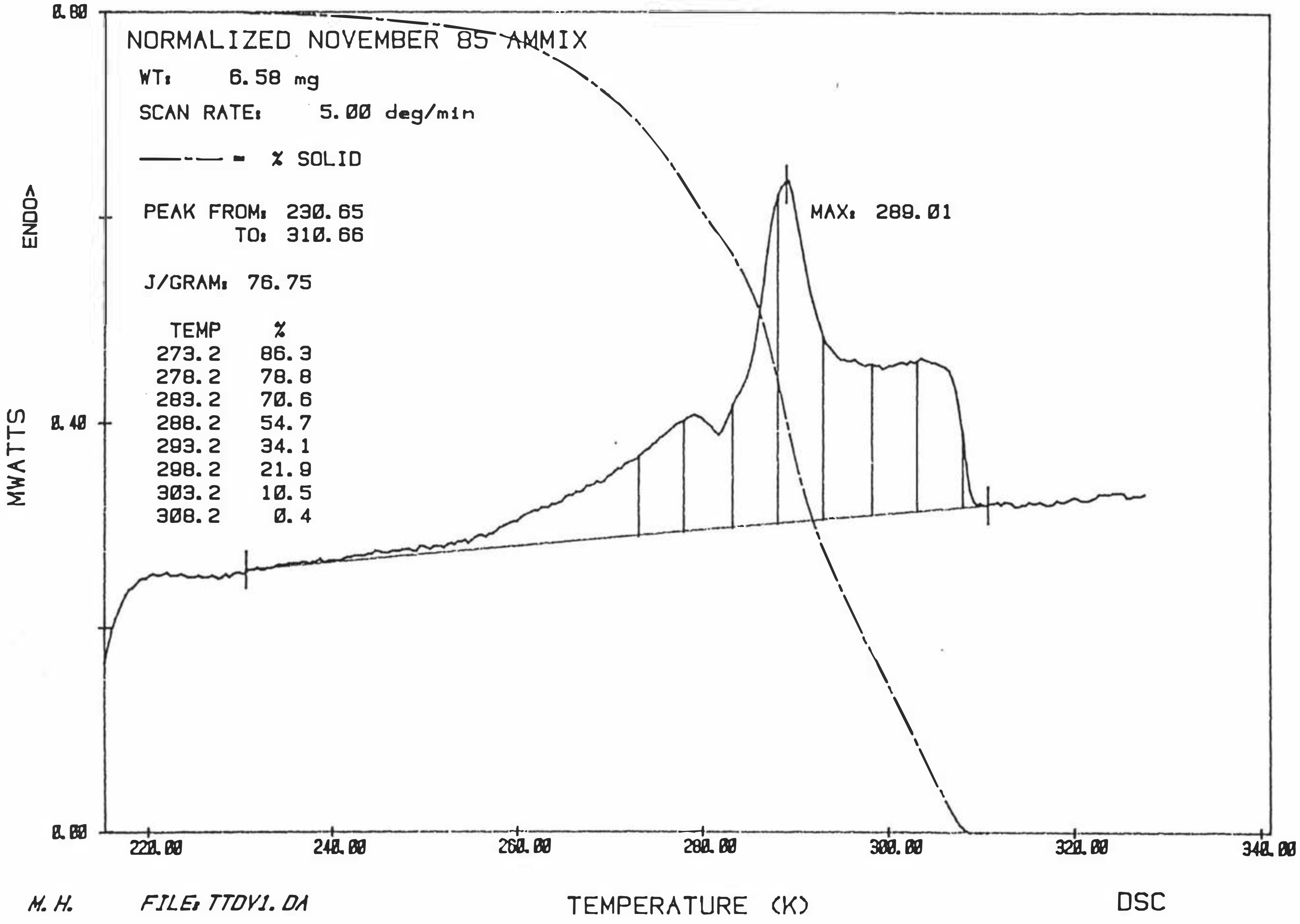
TEMP	%
273.2	83.8
278.2	76.8
283.2	68.4
288.2	56.7
283.2	36.2
288.2	24.2
303.2	13.4
308.2	2.5

