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Rheological Properties of Milkfat and Butter

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ABSTRACT: Butter and milkfat are examples of plastic materials for which texture is a critical factor in determining functionality and consumer acceptance. The methods by which butter rheology is characterized are discussed, including large deformation techniques such as cone penetrometry, compression, sectility and extrusion, and methods which involve testing at low levels of strain. Correlations between instrumental tests and sensory-evaluated properties of the fats are explored. Rheological properties, including hardness, spreadability, setting, work softening, and thixotropy are described, and the models which have been proposed to characterize these behaviors are reviewed. Techniques which have been devised recently to quantitatively relate structural measurements to rheology are also examined. Modification of butter's rheological properties can be accomplished through alterations in composition or in the manufacturing process. These approaches are discussed and evaluated.

Introduction

TEXTURE IS ONE OF THE 4 QUALITY factors which determine butter's acceptability (Bourne 1982). It influences spreadability, taste, mouthfeel, appearance, and butter's suitability for various uses (Mulder and Walstra 1974). This has been an area of great interest and economical importance for dairy industries around the world, with the primary focus being improved butter spreadability. However, the composition and structure of the constituent milkfat are largely responsible for the rheological properties of butter (Haighton 1965; Kawanari and others 1981; Prentice 1972; Shama and Sherman 1968). Therefore, the rheology of milkfat as well as butter are important considerations in quality evaluations.

Butter is a multiphase emulsion, consisting of fat globules, crystalline fat, and an aqueous phase dispersed in a continuous oil phase (Juriaanse and Heertje 1988). The textural properties of butter and milkfat are intimately linked to their underlying structures. Cream undergoes a phase inversion during churning as fat globule membranes are disrupted, globules coalesce, and oil leaks out to form the continuous phase. This continuous oil phase contains crystal aggregates along with remnants of damaged and intact fat globules (Kalab 1985). Milkfat and butter's yield values and viscoelastic behaviors are a result of this 3-dimensional network of fat crystals intimately associated with a continuous oil phase (deMan and Beers 1987). Fat crystal networks are held together by van der Waals forces (Haighton 1963). The extent of solidification, and hence the ratio of solid to liquid fat, is the primary determinant of butter consistency (Rohm and Weidinger 1993). The aqueous phase of butter, which represents between 15 and 20% of the total mass, is present in small droplets less than 10 μm in diameter (Kalab 1985). The presence of this globular water may lead to an increase in the effective viscosity of the system and lends rigidity to the system because of the high energy needed to overcome the surface tension of the globules (Prentice 1992).

Much of our understanding of butter structure comes from polarized light microscopy studies (King 1962, 1964; Vasic and deMan 1966; Walstra 1962), confocal scanning laser microscopy (Heertje and others 1987), and electron microscopy using both ultrathin sections of chemically fixed samples (Knoop, Knoop and Wortmann 1966; Knoop and Schulz 1960; Knoop and Wortmann 1962), fractured surfaces (Knoop and Knoop 1962; Knoop, Knoop and Wortmann 1966; Okada 1962), and freeze-fracture techniques (Buchheim 1978; Precht and Buchheim 1979; Precht and Buchheim 1980; Precht and Peters 1981). For a review of milkfat and butter structures, see deMan and Beers (1987), Precht (1988), and Juriansse and Heertje (1988). This paper will review the techniques used to characterize milk lipid rheology, our current understanding of milkfat and butter rheology and its relationship to structure, and the approaches used to modify the behavior of milkfat and butter.

Milkfat rheology

Most of the tests used to characterize milkfat rheology are empirical in nature and designed to imitate sensory perceptions for quality control operations. These are based mainly on the principles of penetrometry, extrusion, and sectility (Prentice 1972) and involve large deformations which break down the material's structure. The response of the material to an applied stress provides an index for some consistency parameter which is generally used to regulate a step in the buttermaking process or to adjust milk blending operations. The need to try and understand the structural features that give rise to butter's rheological properties was responsible for a shift from using large deformation tests solely for empirical measurements of butter consistency to attempts to evaluate test-independent material properties (Prentice 1972). Tverdokhleb's 1949 and Mulder's 1953 papers were among the earliest to use this new approach (Prentice 1972). Small deformation techniques have also been used to probe a material's response to stress. These have the advantage that strains are low enough to keep the structure intact (Borwankar 1992).

Large deformation testing of milkfat

Penetrometry

The most commonly used test to evaluate butter texture has been penetrometry (deMan and Beers 1987). Brulle (1893) first applied this technique by placing a steel rod just above a butter sample and loading it with weights until it rapidly penetrated the fat. In penetrometry, the depth to which the penetrating body (a cone, needle, or sphere) falls when released for a specified length of time, or the rate at which it falls, is measured (Sherman 1976). Cone penetrometry with constant load is still widely used to evaluate butter texture. It offers a simple and economical method, and the results obtained correlate

well with sensory evaluation (Dixon 1974). Standardized tests and commercial standards of design are also available for cone penetrometry. The most widely used is that of the American Oil Chemists' Society (American Oil Chemists' Society 1960). The shape of a typical cone used in penetrometry is shown in Figure 1.

The depth (d) to which the cone penetrates the sample, in increments of 0.1 mm, is read and is an indicator of consistency (American Oil Chemists' Society 1989). The relationship between consistency and a material parameter that can be related to other tests of butter rheology is a function of various properties of the butter, the geometry of the penetrometer, and penetrometer load. For butter, one material parameter that is fundamental to the quality of the product is its resistance to shear. Dolby (1941a) defined this as hardness. For a penetrometer test, hardness has been defined by Vasic and deMan (1968) as the ratio of load to the area of the impression made by the penetration, on the grounds that "the cone will sink into the fat until the stress exerted by the increasing contact surface of the cone is balanced by the hardness of the fat" (deMan 1983). This definition of fat hardness is akin to the Brinell hardness definition for metals, except that for metals the residual impression area is measured after removing the penetrometer (Tabor 1948). For a simpler cone geometry (sharp-ended cone) where the truncation of the tip in Figure 1 is absent, there is a unique geometric relationship between the depth of penetration and the penetration area. Therefore, the relationship between the applied load (P), the hardness (H), and penetration impression area (A_{imp}) and depth (d) are given by:

$$H = \frac{P}{A_{imp}} = \frac{P\cos(\varepsilon)}{\pi d^2 \tan(\varepsilon)} \quad (1)$$

For the truncated cone (Figure 1), the absence of the tip infers that, at a given penetration depth, penetration area will be greater than that given by Eq. 1. From Vasic and deMan (1968), the hardness for the truncated cone can be expressed as:

$$H = \frac{P}{A_{imp}} = \frac{P}{\frac{\pi d}{\cos(\varepsilon)}\left[2r + d\tan(\varepsilon)\right] + \pi r^2} \quad (2)$$

One advantage of expressing butter consistency as a hardness value, rather than as penetration depth, is that it should normalize consistency values so as to make them independent of the load applied to the penetrometer. This is the rationale behind hardness testing in metallurgy, where the contact pressure defined by hardness in Eq 1 is used to deduce the yield stress of the material (Tabor 1996). However, the yield stress of the material, which is a measure of the resistance to the applied shear stresses, is not the only resistance to cone penetration. The elastic properties of the fat and the coefficient of friction between the cone and the fat will also impede further penetration of the cone (Tabor 1948). In an attempt to obviate the effects of friction, Kruisher and others (1938) advocated the use of flat circular penetrometers with concave sides.

In principle, the truncated cone specified in AOCS Cc16.60 could be used to measure the elastic properties of the fat if a constant speed penetrometer is used (Briscoe and Sebastian 1993). The elastic modulus of butter was measured in this fashion by Diener and Heldman (1968) with a flat circular die at a number of crosshead speeds and at 2 temperatures. However, because of the large strains associated with small angle cone penetrometers (Atkins and Tabor 1965), and the importance of yielding and flow to the end-use properties of butter (Haighton 1959; Prentice 1972; Scott-Blair 1938), considerably greater effort has been devoted to relating hardness values to the yield stress of the material rather than to its elastic properties.

The International Dairy Federation (Walstra 1981) proposed that, for a sharp-ended cone, penetration depths be converted to "apparent yield stress" (AYS) values according to the following relationship:

$$AYS = \frac{P}{A_{proj}} = \frac{gw}{\pi d^2 \tan^2(\varepsilon)} \quad (3)$$

where g is acceleration due to gravity, w is the weight of the cone assembly, ε refers to the cone angle (the same as in Figure 1), and d is the penetration depth. The hardness defined in Eq. 1 and the AYS in Eq. 3 are related to each other simply by a $\sin(\varepsilon)$ term because A_{proj}, the projected area (the area associated with the dotted line in Figure 1) is used in Eq. 3 rather than the impression area (Mohr and Wellm 1948). Haighton (1959) also suggested using a smooth angle cone and converting penetrometer readings into a "yield value" (C) according to the following formula:

$$C = \frac{Kw}{d^n} \quad (4)$$

where w is the weight of the cone, d is the penetration depth, and K is a factor depending on the cone angle (2,). The constant n was found empirically to approximate to a value of 2, but deMan (1976) and Mortensen and Danmark (1981) found that it varied with the structure of the sample. For plastic fats, a value of 1.6 is often used. Using yield values defined in such a manner, an index of butter spreadability (S) can be calculated from measurements of "yield stress" obtained with a constant weight penetrometer before and after working. This index is shown in Eq. 5 where f_u and f_w are the "yield stresses" before and after working respectively

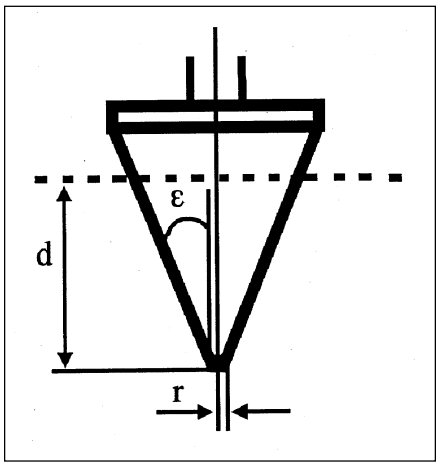

Figure 1—Schematic description of a typical cone used in cone penetrometry (Adapted from deMan, 1976)

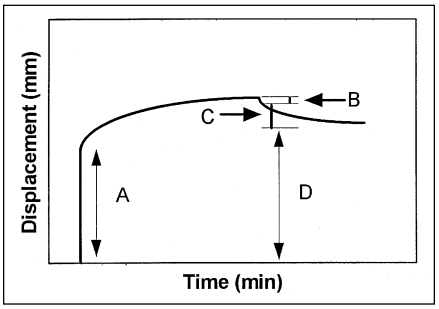

Figure 2—Typical creep curve for a plastic fat. A: instantaneous deformation of loading; B: instantaneous recovery of unloading; C: time-dependent recovery: D: permanent deformation (Adapted from deMan and Beers 1987)

(Haighton, 1965).

$$S = f_u - 0.75\left[f_u - fw\right] \quad (5)$$

Most of the original penetrometers were designed to fall under the constant load of the penetrating body. Kruisheer and others (1938) described one of the first constant speed penetrometers. Tanaka and others (1971) advocated the use of this design in which the penetrating body is mechanically driven into a sample at a constant speed and the force required to do so is measured. Constant speed penetrometry allows for better control over the depth of penetration, and permits a number of hardness values with increases in penetration depth to be calculated from the butter's load-deformation response. An additional advantage of constant speed penetrometers, where the load-deformation response can be monitored upon unloading of the sample, is that additional textural characteristics can be derived from the penetrometer test (Glenn and Johnston 1992; Page 1996).

