Chapter 10
Rheology and Texture of Cream, Milk Fat, Butter and Dairy Fat Spreads

Braulio A. Macias-Rodriguez and Alejandro G. Marangoni

1 Introduction

'Rheology' is a branch of physics concerned with deformation and flow experienced by complex fluids and soft materials such as foods when acted on by forces. Such forces may be 'naturally' exerted (e.g. gravitational or interaction forces holding a structure) or deliberately applied during their industrial process, use or consumption. Without exception, rheological phenomena occur in cream, milk fat, butter and dairy blends where it plays essential roles in fundamental, technological and sensorial aspects. Specifically, rheological properties provide information about interaction forces and reversible/irreversible flow of the structural elements of the mesoscopic network. It also relates to the application, "in-use" textural and sensorial properties (e.g. incorrect blending of milk fat fractions leads to macroscopic softening attributed to eutectic formation). Furthermore, it contributes to understanding the effects of formulation and processing. This information is used to establish rheology-structure relationship (e.g. develop models linking shear modulus and microstructure), rheology-texture relationships (e.g. describe firmness in terms of shear compliance), and rheology-formulation-processing relationships (e.g. assess the effect of cooling on firmness), all equally important to understand, control and improve product quality and process performance.

In this chapter, we highlight the above-mentioned aspects, while focusing largely on the characterization of rheology and texture of cream, milkfat, butter and dairy spreads and in some cases in their relationship. At this point, it is important to make a distinction that rheological properties are inherent to the tested material, while textural attributes are not. Texture, earlier coined 'psycho-rheology' by Sir Scott

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B. A. Macias-Rodriguez (✉) · A. G. Marangoni
Department of Food Science, University of Guelph, Guelph, ON, Canada
e-mail: amarango@uoguelph.ca

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Blair (considered the founding father of food rheology by many researchers), is a multifaceted field of study (Scott Blair, 1947). In the words of Szczesniak (2002), "*Texture is the sensory and functional manifestation of the structural, mechanical and surface properties of foods detected through the senses of vision, hearing, touch and kinetics*". Although it is more reasonable to measure rheological material functions, these properties are frequently unable to describe features only captured in the realm of texture. Such complexity arises due to the highly heterogeneous and multiscale structure of foods dictated by their formulation and processing regimes, and their deformations that they undergo during processing, use and oral processing (this latter aspect concerns thin-film rheology or tribology as covered at length in Chap. 11).

Considering the contribution of both rheology and texture to the understanding of cream, milk fat, butter and dairy spreads, it is the aim of this chapter to offer an integrated account of both fields. To achieve this, we summarize major empirical and fundamentals methods to measure rheological properties and textural attributes, detail some relations to calculate relevant parameters, and provide and contrast previous studies when possible. We take this approach due to the high heterogeneity of the literature. Making clear and meaningful connections among all studies is an elusive task due to arbitrary testing conditions and deformations applied to the materials under investigation. We also describe the structures of cream, butter and milk fat, and their proposed link to rheology and texture, with particular emphasis on milk fat crystal networks. In milk fat, these properties and attributes depend in a complex manner on at least three factors: volume fraction (or solid fat content), crystal microstructure and crystal interactions (Narine & Marangoni, 1999a). Finally, we summarize some of the major formulation and processing approaches taken to tailor the rheology of these products.

2 Technological Implications of Rheology and Texture of Cream, Milkfat and Derived Products

The study of rheology and texture in cream, milk fat and their derived products: butter, recombined butter and milkfat blends has born out of the necessity for assessing, controlling and improving their industrial process, quality, consumer acceptability and even for preventing fraudulence.

Cream, the starting point of manufacture of milk fat and butter, is an extremely complex system from a rheological standpoint, far more complicated than milk due to their higher solid fat content, especially at low temperatures. The quality of cream is judged based on sensory perceptions such as "body", a property that the consumer falsely associates with "richness", is a term that is difficult to be precisely reconciled with rheological properties, though it shows strong correlation with viscosity (Scott Blair, 1958).