M. H. *FILE: TUIW1. DA*

DATE: 86/10/01 TIME: 02:09

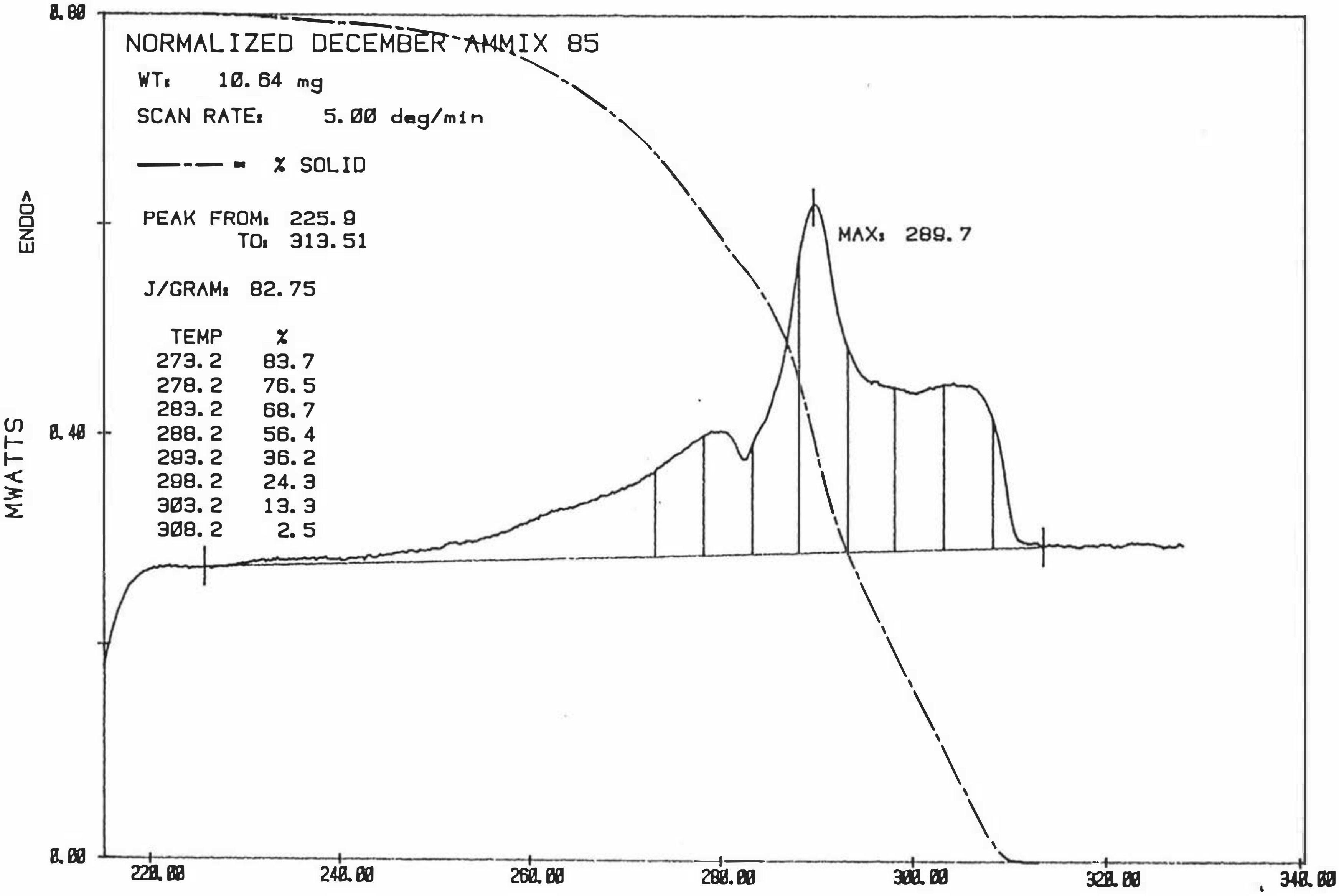


TEMP	%
273.2	81.6
278.2	73.9
283.2	64.2
288.2	49.8
293.2	30.7
298.2	19.5
303.2	9.4
308.2	0.7



M. H. FILE: TTDV1.DA

DATE: 86/09/19 TIME: 13:26



NORMALIZED DECEMBER AMMIX 85

WT: 10.64 mg