Compression

The use of compression for deriving useful technological and end-use properties from milkfat and butter samples also has a long history (Davis 1937; Dolby 1941a; Mohr and Wellm 1948; Scott-Blair 1938). In such a test, a compression sample is prepared (typically a cylinder or a prism) and is placed between 2 flat platens. In this way, a uniform stress is applied to the top and bottom surfaces of the sample. Extraction of empirical or fundamental parameters used to classify the properties of the sample is therefore more straightforward than with a penetrometer.

Typically, the compression test is used in creep tests, so that a constant load is applied to the top platen and the deformation of the butter sample over time is recorded (not necessarily a constant rate of deformation). An example of a creep curve (where compliance is plotted against time) is given in Figure 2. Two parameters that are often extracted are: A (from the beginning of the creep curve) the instantaneous elastic compliance, from which a modulus is calculable; and E (from the end of the creep curve) the limiting viscosity, from the reciprocal of the slope. Scott-Blair (1938) used the mean viscosity over the course of 50% compression of the sample in a creep test to define the spreadability of butter, although he remarked that spreadability was in reality a psychological property. The fundamental parameters that can be obtained from creep compliance tests have been related to molecular mechanisms (Davis 1973; deMan and others 1985; Shama and Sherman 1970).

Compression tests can also be used in constant speed tests, where the top platen moves down on the top sample surface at a constant rate of travel, and the load is monitored as well as the deformation. A load-deformation curve for a milkfat sample (crystallized for 24 h at 5 °C) is shown in Figure 3. Three parameters can be derived from the curve. The initial stiffness can be used with the sample dimensions to obtain a compressive modulus for the milkfat, while yielding of the sample is readily apparent at the end of this elastic regime, so that a yield stress can be determined from F_y. Dixon (1974) stated that measures of butter firmness and plasticity could be derived in this manner. Once the applied stress has exceeded the yield stress, the fat will flow outwards due to continued movement of the top plate. If contact between the platens and milkfat is frictionless, the change in force with decrease in sample height can be used to derive an apparent biaxial extension viscosity (Casiraghi and others 1985) which can be related to "pseudoviscosities" obtained from other large deformation tests.

Although the compression test is less complex to analyze than penetrometry, complications can arise from experimental artifacts so that different values for mechanical properties can be obtained from identical butter samples. Dixon (1974) observed that compression samples should not be too long (to prevent bowing), nor too short (to prevent end-effects). One end-effect in compression is the constraint of lateral spreading of the butter sample that can arise from the coefficient of friction between the platens and the sample (Casiraghi and others 1985). This generates different stress-strain curves for identical samples of different height-to-width ratios. Comprehensive studies of the effects of such constraint has been provided for cheese (Charalambides and others 1995; Culioi and Sherman 1976), but such studies do not appear to have been performed for milkfat or butter.

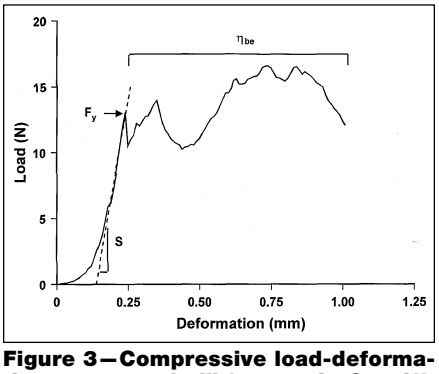

Figure 3—Compressive load-deformation response of milkfat sample; S = stiffness, F_y = yield force, and η_{be} is apparent biaxial extensional viscosity

Sectility

Plastic fats have also been characterized by sectility measurements (Dolby 1941a, 1941b; deMan and Wood 1958a; Dixon and Williams 1977; Mohr and Wellm 1948). This involves forcing a stretched steel wire through a sample. The load required for the wire to cut through the sample at a constant rate can be used to provide a measure of firmness (Dolby 1941a). A more common practice nowadays, though, is that the wire is driven through the sample at a constant speed and the counteracting force is measured (Hayakawa and others 1986).

Dolby (1941a) showed, at a cutting rate of 6 mm/min, that the cutting force required to pass through butter was approximately linearly related to wire diameter and cutting length of the wire. The analysis of Luyten and others (1991) would infer that the deviation from linearity is an experimental artefact, and that exactly linear relationships should be observed. As a result, Luyten and others (1991) were able to extract fracture toughness values for cheeses of different maturity using the sectility test. The question of whether butter or milkfat (which readily yield) would have toughness values is debatable (deMan 1969), but the generation of cracks in large butter masses (Brady and others 1978; deMan 1976) infers that a value should be measurable. A reevaluation of Dolby's (1941a) experimental points (his Figure 3) according to the analysis of Kamyab and others (1998) indicates that butter does have a fracture toughness value, but at 60 J/m^2, this reevaluation appears high based on a comparison with values obtained from precise constant-cutting-speed experiments on cheese (Kamyab and others 1998; Luyten and others 1991). Nevertheless, this toughness value does permit accurate prediction of Dolby's cutting forces for samples of different thickness (his Figure 2, Dolby, 1941a).

Sectility tests have also been used to derive a yield stress for cheese (Goh and others 2000; Kamyab and others 1998). However, performing sectility measurements on butter at different cutting rates was used by Dolby (1941b) to show that, at 12.5 EC, butter does not exhibit a yield value and that a pseudoviscosity is a more appropriate descriptor of butter properties (Dixon and Williams 1977). Mulder and Walstra (1974) showed that, for a range of butter consistencies, the ratio of apparent yield stress to pseudoviscosity was a constant.

Extrusion

Extrusion devices have also been used to evaluate butter texture, albeit to a lesser extent than the other techniques. Since the action of spreading butter requires flow of the butter, then a process requiring flow and thus designed to mimic the action of spreading, should provide measurements that relate to spreadability (Prentice 1972). Prentice (1954) argued that most of the methods available to evaluate butter firmness involved very slow rates of deformation and, therefore, reflected the material's yield value. However, the action of spreading butter involves rapid deformation and substantial flow. To achieve rapid deformation under test conditions, he designed an extruder which was sold commercially as the FIRA/NIRD Extruder (H.A. Gaydon and Co. Ltd., Surrey, England). This has been the instrument of choice in extrusion studies, although Vasic and deMan (1967) also described an extrusion attachment for a Kramer shear press. A schematic diagram of an extruder is shown in Figure 4.

In extrusion studies, a fat sample is extruded through an orifice at a constant speed and the thrust (force required to sustain motion) is recorded. There are 2 types of forces acting in an extruder (Prentice 1972). When the rate of extruder piston movement remains constant, a constant force is required to actually extrude the sample through the orifice. This is independent of the volume of sample in the extruder's barrel. Extrusion friction of the butter along the walls of the barrel represents the second force component. The frictional force is proportional to the amount of sample in the barrel. As the extrusion proceeds and the barrel empties, there is less sample friction and so the overall thrust decreases. When the extruder is almost empty, frictional forces no longer make a significant contribution and the force remaining is solely that required to maintain extrusion (extrusion thrust) (Prentice 1972). Extrusion thrust has been inversely correlated with spreadability, and extrusion friction may be directly proportional to stickiness (Kulkarni and Rama Murthy 1987).

Comparison of techniques

Large deformation techniques are generally simple and rapid and require relatively inexpensive equipment. These instrumental methods continue to be used because they correlate with some subjective measure of butter consistency. Dixon (1974) and Kawanari and others (1981) showed that strong relationships existed between various parameters derived from such tests, suggesting that similar physical properties were being measured by the different techniques. A major criticism of these large deformation tests is that it is difficult to correlate measured parameters with fundamental properties of the material (Shellhammer and others 1997). Because the structure is broken down and the specific conditions of stress and strain in a test sample are often intractable, it has been stated that fundamental rheological information cannot be obtained (Shukla and others 1994). Also, because the concept of texture is complex, describing it with a single parameter like "yield stress" or "hardness" may not be appropriate (Mortensen and Danmark 1982b). However, as remarked by Scott-Blair (1938), measurement of recognizable physical properties in absolute units, such as apparent modulus, yield stress, or viscosity, may be preferable to measurement of ill-defined empirical parameters just because they are better correlated to texture.