Milk fat, a natural product obtained from cream, is the major constituent of butter. To broaden the range of functionality of milk fat, it can be separated into fractions with different chemical make-up and melting ranges that affect rheological and textural properties of butter and dairy spreads (Van Aken & Visser, 2000). In these products, quality is largely dependent on firmness or hardness, i.e. resistance to deformation or penetration, and spreadability, i.e. the ease with which the material spreads on bread or another substrate (Prentice, 1993). For example, a "good" butter should not be too firm otherwise, it would tear the bread, nor too spreadable, otherwise it would not remain as a continuous layer on the surface of the bread and appear "oily" or "sticky". It should be neither tough nor crumbly or brittle. A "good" butter should appear "vivid" (i.e. *show some elasticity*) when spread on bread (Scott Blair, 1953). The terms 'hardness' and 'firmness' are used interchangeably throughout the chapter, though some authors suggest the use of 'firmness' for recoverable viscoelastic deformations and 'hardness' for non-recoverable plastic deformations (Faber, Jaishankar, & McKinley, 2017a). The notion of plastic deformation is applicable to butter since it is not completely deprived of elasticity when sheared during spreading. Textural attributes can be correlated to rheological properties (e.g. modulus, compliance, viscosity).

Due to its practical importance, the texture and rheology of butter has been a subfield of research which has laid the foundations of fat rheology. Much work has been published on sensory panels involving craftsmen, *ad hoc* methods and development or application of empirical and fundamental methods aimed to grade or measure firmness and spreadability and determine moduli and viscosities (Prentice, 1993; Scott Blair, 1954, 1958; Wright, Scanlon, Hartel, & Marangoni, 2001). These reports have also investigated the influence of processing and crystallization conditions on textural attributes and rheological properties, supporting their relevance in product quality (Mulder, 1953; Prentice, 1984a, 1993; Scott Blair, 1954, 1958).

3 Structure of Cream, Milk Fat and Butter

Structurally, cream resembles milk with the major difference being the higher content of fat globules in cream. It has been suggested that cream contains globules displaying a bimodal size distribution, with larger globules being more abundant (Prentice, 1993). The distance between the globules, whose average size ≈3 μm, is marginal ≈0.35 μm for creams with fat content of 48% (Prentice, 1993; van Vliet & Walstra, 1979). Increasing and reducing the fat content, reduces and increases the distance between globules, respectively, which alters the viscosity of the cream (Prentice, 1993). At the molecular level, milk fat is composed of an extremely heterogenous triacylglycerols (TAG) mixture. At the nanoscale, TAGs crystallize into lamellae and then into platelets—the fundamental crystal unit. At the submicron and microscopic scale, platelets aggregate into clusters or flocs that make up the microscopic crystal network in which liquid oil is embedded. The microstructure has a tremendous bearing on rheological properties (DeMan & Beers, 1987; Heertje, 1993; Narine & Marangoni, 1999a; Tang & Marangoni, 2007). Within the microstructure, crystal aggregates differing in size (0.1–140 μm) and morphology and being held together by a wide spectrum of bonds of variable degrees of strength and reversibility (van den Tempel, 1961; DeMan & Beers, 1987; Narine and Marangoni 1999e; Shama & Sherman, 1970). Furthermore, butter comprises a water phase dispersed in a continuous oil phase containing crystalline aggregates and fat globules (partly broken or intact). This structure is imparted by churning, physical working

Fig. 10.1 Schematic structure of cream, milk fat and butter. Gray globules correspond to oil droplets, white globules represent water droplets and clusters correspond to crystalline fat

and crystallization, where the membrane of fat globules collapses, globules coalesce, oil leaks out and crystal aggregates form. Figure 10.1 shows a schematic representation of the microstructures associated with cream, milk fat and butter respectively.