SCAN RATE: 5.00 deg/min

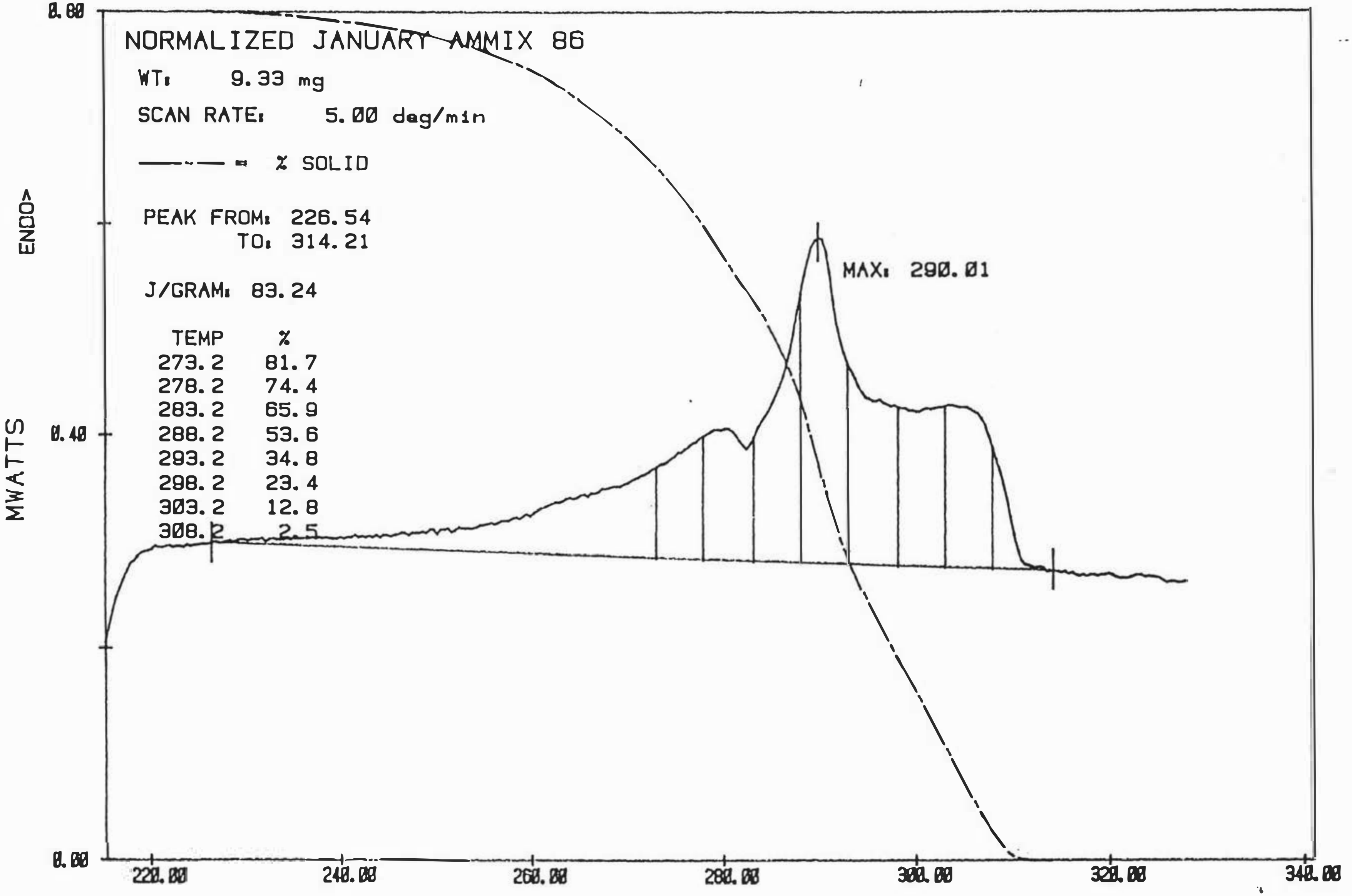
—·—·— = % SOLID

PEAK FROM: 225.9
TO: 313.51

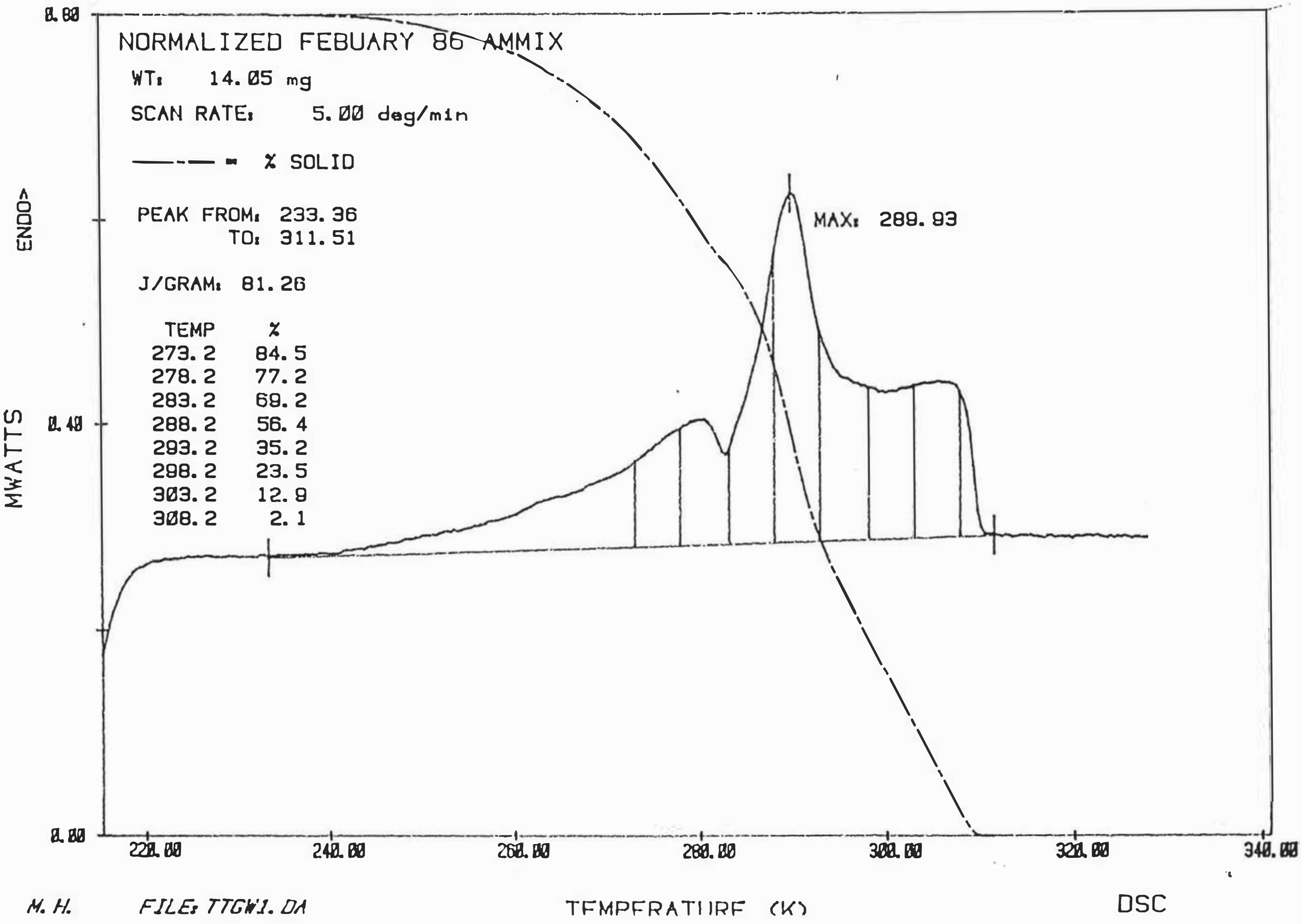
J/GRAM: 82.75

TEMP	%
273.2	83.7
278.2	76.5
283.2	68.7
288.2	56.4
293.2	36.2
298.2	24.3
303.2	13.3
308.2	2.5

MAX: 289.7