Correlation of large deformation tests with sensory evaluation

Despite the limitations of empirical testing, results often do correlate well with sensory evaluation. For example, the correlation between 3 instrumental methods to assess consistency, including cone penetrometry, disc penetrometry and sectility, and spreadability estimated by a panel of judges was approximately –0.9 (Mortensen and Danmark 1982b). Correlations were found in the comparison of apparent yield values determined from cone penetrometry and constant load and spreadability evaluated by panelists using magnitude estimation. Sectility was found to correlate best with the sensory perception of hardness, while apparent yield values correlated with the assessment of spreadability (Rohm 1990; Rohm and Ulberth 1989). Spreading, biting, and chewing involve breaking down butter's structure, so large deformation tests are useful in understanding textural properties (Borwankar 1992). Butter texture has been evaluated in sensory studies using structured interval scales (deMan and others 1979; Mortensen and Danmark 1982b), unstructured intervals scales (Dixon and Parekh 1979; Pokorny and others 1984), and magnitude estimation (Rohm and Ulberth 1989). These types of analysis are notoriously complicated, expensive, and time-consuming (Pokorny and others 1984), so the possibility of replacing sensory evaluation with an instrumental method is very attractive (Kamyab and others 1998). Attempts to correlate instrumental tests with sensory attributes of fats have been numerous (deMan and others 1979; Dixon and Parkeh 1979; Shama and Sherman 1968; Vasic and deMan 1968).

A number of correlations between empirical and sensory tests have been reported (Dixon and Parekh 1979; Dixon and Williams 1977; Mohr and Wellm 1948; Mortensen and Danmark 1982b). For example, Haighton (1969) reported that both cone penetrometry and extrusion tests predicted the consumer assessment of texture quite well. Butter cold spreadability was evaluated by a trained panel, and the results correlated well with cone penetrometry data (Rousseau and Marangoni 1999). Mortensen and Danmark (1982b) found that yield stresses, determined from both penetrometry and sectility, correlated well with spreadability determined by a consumer panel. Figure 5 shows the relationship found between yield stress and sensory spreadability.

Some instruments have been specifically designed to mimic sensory evaluations of butter texture. Kapsalis and others (1960) developed the Consistometer, based on a design by Huebner and Thomsen (1957); Dixon (1966) described a triaxial compression test in

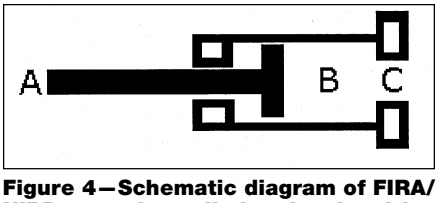

Figure 4—Schematic diagram of FIRA/NIRD extrusion cylinder showing drive shaft and plunger (A), extrusion cylinder (B), and orifice (C) (Adapted from Prentice 1954)

which both shear and deformation could be determined; and Davey and Jones (1985) evaluated the use of a sliding pin consistometer. Pompei and others (1988) developed and compared 2 imitative methods which used an Instron Machine to simulate manual spreading. In each of these cases, some parameter was found to be reasonably correlated with sensory assessments of butter spreadability or hardness ($P < 0.05$).

Small deformation testing of milk lipids

Many studies have demonstrated that butter exhibits viscoelastic behavior at small stresses (Chwiej 1969; Pijanowski and others 1969; Shama and Sherman 1970; Sherman 1976; Shukla and Rizvi 1995). Viscoelasticity can be probed by evaluating the relationships between stress, strain, and time, using small deformations. This should be carried out within the region where the relationship between stress and strain is linear, and when the sample's structure remains intact. Typically, this occurs at critical strains of less than 1.0% (Mulder and Walstra 1974), although the linear viscoelastic region (LVR) may be limited to strains less than 0.1% (Rohm and Weidinger 1993). Figure 6 shows a stress sweep for a sample of milkfat. The initial flat portion of the curve is the LVR, where the storage modulus (GN) is independent of the applied stress (Shukla and Rizvi 1995).

As with parameters derived from large strain tests, the rheological parameters within the LVR are strongly dependent on temperature (Rohm and Weidinger 1993; Shukla and Rizvi 1995). Also, oscillation frequency affects the ratio of viscous to elastic behavior (tan δ). At higher frequencies, a more solid-like response is observed (Drake and others 1994; Rohm and Weidinger 1993). With increasing frequency the complex viscosity (η^*) and viscous modulus (G'') of butter decrease, while the elastic modulus (G') increases (Diener and Heldman 1968; Shukla and Rizvi 1995).

There are a number of advantages to using dynamic mechanical testing in rheological studies. Low shear rates are involved, only a small sample is required, and both the elastic and viscous components of a material are probed simultaneously (Ferry 1980). Milkfat viscoelasticity has been studied using a number of configurations and geometries, including a parallel-plate viscoelastometer operated in the simple shear mode (Chwiej 1969; Pijanowski and others 1969; Shama and Sherman 1970). Sone (1961) compared the determinations of viscosity, elasticity, and yield value using a parallel plate plastometer, vibrating-plate viscometer, and cone and plate viscometer for butters under different conditions. Elliot and Ganz (1971) used a Weissenberg rheogoniometer in the static and dynamic shear modes to probe butter texture with a cone and plate configuration.

Rheological behavior of milk lipids

Modelling butter rheology

Although "hardness" and "spreadability" are ill-defined concepts, from a consumer perspective, they are relevant qualities. Attempts have been made to resolve butter's rheological properties in more meaningful ways. A long-standing matter of controversy has been whether butter should be classified as a plastic material with a yield value, or as a fluid with very high apparent viscosity under low stress conditions (Dolby 1941b; Prentice 1972). It is now generally agreed that solidified milkfat and butter display non-Newtonian behaviors and behave as plastics with yield values, above which the materials flow (deMan and Beers 1987; Sone 1961). Milkfat contains potentially thousands of different triacylglycerol species, each with their own melting temperature. The overall dropping point of milkfat is approximately 34 °C. However, because the triacylglycerols in milkfat have melting temperatures between –40 °C and 40 °C, milkfat demonstrates a very broad melting range. Figure 7 shows the solid fat content of milkfat as a function of temperature and the effect of solid fat content on milkfat hardness determined by cone penetrometry.

Figure 7 highlights the problem of excessive hardness found in milkfat and butters at refrigeration temperatures (5 to 8 °C). Generally, a fat possessing between 20 and 40% solids will exhibit good spreadability. Figure 7 shows that there is a limited temperature range over which desirable plasticity is achieved from a consumer perspective.

Over the melting range of milkfat,

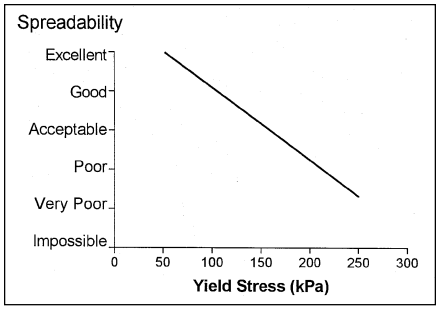

Figure 5—Relationship between yield stress of butter (determined by disc penetrometery, sectility, and cone penetrometry) and spreadability (Adapted from Mortensen and Danmark 1982)

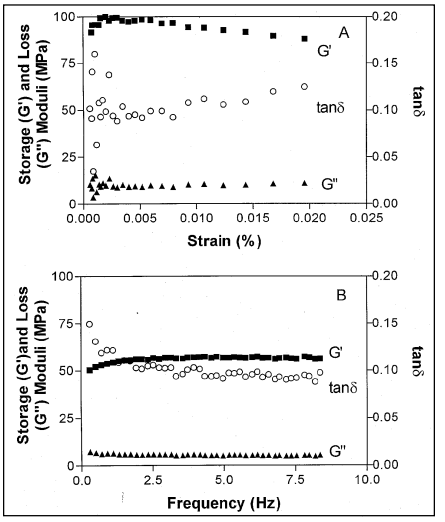

Figure 6—A. Storage (GN) and loss (GO) moduli and loss tangent (tan$^{\delta}$) of milkfat as a function of strain during a torque sweep at a frequency of 1 Hz. B. Storage (G′) and loss (G″) moduli and loss tangent (tan$^{\delta}$) of milkfat as a function of strain (%) during a frequency sweep at 8.0x10^{-3} % strain

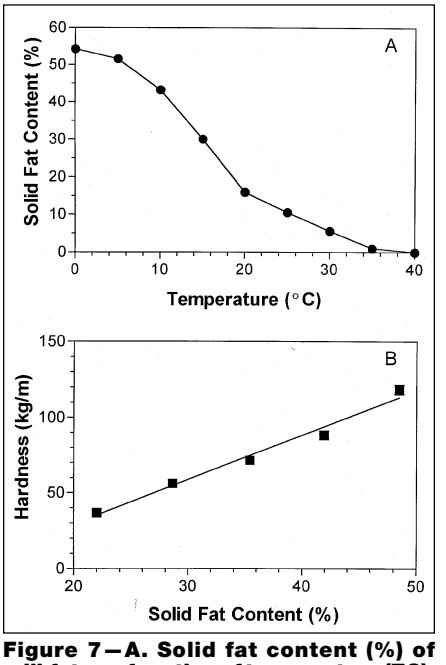

Figure 7—A. Solid fat content (%) of milkfat as a function of temperature (EC). B. Milkfat hardness (kg/m) determined from cone penetrometry versus solid fat content (%)

butter behaves as a viscoelastic material, possessing solid and liquid-like characteristics (Jensen and Clark 1988; Kleyn 1992; Shama and Sherman 1968; Shukla and Rizvi 1995; Sone 1961). Shama and Sherman (1968) have gone so far as to state that much of butter's rheological behavior can only be explained using theories of viscoelasticity. Nevertheless, the need for simplification of the rheological description of butter and milkfat, coupled with the fact that under conditions employed in some rheological tests a dominant mode of deformation may exist, means that a minimum number of rheological parameters are desirable for description of the rheological behavior of milk lipids.

The simplest model for the rheology of milk lipids is to assume elastic-perfectly plastic behavior (Figure 8a). When stresses are below the yield stress (F_y in Figure 8b), the sample behaves elastically, with a given modulus of elasticity. Once the yield stress is attained, the sample flows and continues to flow until the stress is lowered below the yield stress. Two parameters are therefore required to describe the behavior of this solid: the elastic modulus and the yield stress; these can be readily obtained from a compression test. Where elastic deformations are small compared to the total deformation, the solid can be essentially classified as a rigid plastic material (Johnson 1996), so that only 1 parameter is needed to describe the rheological behavior—the yield stress. Support for such a simplified treatment of butter comes from the penetration tests of Kamel and deMan (1975). They observed that yield force was linearly related to the area of the penetrometer, inferring that additional toughening mechanisms, which are evident in other dairy products such as cheese, are absent in butter (deMan 1969). However, given the distribution of melting points in Figure 7a, it is to be expected that viscous elements will need to be added to the model of Figure 8a to more accurately describe the rheological behavior of milk lipid systems.

Elliott and Ganz (1971) and Elliott and Green (1972) proposed that unctuous materials, including butter, can be qualitatively described by a modified Bingham Body. The model proposed consisted of viscous, plastic, and elastic elements in series and proved to be valid for both steady shear and oscillation studies. Elliott and Ganz's model is shown in Figure 8c, and its stress-strain behavior in Figure 8d. Although ostensibly only 1 extra parameter, the viscosity, is added to the elastic-perfectly plastic model, a static yield stress and a lower moving yield stress must be employed in order to represent the real behavior of unctuous systems (Elliott and Green, 1972).

A more complex model was proposed to describe the small strain behavior of butter when loaded with a small circular die (Diener and Heldman 1968). The viscous Maxwell-Bingham rheological model postulated by Diener and Heldman (1968) to represent specific structural elements within butter is shown in Figure 8e. The model consists of a plastic and a viscous element in parallel, coupled in series with a viscous element in parallel with a combination of a viscous and an elastic element. The elasticity was attributed to the fat globule membranes and the viscous nature related to flow of the surrounding liquid fat. Liquid fat, as well as the aggregated solid fraction, are responsible for the viscoelastic nature of plastic fats (Drake and others 1994). The continuous network of fat crystals themselves is postulated to bear the stress below the yield stress and so contribute solid or elastic properties (Narine and Marangoni 1999a). Electron micrographs show that globules can be deformed considerably without losing their structural integrity (Precht 1988). However, evidence has shown that during churning most of the membrane material is lost and passes into the buttermilk (Knoop and Wortmann 1962).

Relating rheology to structure

The attempt by Diener and Heldman (1968) to relate the macroscopic rheological models to specific structural components within the butter empha-

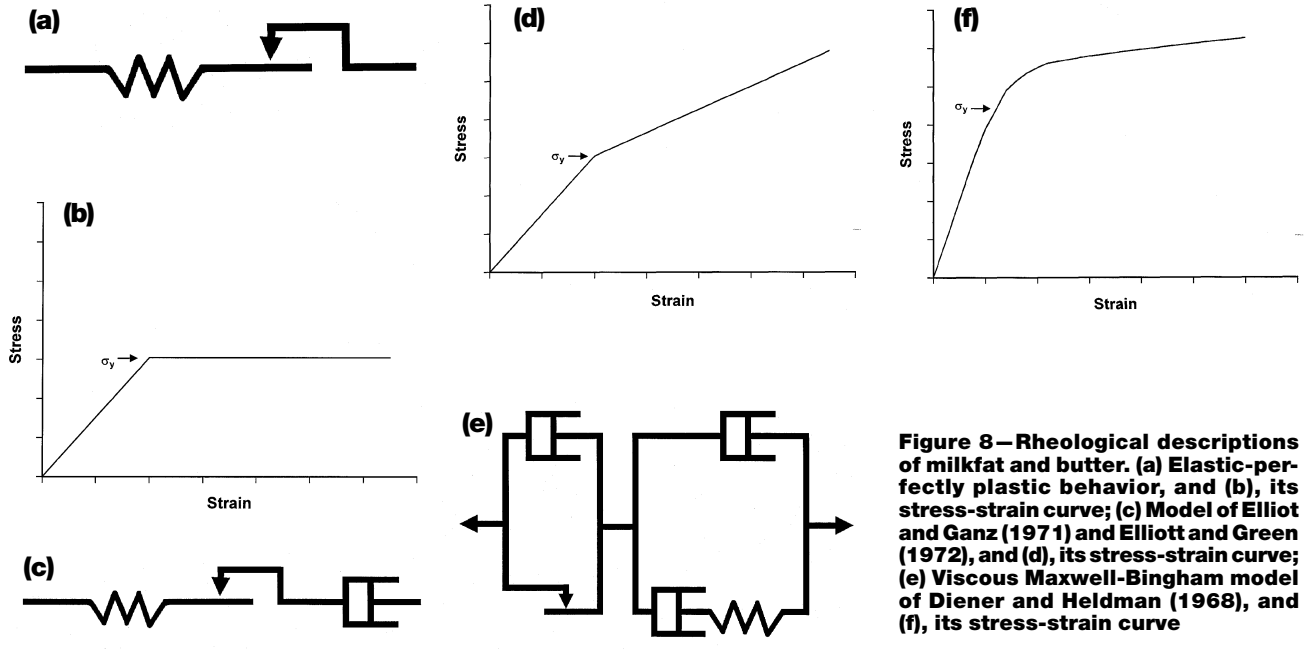

Figure 8—Rheological descriptions of milkfat and butter. (a) Elastic-perfectly plastic behavior, and (b), its stress-strain curve; (c) Model of Elliot and Ganz (1971) and Elliott and Green (1972), and (d), its stress-strain curve; (e) Viscous Maxwell-Bingham model of Diener and Heldman (1968), and (f), its stress-strain curve

sizes that any modeling of the mechanical properties of a network must have as its starting point a good definition of the structural levels that exist within the network. The hierarchical organization of structural levels in fat crystal networks is best elucidated through an examination of the structural levels defined as the network is formed when the fat crystallizes from the melt (de-Man and Beers 1987; Narine and Marangoni 1999a). Growth of the solid network begins with initial nucleation sites, which grow into larger crystals as additional triacylglycerol molecules crystallize. Given the large negative entropy of fusion of milkfat ($\Delta S_f/k$ ~−25, compared with water, −2.8), nucleation events are expected to dominate (Guy 1972), so that there is likely to be further nucleation during crystal growth. These larger crystals grow into primary particles, or microstructural elements (collection of primary crystallites), of approximately the same size (< 10μm), which then aggregate into larger clusters, or microstructures (>100 μm) (Figure 9). The microstructural elements are arranged in a fractal manner in the length range bounded by the size of 1 microstructural element and the size of 1 microstructure. The clusters themselves pack in a regular, homogeneous, space-filling manner to provide the largest structural building block of the fat crystal network (Figure 10). Interspersed between the microstructures and microstructural elements is the liquid phase (oil) of the network.

Our group has proposed a scaling theory (Marangoni and Rousseau 1996; Narine and Marangoni 1999b) to quantitatively relate the Young's modulus (E) of a fat to the fractal arrangement of microstructural elements within microstructures (characterized by D) and the volume fraction of solid fat (M), namely:

$$E = \lambda \Phi^m \quad (6)$$

where, in 3-dimensional space,

$$m = 1/(3-D) \quad (7)$$

This theory was based upon the assumption that, when the network is stressed, the links between the microstructures are more likely to be stressed than the microstructures and structures within them. This is reminiscent of the old adage "the strength of a chain lies in its weakest link." The weakest links here are the links between the microstructures. This theory is simply and appropriately called the weak-link theory (Shih and others 1990). Figure 11 shows a schematic of a fat network under compression when the weak-link theory is applicable.

The fractal dimension of the microstructural network can be determined rheologically by diluting the fat with an oil that does not appreciably dissolve the fat under the test conditions (Marangoni and Rousseau 1996). For milkfat, dilutions in the range 70 to 100% (w/w) milkfat were appropriate for this type of analysis (Marangoni and Rousseau 1996). Upon measurement of the storage modulus using small deformation dynamic rheological techniques under shear (G′) or compression (E′), and the solid fat content by pulsed NMR, it is possible to plot:

$$\log E' = \log\lambda + m\log\Phi \quad (8)$$

where Φ = SFC/100. From the slope and y-intercept of such a plot, D and λ can be determined (Figure 12).

Polarized light microscopy (PLM) images of a fat crystal at the microstructural level can be used to determine the fractal dimension. However, because the images of fat networks that are acquired from PLM are not suitable for analysis by the traditional methods of fractal dimension calculation, a new method to calculate fractal dimensions was created (Narine and Marangoni 1999b). This new method was developed utilizing the theory of mass fractals, and the following equation:

$$N = c(R)^D \quad (9)$$

where N is the number of reflections present in the region of interest R and c is a proportionality constant. R is bounded by the diameter of 1 microstructural element (a) and the diameter of 1 microstructure (>). The method to calculate the fractal dimension of the fat crystal consisted of counting the number of reflections, N, in a region of interest of length R for various values of R, not exceeding the size of 1 microstructure (Figure 13). Then, log(N) vs log(R) is plotted, yielding log(c) as the intercept and D as the slope (Figure 14). Reasonable agreement between rheologically calculated values of fractal dimension using the weak-link theory and

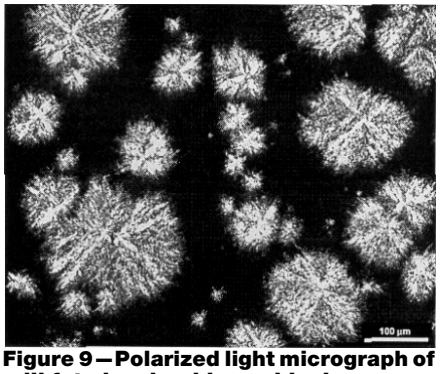

Figure 9—Polarized light micrograph of milkfat showing hierarchical arrangement in fat crystal network