TEMP	%
273.2	81.7
278.2	74.4
283.2	65.9
288.2	53.6
293.2	34.8
298.2	23.4
303.2	12.8
308.2	2.5



NORMALIZED FEBUARY 86 AMMIX

WT: 14.05 mg

SCAN RATE: 5.00 deg/min

—-— = % SOLID

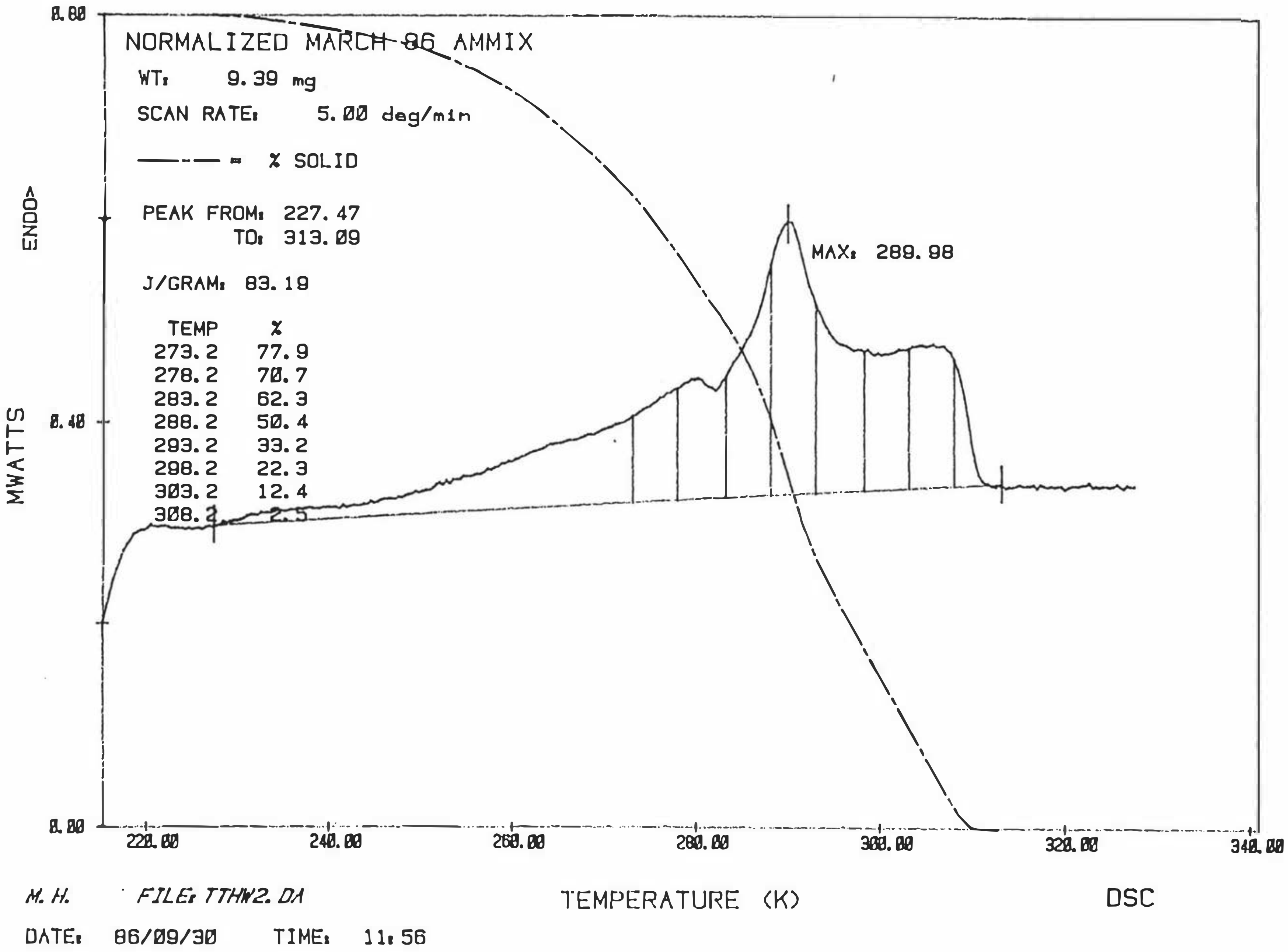
PEAK FROM: 233.36
TO: 311.51

J/GRAM: 81.26