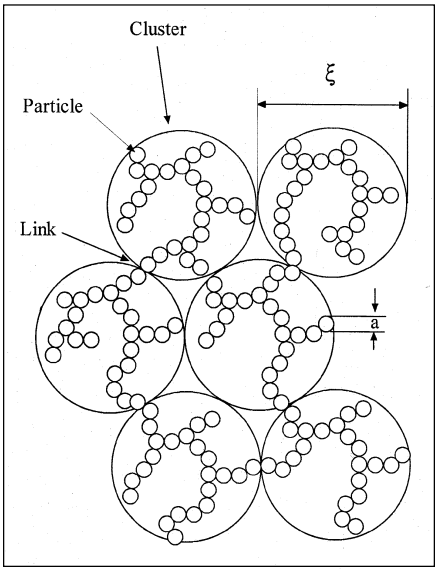

Figure 10—Schematic model of fat crystal networks

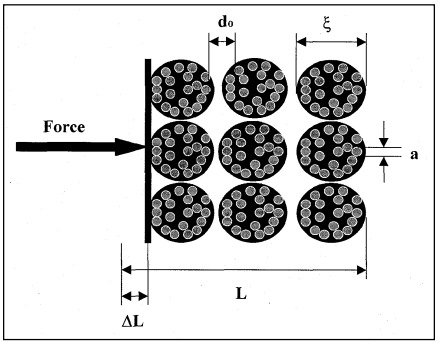

Figure 11—Schematic model of fat crystal networks under shear

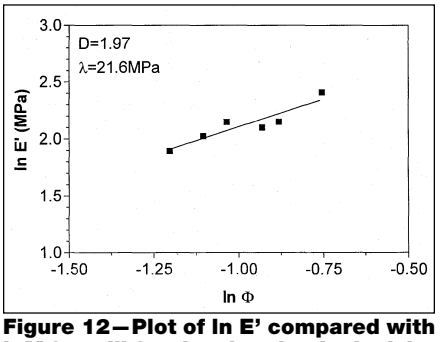

Figure 12—Plot of ln E' compared with lnM for milkfat showing rheological determination of D

fractal dimensions calculated microscopically was apparent (Narine and Marangoni 1999b). This seems to indicate that the fractal dimension was indeed a fundamental constant of the solid fat network, akin to a bonding parameter or lattice constant.

Our work (Narine and Marangoni 1999b) suggests that fat systems with high fractal dimensions demonstrate a higher order of packing of microstructural elements within microstructures than those with lower fractal dimensions. Therefore, the fractal dimension of a network is a measure of the order in the spatial distribution of solid mass in the network, with higher fractal dimensions leading to a more ordered distribution.

Figure 15 shows the shear storage modulus, G′, normalized by the pre-exponential constant λ, plotted against the fractal dimension of more than 20 different fat systems whose fractal dimensions were determined rheologically. From this figure, we can deduce that an increase in fractal dimension implies a decrease in the elastic modulus of the system. Therefore, by altering the processing conditions for the crystallization of a particular fat system, the rheological properties of the network may be altered by using the microstructural parameters D, λ, and M as indicators.

While the value of the fractal dimension of the fat network as an indicator of the mechanical strength of the network cannot be denied, it must be understood that the value of the pre-exponential term λ (and the solid fat content) is also equally important. Our group has shown that for spherical microstructures (Narine and Marangoni 1999c; Marangoni 2000),

$$\lambda \approx \frac{A}{\pi a \gamma d_o^2} \qquad (10)$$

where A is Hamacker's constant, a is the diameter of a microstructural element, γ is the macroscopic strain imposed during the rheological test, and d_o is the average equilibrium distance between microstructures (Figure 11). This model therefore identifies key network parameters important in determining the value of λ. Furthermore, the model agrees well with experimental observations (Marangoni 2000). Eq. 10 therefore provides impetus for the development of phenomenological investigations of relationships between triacylglycerol composition and polymorphism and parameters of our model.

Specific rheological characteristics: spreadability and hardness

Butter hardness and spreadability are inversely related parameters and are 2 of the most important aspects of texture. They have been the 2 most commonly measured sensory properties (deMan and others 1979), as they greatly influence consumer acceptability. Prentice (1972) argued that spreadability is the only rheological property of practical importance. Indeed, butter spreadability is probably the rheological property that consumers are most familiar with. Butter notoriously possesses poor spreadability at refrigeration temperatures, and poor structural stability at room temperatures (Kaylegian and Lindsay 1992). At room temperature, butter also demonstrates oiling off and moisture migration (deMan and Wood 1958b, Shukla and others 1994). Vasic and deMan (1965) reported that the change in butter's solid fat content between 10 and 20 °C is very pronounced, resulting in a very limited temperature range within which there is desirable spreadability. Creep analysis showed lower instantaneous and retarded elasticities and less viscous flow at higher temperatures (deMan 1985).

These effects can mainly be explained by the effect of temperature on solid fat content (Shukla and Rizvi 1995). At lower temperatures, more triacylglycerols crystallize into the solid fat network. The degree of milkfat crystallinity is the largest determinant of the rheological properties of butter (Rohm and Weidinger 1993). For easy spreading, butter should contain between 20 and 40% solids (deMan 1962) and, in general, butters with "yield stresses" below roughly 125 kPa have satisfactory spreadability (Mortensen and Danmark 1982b). Rohm and Raaber (1991) found the preferred spreadability range in butter to correspond to a range in apparent yield values (determined according to International Dairy Federation [1980]) of approximately 30 to 60 kPa. Knoop (1963, 1964) related butter spreadability to its structure using cutting resistance measurements (1964) and electron microscopy (1963). A more homogeneous structure was linked to a firmer consistency, while improved spreadability was correlated with a structure in which more corpuscles, representing fat crystals or aggregates (Precht and Buchheim 1979, 1980) were observed.

Butter texture depends on many interrelated parameters, and no single factor appears capable of explaining its consistency (Precht 1988). Milkfat's fatty

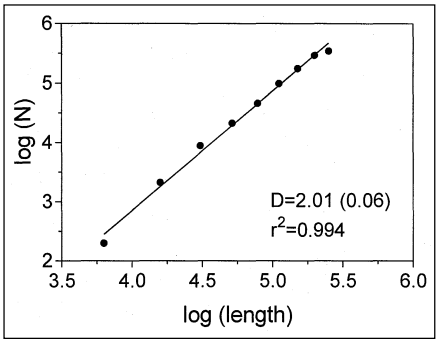

Figure 14—Plot of log(N) as compared to log (length) for milkfat showing the determination of D by particle-counting approach

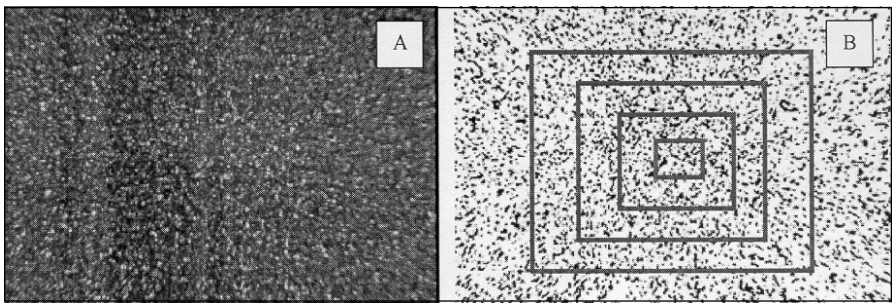

Figure 13—Polarized light micrograph of AMF at 5 °C (A) and thresholded micrograph showing particle counting approach to determination of D (B)

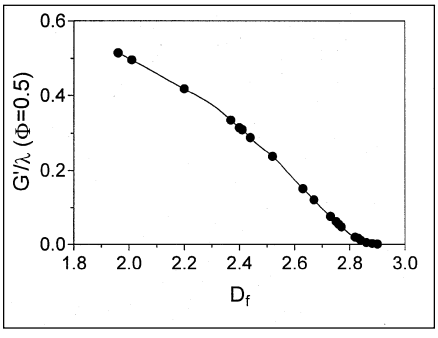

Figure 15—Plot of G′ normalized by the pre-exponential constant 8 versus D for many different fat systems

acid composition and positional distribution influence the melting point, and therefore are of major importance (Kleyn 1992). The iodine value and average fatty acid chain length account for much of the variation in butter firmness. A change in iodine value of 3% can effect a 50% change in firmness (Hayakawa and others 1986). Winter butter is notoriously harder than summer butter because of seasonal variations in cow feed which result in a more saturated fat overall during the winter (Prentice 1972). MacGibbon and McLennan (1987) found large increases in the hardness of New Zealand butters through the spring. Hardness levelled off during the summer and gradually declined in autumn. Variations in the original milks' compositions explained much of this trend (MacGibbon and McLennan 1987). Typically, continuously churned butter is also harder and less spreadable than conventionally batch-churned butter (deMan and Wood 1958a).

Specific rheological characteristics: setting, work softening, and thixotropy

Brownian motion and van der Waals forces cause fat crystals, which are suspended in the liquid fat, to aggregate into 3-dimensional networks (van den Tempel 1961). This aggregation can continue in freshly made butter for months, resulting in an increase in firmness (Precht 1988). The extent of this setting depends on a number of variables, including composition, storage temperature, storage time, the butter's initial hardness, and the conditions during manufacturing (deMan 1976; Precht 1988; Prentice 1972). The strength of the network continues to increase because of continued crystallization (Shama and Sherman 1968). Setting is evidenced by electron microscopy which shows newly formed fat crystals arising in butter over the course of 10-d storage (Buchheim and Precht 1979).

Butter exhibits work softening when large shearing forces are applied (Shama and Sherman 1970). The creep curve for a plastic fat shown in Figure 2 demonstrates work softening and thixotropy. The initial elastic response (A) of plastic fat networks (deMan and Gupta 1985) represents the stretching of the bonds between microstructural elements (Narine and Marangoni 1999a) and can be characterized by a Hookean spring (deMan and Beers 1987). If the applied stress is greater than the yield stress, most breakdown of milkfat and butter structure occurs virtually instantaneously. A plot of shear stress in contrast to time shows a rapid decrease in stress initially upon working, indicating structure breakdown (Cornily and leMeste 1985). After the initial deformation, the strain continues to increase, in a time dependent fashion, as bonds between crystals in the fat network break and reform. This area of the curve can be represented by a series of Voigt-Kelvin units (spring and dashpot in parallel), similar to Diener and Heldman's description (Figure 8e). The strains that result are retarded by the dashpot (deMan and Beers 1987). Both the time of loading and the extent of loading influence the response (deMan and Beers 1987). The amount of breakdown is largely limited by the properties of the butter and not by the intensity of working (deMan 1969).

Because of the thixotropic nature of milkfat, after working some of the original firmness is recovered (deMan 1969; Vasic and deMan 1968; deMan and Gupta 1985; Mortensen and Danmark 1982b). This slow recovery of firmness is evidenced by an increase in the elastic modulus with time (Shama and Sherman 1970). As a result of thixotropy, plastic fats demonstrate a hysteresis loop. Thixotropic hardening is closely related to setting in which freshly made butter continues to increase in hardness for some time after manufacture (Precht 1988). The thixotropic hardening of butter after working is shown in Figure 16.

In creep-compliance-time studies, Shama and Sherman (1970) found that the elastic modulus of butter decreased less than the apparent viscosity with working. Most of the instantaneous elasticity was recovered after working. However, there was less recovery of the Newtonian viscosity. Shukla and Rizvi (1995) studied the dynamic properties of butter by looking at the effects of storage time (and temperature) on the complex modulus G*. The firmness increased for butters with storage time, probably because of rearrangements in the crystalline network (Shukla and Rizvi 1995).

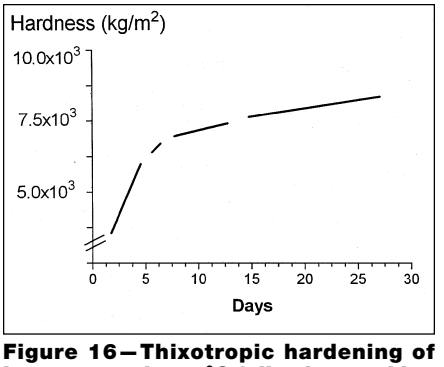

Figure 16—Thixotropic hardening of butter stored at 5 °C following working (Adapted from deMan and Wood 1959)

Setting, work softening, and thixotropy have been explained in the context of 2 types of bonds hypothesized for fat crystal networks (van den Tempel 1961; Haighton 1963). Primary bonds are stronger and irreversible, whereas secondary bonds are relatively weak and are reversible (van den Tempel 1961; Haighton 1963). Primary bonds, which have higher energies, contribute more to the network's stiffness than secondary interactions. Working may disrupt the primary interactions. Shama and Sherman (1970) attributed the difference in shear modulus, before and after kneading of butter, to the breaking of primary bonds. Thixotropy may be related to broken secondary bonds which reversibly reform after working (deMan and Beers 1987). DeMan and Wood (1959) assumed that the smaller crystals in butter cause thixotropy because they are present in higher amounts, are more mobile, and consequently can form secondary structures.

The allocation of all attractive forces in the fat crystal network into 2 categories may be useful; however, it is arbitrary and doesn't accurately reflect the bond strengths present (Shama and Sherman 1970). Shama and Sherman (1970) argued that butter's behavior should be characterized instead on the basis of a spectrum of bond strengths. The attractive forces between adjacent particles in a network are proportional to some power of the particle diameter, with the exact power depending on the geometry of the particle (Vold 1954). Shape and composition also affect the magnitude of van der Waals interactions in fat crystal networks (van den Tempel 1961). Therefore, since not all particles are the same size, not all the attractive forces will be the same.

Prentice (1972) explained butter's deformation under stress and strain according to 3 distinct alterations in structure. When small stresses are applied, they may distort the network and, consequently, potential energy is stored. This is a reversible, elastic-type deformation. Secondly, larger stresses cause extensive rearrangement of the crystals, or cause fracturing. This type of deformation is not reversible and may correspond to van den Tempel's (1961) primary structure. Thirdly, work

softening can occur as a result of crystal melting (Prentice 1972; Sone 1961). Mechanical energy applied to the fat may be converted into heat which melts some crystals. Recrystallization of the melted crystals may occur in time, since melting is thermodynamically reversible. However, recrystallization proceeds slowly and may not return the network exactly to its original structure. This melting and recrystallization effect may correspond to secondary or recoverable structure (Prentice 1972).

Table 1—Methods by which butter's textural and rheological properties can be modified

Alteration of Butter Composition	Treatment Applied During Manufacture	Treatments Applied After Butter Churning
Adjustments to cow feed • oil seed supplementation • encapsulated unsaturated oils	Method of manufacture • conventional as compared to continuous processes	Storage conditions • time • temperature
Blending with unsaturates	Cream agitation during cooling	Mechanical working
Milkfat fractionation	Rate of cooling	
Milkfat interesterification • chemical • enzymatic	Recycling • addition of seed crystals	
Other changes to butter composition • water content • air content • addition of surfactants	Cream ripening process	

Modification of rheological properties

Butter's functional properties can be improved by a number of treatments. Most are aimed at improving cold spreadability while maintaining stability at room temperatures. Table 1 presents the most common methods of modifying butter's textural and rheological properties. These are categorized under the 3 broad approaches which are taken: compositional alterations, treatments applied during manufacture of the butter, and treatments applied to the butter after churning.

Alteration of Composition

The chemical nature of cream ultimately has a very strong influence on butter consistency (Bornaz and others 1993). Differences in fat composition, depending on the stage of lactation, can affect milkfat's consistency (Kleyn 1992). Also, winter butter is notoriously hard and brittle. These characteristics result because of seasonal variations in cow diets which lead to fats with higher melting points and lower iodine numbers. Recommendations to improve winter butter spreadability include altering milkfat composition by changing the feeding conditions of dairy cows (Nielsen 1971). This involves feeding highly unsaturated oils. The oleic acid content of butter can be increased with a simultaneous decrease in the level of saturates by feeding whole oilseeds to cows (DePeters and others 1985; Mohamed and others 1988). Unfortunately, this also results in an increased level of trans fatty acids and a decreased level of short chain saturates (Lin and others 1996a). Vegetable oils can also be encapsulated in formaldehyde-treated casein. The encapsulated oil is protected against hydrogenation in the cow's rumen so that it is incorporated into the fat (Scott and others 1970). By feeding formaldehyde-treated canola seeds, Ashes and others (1992) successfully increased the level of oleic acid in butter and decreased the medium chain-saturated fatty acids. There are concerns, however, that the formaldehyde could be transferred to the milk. Lin and others (1996a, 1996b) studied the effects of incorporating calcium-protected high oleic sunflower oil into cow diets. The resulting decrease in saturates, increase in monoenes, and little change in the polyunsaturates corresponded with improved butter spreadability. While studies have shown that modified feeding is successful, it is impractical on a large scale (Nielsen 1971).

Blending milkfat with vegetable oils also serves to increase the overall level of unsaturation and decrease the melting point (Ahmed and others 1979; Amer and Myhr 1972; Wilbey 1994). Rousseau and Marangoni investigated the effects on physical properties when milkfat was blended with canola oil (1996a, 1996b, 1996c). The hardness index of the blends decreased with increasing amounts of canola oil, and changes were noted in the blends by both large and small deformation measurements. Amer and Myhr (1972) replaced 30% of the milkfat in butter with sunflower oil and found improved cold spreadability. Unfortunately, at room temperatures the samples with additional unsaturates were too liquid in nature (Amer and Myhr 1972). In addition, legislation is very strict in most regions of the world with regard to the legal definition of butter. Large changes in the composition of milkfat and blending with nondairy fats raise concerns about the standards of identity. Dairy spreads with vegetable oil are sold in several countries, but cannot legally be called butter (Gupta and deMan 1985).

Milkfat can be fractionated based on triacylglycerol melting points, or interesterified to alter butter rheology. Butter spreadability has been improved by fractionating milkfat and then recombining the fractions in various proportions (McGillivary 1972; Makhlouf and others 1987; Deffense 1989; Kaylegian and Lindsay 1992). The addition of low-melting milkfat fraction to milkfat reduced the hardness of butter by increasing the levels of short chain fatty acids and oleic acid (Kulkarni and Rama Murthy 1987). Kaylegian and Lindsay (1992) found success recombining a high proportion of low-melting triacylglycerols from multiple-step dry fractionation and small proportions of both high-melting triacylglycerols and very high-melting triacylglycerols obtained by acetone fractionation. The recombined butter exhibited good spreadability at 4 °C and maintained its physical structure at room temperature. The very high-melting triacylglycerols seemed to provide key structural functionality in the spreadable butters (Kaylegian and Lindsay 1992). The viscoelastic behavior of high-melting fraction of milkfat was characterized by a general Maxwell model with 1 spring and 2 Maxwell elements (Shellhammer and others 1997). Shukla and others (1994) found that butters with additional high-melting triacylglycerols had higher solid fat contents and complex viscosities at higher temperatures, which improved the stability and eliminated oiling off and moisture migration. This offers hope for improving butter behavior at ambient conditions. Fractionation appears to be the best alternative to improving functional properties of butter (Shukla and others 1994). Still, butters made from milkfat frac-

tions are relatively rare in the market place (Taylor and Norris 1977). This may largely be a result of the high cost associated with fractionation operations (Gupta and deMan 1985).

Weihe (1961), Mickle and others (1963), and Rousseau and Marangoni (1996a,b,c) used chemical interesterification to improve butter cold spreadability by altering the milkfat's fatty acid distribution (Frede 1989). Enzymatic interesterification can also be used (Rousseau and Marangoni 1998a, 1998b, 1998c), although it is considered too costly to be economically feasible (Kleyn 1992). Kalo and his group (Kalo and others 1986a,b, 1990) found few differences between chemically and enzymatically interesterified milkfats in terms of their chemical compositions and melting properties. Rousseau and Marangoni (1999) found both chemical and enzymatic interesterification to be excellent methods of improving butter's cold spreadability. Penetration depths, determined according to the AOCS Method Cc 16-60 (AOCS 1989), increased from 7.4 ± 1.1 $10mm^{-1}$ in anhydrous milkfat at 5 °C to 20.0 ± 3.8 $10mm^{-1}$ and 59.0 ± 5.9 $10mm^{-1}$ upon enzymatic and chemical interesterification respectively (Rousseau and Marangoni 1999). The chemical process led to greater changes in physical and sensory attributes than the enzymatic method, possibly because it resulted in greater changes in composition and solid fat content. Although both methods were successful, unfortunately both led to butters with decreased flavor intensities (Rousseau and Marangoni 1999). This loss of butter flavor is a common problem with interesterification (Kleyn 1992).