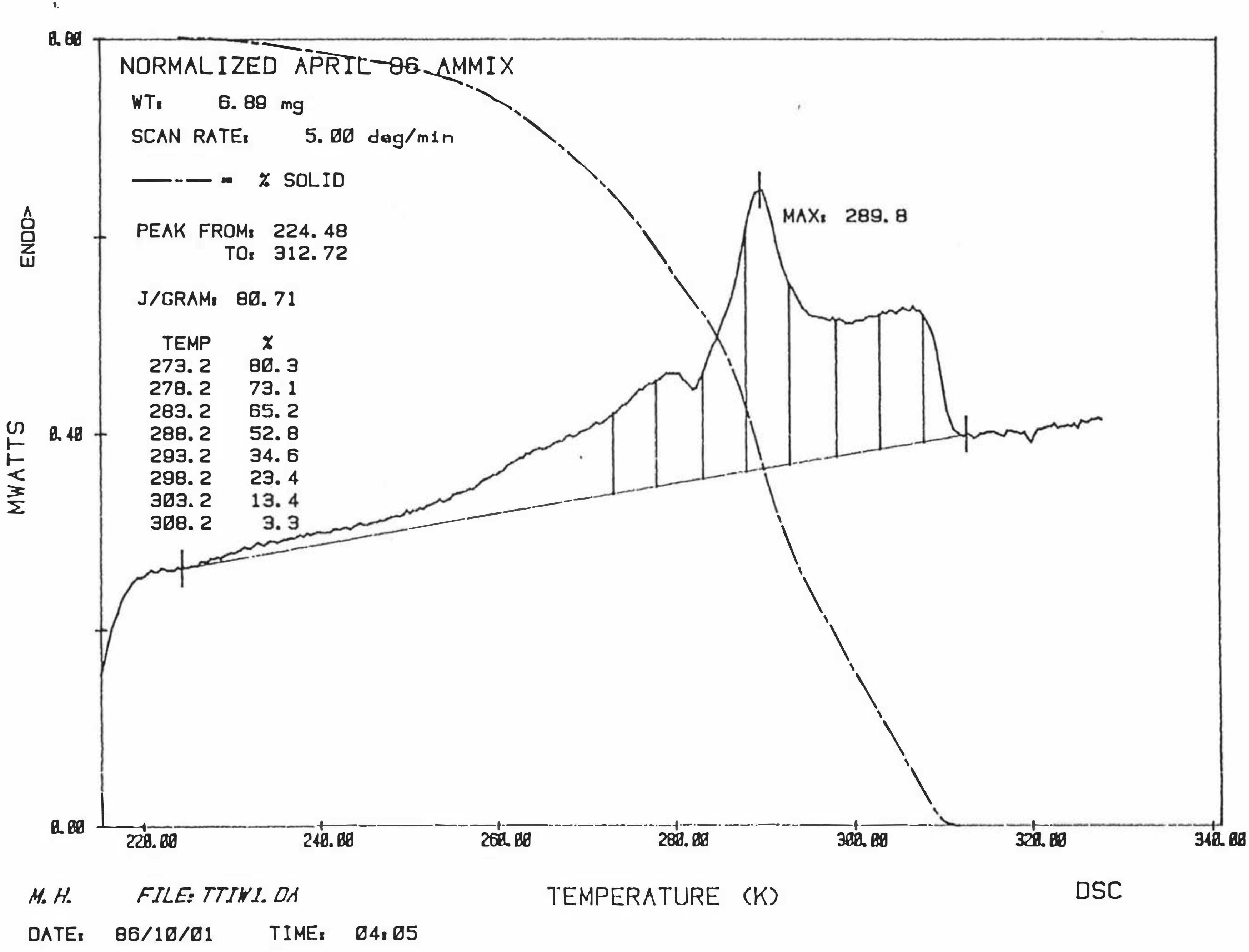
TEMP	%
273.2	84.5
278.2	77.2
283.2	69.2
288.2	56.4
293.2	35.2
298.2	23.5
303.2	12.9
308.2	2.1

MAX: 289.83

M. H. FILE: TTGW1. DA



TEMP	%
273.2	77.9
278.2	70.7
283.2	62.3
288.2	50.4
293.2	33.2
298.2	22.3
303.2	12.4
308.2	2.5



NORMALIZED APRIL 86 AMMIX

WT: 6.89 mg

SCAN RATE: 5.00 deg/min

PEAK FROM: 224.48
TO: 312.72

J/GRAM: 80.71

TEMP	%
273.2	80.3
278.2	73.1
283.2	65.2
288.2	52.8
293.2	34.6
298.2	23.4
303.2	13.4
308.2	3.3

M. H. *FILE: TTIW1. DA*

DATE: 86/10/01 TIME: 04:05

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