Other researchers have tried to modify butter consistency by adjusting moisture and air contents. Kulkarni and Rama Murthy (1985) found that penetration values, determined according to the American Oil Chemists' Society recommendations, increased significantly when the moisture content of butter at 5 and 15 °C was increased from 12 to 15%. Not surprisingly, a more drastic increase in moisture from 12 to 35% completely changed the rheological properties of butter, determined both by objective and subjective tests (Kulkarni and Rama Murthy 1985). Additional water also increases the potential for microbial spoilage and hydrolytic rancidity, and raises concerns about legal standards of identity. Structural stability at higher temperatures is also a concern.

Butter typically has an air content between 3 and 7%. By treating under reduced pressure, as in a vaculator, air content can be reduced. Butter worked under reduced pressure appears glossy and has a smooth texture (Swartling and others 1956). Strangely, despite the fact that this butter seems to have a harder consistency, it is reported to have improved organoleptic plasticity (Swartling and others 1956). This contradiction has been explained by suggesting that reducing the air content results in a more compact and therefore harder structure. However, the free butter oil, which was originally adsorbed onto the air bubbles, may now alter butter's flow properties (Swartling and others 1956).

Hardness is significantly reduced by adding air to butter (Hayakawa and others 1986). Gupta and deMan (1985) reported that the addition of air is more effective at higher temperatures and equivalent to the effects of working. A gas such as nitrogen can be whipped into butter to improve its spreadability. However, this can lead to a crumbly texture and loss of butter aroma (Kleyn 1992). In whipped butter, an increase in overrun (between 10 and 125%) results in a significant increase in spreadability (Foley and Cooney 1982; Vyas and Hedrick 1963). However, Fisker and Jansen (1970) found that the spreadability wasn't improved significantly in aerated butter. A number of factors, including the production process, time of gas incorporation, and fat composition, determine the achievement of successful spreadability in whipped butter (Precht 1988; Vyas and Hedrick 1963).

Gupta and deMan (1985) argued that the addition of air and surfactants to milkfat were the most feasible approaches to improving butter texture. Conversely, Hayakawa and others (1986) concluded that the effect of surfactants on the rheological properties of butter is small and of little practical significance. Kapsalis and others (1963) improved butter spreadability with some surfactants, although others made the butter brittle and sticky. The effect was attributed to the surface active properties of the additives (Gupta and deMan 1985). With storage, the effects of the additives were overcome, thus they delayed but did not prevent normal butter setting. Ultimately, the surfactants had no effect on the solid fat contents of the butters and dropping points were only reduced by a maximum of 0.9 °C (Kapsalis and others 1963). Gerson and Escher (1966) added 1% monoglycerides to cream before churning and achieved a 30% improvement in spreadability. Unfortunately, uniform distribution of the surfactants is difficult to achieve (Kapsalis and others 1963), and most of the surfactants are lost in the buttermilk.

Treatments during manufacturing

Figure 17 outlines the typical steps involved in buttermaking.

The first step in buttermaking involves centrifugation and separation in order to increase the fat content of the cream to approximately 40%. Following pasteurization, the cream is cooled. The cooling rate here can ultimately influence the consistency of the butter produced because it affects the ratio of solid: liquid fat going into the aging treatment. Also, rapid cooling leads to many small crystals and a crystal surface area which is larger than during slow cooling. As a result, when cooling proceeds rapidly, more liquid fat will be adsorbed to the crystal surfaces. Less liquid fat is available to form the continuous oil phase during churning and working, and a firmer butter results (Boudreau and Saint-Amant 1985).

The cream aging and churning operations are most critical in the achievement of desirable butter texture. Pasteurized cream is typically ripened before churning (Prentice 1972). Such temperature pretreatments may be the most economical and successful method of influencing butter consistency (Precht 1988). Dolby (1954), for example, found that butter made from cream held at 15.6 °C and churned at 7.2 °C contained more free liquid oil and was softer than butter held and churned at 7.2 °C. Generally, it is recommended that cream for winter butter be cooled to 10 °C after pasteurization and held overnight between 10 and 12.8 °C (Nielsen 1971). Although cream ripening is a very complex process and little fundamental knowledge is available, it has been used industrially since 1935 (Bornaz and others 1995). One commercial example of this is the Swedish or Alnarp "6–12–6" method (Alpha-Laval 1987). This and other cold-warm-cold processes result in butters with higher contents of liquid fat than samples ripened directly at lower temperatures (Szakaly and Schaffer 1988). Various explanations for the success of such treatments generally relate to the effects of liquid fat on crystal formation (Precht 1988). Melting of the high-melting fat crystals during the warming process is probably re-

sponsible for the observed reduction in hardness (Precht 1988).

Churning involves agitation of the cream and leads to partial phase inversion and agglomeration of the partially crystalline fat and ruptured fat globule remnants. The specific churning procedure has a large impact on butter consistency (Black 1975; Kawanari and others 1981; Sone and others 1966; Vasic and deMan 1968). Traditionally, butter was batch manufactured by churning in large metal churns. Today, the continuous technologies predominate, including accelerated churning (Fritz-type), phase inversion, and emulsification types of buttermaking. Butter prepared in the continuous machines is notoriously harder than that made by the conventional process (deMan 1976). This is partly due to different effects on the structural integrity of the fat globules during production. When butter is batch produced, a relatively high proportion of the fat phase (2 to 46%) may remain in the globules after churning. During the continuous Gold'n flow process, however, the globule structure is completely destroyed and all the fat exists as free fat (Kawanari 1996).

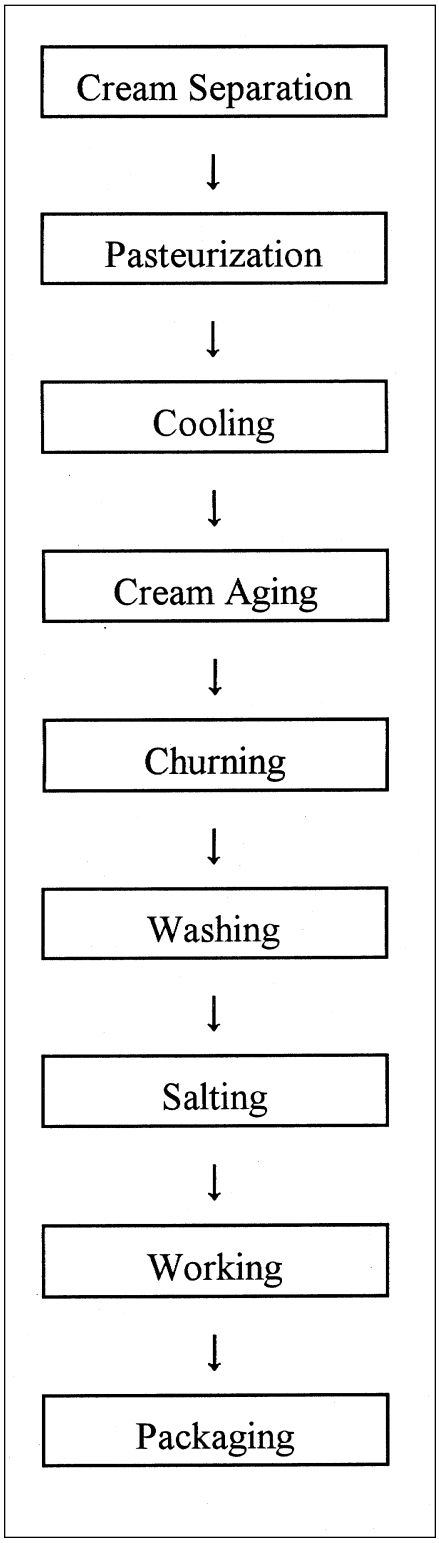

Figure 17—Flow diagram showing steps involved in buttermaking

Differences between conventionally and continuously made butters have specifically been attributed to differences in the degree of crystallinity of the fat and fat crystal morphologies (deMan and Wood 1958a; Sone and others 1966). While conventionally made butter is mechanically treated after the fat has crystallized, in the continuous process most of the mechanical treatment takes place before crystallization. This is one possible explanation for some of the differences observed in butters made by each process. Mechanical agitation during cream cooling influences crystal size by increasing secondary nucleation and impedes agglomeration and interlocking of crystals. This gives more discrete crystals and a less firm fat at any given solid fat content (Sherman 1976).

Cooling also occurs more rapidly in the scraped surface heat exchangers of a continuous buttermaking operation than in the traditional batch process (deMan 1963b). The rate of fat cooling during manufacture is important because it dictates the number of nuclei formed during crystallization and influences the size to which the crystals will grow (Bailey 1951). Rapid cooling influences the size of fat crystals and, in turn, the texture of butter (Deffense 1987; Haighton 1976). Rapid cooling of milkfat leads to higher solid fat contents and a firmer product (Foley and Brady 1984). Unfortunately, it is difficult to evaluate the effect of 1 parameter, such as cooling rate, on butter texture since there are a number of interrelated parameters which influence the texture simultaneously. For example, solid fat content, crystal size (deMan 1976), and mixed crystal formation (Mulder 1953) are all affected by temperature treatment.

Rapid cooling leads to smaller crystals and higher solid fat contents, 2 factors which lead to an increase in butter hardness (deMan 1963b; Parkinson and others 1970; Sone and others 1966). An increase in crystal size seems to cause a decrease in the hardness index of fats (Feuge and Guice 1959). Viscoelastic testing showed that the shear modulus of a plastic fat was inversely proportional to the third power of the particle diameter (Shama and Sherman 1968). DeMan (1963b) reported the formation of many crystals with diameters of 1 µm or less in rapidly cooled milkfat, compared to the formation of fewer crystals with diameters up to 50 µm when the fat was cooled slowly.

The fat crystals of conventionally made butter are larger and more irregularly shaped than those resulting from a continuous process (Vasic and deMan 1968). The morphology of the crystals seems to influence butter consistency (Sone and others 1966). Spherically shaped crystals, for example, cause less resistance to flow than plate-, disc- or needle-shaped particles (deMan 1964). There is debate concerning how relevant polymorphism is to butter texture (Precht 1988). Polymorphism influences crystal shape (deMan and Beers 1987), and in that regard it is an important consideration.

Some attempts have been made to improve butter consistency by recycling. Recycling involves adding milkfat crystals to the cream during churning to seed the growth of larger, desirable crystals (Black 1975). This can result in a softer fat (Joyner 1953; Black 1975), although recycling adversely affects the product's appearance (Black 1975).

From the discussion on structure and butter rheology above, it is expected that quantitative parameters which characterize the microstructural arrangements of the butter (d_o, average equilibrium distance between microstructures; a, dia of microstructural element, and D; fractal dimension) will change as a result of changes in processing conditions. By defining the network characteristics responsible for the mechanical strength of the fat network, an array of indicators are available to butter processors, and these can be monitored during developmental stages of tailored fat crystal networks as well as being key parameters for quality

control during processing. As a result, processing conditions, such as cooling rates, can be manipulated to alter the microstructure so as to attain desirable textural characteristics. For example, when milkfat is cooled from the melt to 5 °C, at a rate of 0.1 °C/min, a spherulitic microstructural texture is observed (Figure 18A). This microstructure arises due to a low number of evenly distributed nucleation events. Under these slow crystallization conditions, crystal growth predominates over nucleation, thus resulting in a small number of large microstructural features. On the other hand, when milkfat is cooled from the melt to 5 °C at a rate of 5 °C/min, a granular microstructural texture is observed instead (Figure 18B). This granular texture arises due to a large number of randomly distributed nucleation events. Under these fast crystallization conditions, nucleation events predominate over crystal growth processes, thus resulting in a high number of small microstructural features. These microstructural features are distributed in a less orderly fashion than in the case of slow cooling.

Figure 19 shows the results of the microstructural analysis carried out rheologically for slow and fast cooled milkfat. The fractal dimension of the fat crystal network in milkfat decreases from 2.5 to 2.0 when the cooling rate is increased. Concomitantly, the particle-related constant λ increases. These results demonstrate how a faster cooling rate leads to a decrease in the order in the spatial distribution of mass within the microstructural network, which would result in a lower value of D, and a decrease in the average particle dia, which would result in a higher value of λ, as predicted by our model (Marangoni 2000). Fractal dimensions determined by particle counting were 2.45 and 1.95 for slow- and fast-cooled milkfat, respectively. This was in good agreement with the rheologically determined fractal dimensions.

From the expressions for λ and E, it is also apparent that using a defined rheological model alongside information on the microstructure of the fat network, the large deformation properties should be predictable (notwithstanding rate effect differences between various rheological tests). For the simpler rheological model (Figure 8a), when the applied stress is below milkfat's yield stress, any load on the fat is primarily borne by the existing microstructural elements, including the weak links interconnecting them. At the point where the bonding between microstructural elements gives, the load is transferred to the liquid phase and so a plastic response is apparent (Figure 3 and 8a). This event occurs at the yield stress and after a certain amount of strain has occurred in the butter, denoted by (Σ_y Therefore, the yield stress of the milkfat is related to its microstructure by:

$$\sigma_y = E\gamma_y \propto \Phi^m \qquad (11)$$

Based on this simple model of milkfat structure (Figure 8a), it is to be expected that the compression storage modulus (E') is directly proportional to the yield force (Narine and Maragoni 2001) (Figure 20). Thus it is possible to map the effects of structure to small deformation rheological behavior, and from there to large deformation rheological behavior (albeit empirically at the moment), and therefore possibly the texture of the butter (Rouseau and Marangoni 1999).

Work is ongoing in our laboratory to establish relationships between crystallization behavior, structure, and macroscopic rheological properties in a variety of fat systems.

Treatment of Butter After Churning

The commercial production of butter involves a plasticizing step which is important in the achievement of desirable butter texture (Joyner 1953). Working serves to disperse the water and salt in the continuous oil phase and continues the expulsion of oil and fat crystals from the fat globules (Boudreau and Saint-Amant 1985). High shearing rates break down the fat crystal networks although, after mixing, setting will occur and butter firmness will continue to increase (deMan 1976). Butter can be worked after storage and once further setting has occurred, although this is not very feasible since butter is packaged immediately after churning in

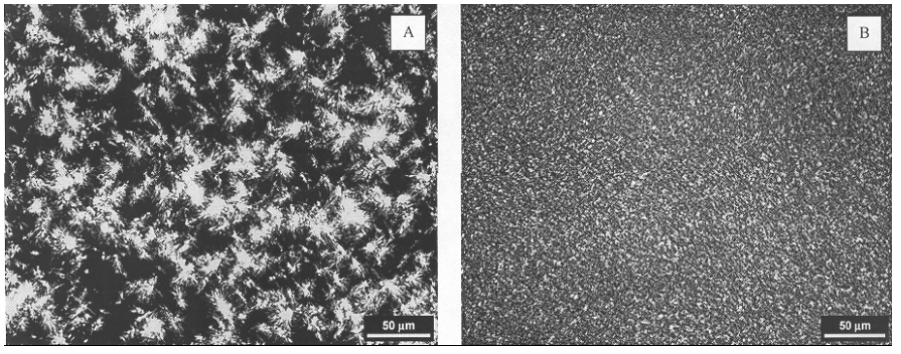

Figure 18—Polarized light micrographs of milkfat cooled to 5 °C at of 0.1°C/min (A) and 5 °C/min

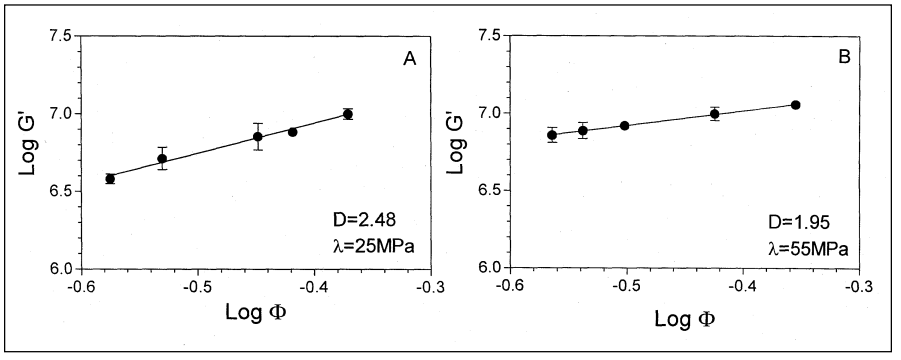

Figure 19—Rheological determination of D for milkfat slow (A) and fast (B) cooled to 5 EC

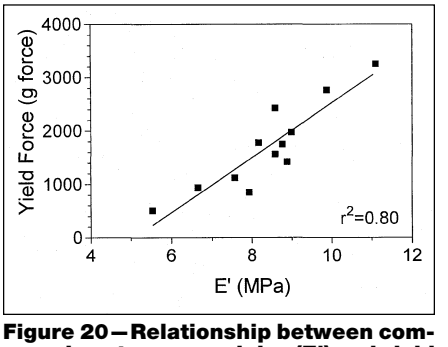

Figure 20—Relationship between compression storage modulus (E') and yield force of milkfat

continuous operations (Kleyn 1992). Working serves to decrease the hardness of butters, although with kneading (Sone and others 1966) and reworking (Gupta and deMan, 1985) butter can also became increasingly sticky. There is also a limit beyond which working has no effect (Gupta and deMan, 1985). The amount of structure breakdown with working depends on the properties of the butter, not the intensity of working (deMan 1969).

Post-manufacturing storage and handling influence butter firmness (deMan 1969; Precht 1988). Specifically, storage time and temperature are 2 important considerations. Setting occurs with time and can continue for months after manufacture (deMan and Wood 1959). The original hardness of butter after churning determines the extent of this setting (deMan and Wood 1959). Setting also depends on the fat composition and manufacturing conditions (Precht 1988). Setting was more extensive in conventionally made butter than that made in the continuous process (deMan and Wood 1959). Kulkarni and Rama Murthy (1985) found that buffalo butter stored between -20 and 15 °C exhibited changes in its rheological properties with time. At a constant temperature, butter viscosity and yield stress changed the most during the first 2 d of storage. The rate of change was higher at lower storage temperatures (Kulkarni and Rama Murthy 1985).

The effects of storage temperature on butter texture can be very important. For example, a decrease in temperature of only a few degrees can double butter's hardness (Mortensen and Danmark 1982a). Using dynamic mechanical analysis, Shukla and Rizvi (1995) related the liquid fat contents at different temperatures to the viscoelastic behaviors of butter and butter enriched with high-melting triacylglycerols. They plotted the complex modulus, which can be correlated with the degree of firmness, against the amount of liquid fat at each temperature. Higher solid fat contents and complex viscosities at higher temperatures resulted in increased stability at room temperatures in the enriched samples (Shukla and Rizvi 1995). Butters stored at 5 °C had higher failure stresses and moduli than those stored at –30 °C (Kawanari and others 1981). Temperature effects on butter texture are related primarily to changes in solid fat content with temperature (Precht 1988). Crystallization temperatures influence the firmness values, crystal morphology, and amount of solid fat (Foley and Brady 1984).

Conclusions

THE AREA OF MILK LIPID RHEOLOGY has been dominated by a desire to improve butter's cold spreadability. Out of this have come some successes in characterizing butter consistency with empirical tests and relating these results to sensory-evaluated parameters like spreadability. However, milkfat and butter are complex systems. Characterization and optimization of butter consistency is complicated by a number of factors. These include regional and seasonal variations in milkfat composition, the strong time and temperature dependence of milkfat's rheological properties, the fact that many parameters in butter are influenced simultaneously, and strict legal standards of identity for butter. However, interest in resolving the structure of the underlying fat crystal networks is growing.

Holcomb (1991) provided a compilation of references concerning the structure and rheology of dairy products. Unfortunately, there have been relatively few attempts to correlate structure and rheology. Attempts to relate the structure of fat crystal networks to their mechanical properties have been recently reviewed by Narine and Marangoni (1999a, 2001). Advances have been made recently in relating the underlying microstructure of fat crystal networks to the mechanical properties using the techniques of fractal analysis (Narine and Marangoni 1999b, 1999c). Simultaneous advances in theoretical analyses of large deformation tests in measuring undisturbed structure by small deformation rheological studies and in microscopy offer the exciting possibility of linking milkfat and butter structure to rheology, and ultimately to consumer preference.

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