4 Rheological and Textural Characterization

Evaluation tests can be broadly classified into three main categories: imitative, empirical, and fundamental tests-based on its foundations and the information obtained from them (Scott Blair, 1958). Each type of test has its own merits and limitations. Imitative tests attempt to resemble the conditions the material will be subjected to during their use, such as machines that imitate spreading of butter on bread by measuring shear imposed by a knife edge. Although they show some correlation with sensory scores or empirical methods, they lack a solid foundation and methodology, control of deformations and quantitative measures. Empirical tests imitate more closely the basic motions of deformations applied during processing and product usage. Their measures (typically textural attributes such as firmness, spreadability) depend on instrument configuration and correlate well with sensory assessment of texture. They are useful for quality control and product development routines such as for adjusting milk fat blending or butter-making. Fundamental tests are rigorously defined in physical and mathematical terms, and aid the measure of true or apparent (for nonhomogeneous flows) bulk properties. They are used for research and development purposes and require a certain degree of expertise. In the following section, we describe the principles of the main empirical and fundamental methods developed early and still in use to measure the rheology of cream, milk fat, butter and dairy fat blends. We also briefly discussed emerging rheological approaches and techniques. It would be impractical to review the many discontinued empirical methods (at least in research grounds). For the interested readers, an extensive account of such methods appears in (Deman, 1983; Mulder, 1953; Prentice, 1984a, 1984b, 1993; Scott Blair, 1954, 1958).

4.1 Imitative and Empirical Tests

4.1.1 Indentation and Penetration Tests

Indentation and penetration have been by far the most popular methods to evaluate the texture of butter, milk fat and edible fats in general. They offer simple and inexpensive characterization which is useful for investigating the effect of processing conditions on hardness and correlate well with sensory panels (Van Aken & Visser, 2000). They are based on the resistance of a material to be "pierced" or indentated by a test body: rod, cone, sphere, needle, etc. The resistance is measured as load, depths or rates of indentation/penetration of the testing body. Some of the early used approaches can be more or less described in chronologically order as the "*oleogrammeter*" developed by Brullet (a vertical rod applied on hardened surfaces of fat loaded with increasing weights aimed to detect butter-margarine adulteration), compression of cylinders of butter (under constant loads and fixed times to establish correlations between hardness and melting point), penetration studies with vertical rods of different dimensions to estimate butter temperature relationships, Kruisheer's penetrometer, Mohr and Wellm's cone- and sphere-yield tests (to assess used for in-container butter) (Scott Blair, 1954). To date, cone penetrometry remains the most popular method to measure the texture of butter or dairy spreads (Wright et al., 2001). A schematic representation of a typical cone is shown in Fig. 10.2.

Conical configurations varying in loads and angles allows to cover a range of textures. Most studies included constant load experiments and to less extent constant rate experiments. Both methods show good agreement with one another (Haighton, 1959; Hayakawa & DeMan, 1982). Results are reported as penetration depths or converted into yield values, hardness or spreadability indexes, using various equations dependent on the testing body and test conditions (Haighton, 1959).

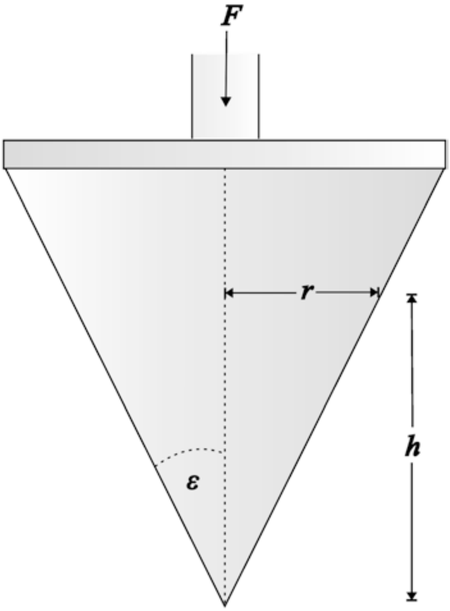


Fig. 10.2 Schematic representation of a cone penetrometer. Applied force *F*, cone radius *r*, arbitrary penetration height *h*

Considering that most of the force is used to overcome the yield point (the stress at which deformations are a combination of elastic ‘reversible’ and plastic ‘irreversible’ deformations) and provided that the motion is slow, an empirical yield value is defined as the force load per unit cross-sectional area of the cone as given by,

$$\text{yield value} = \mathrm{K'W / p^n} \tag{10.1}$$

where K' is a constant dependent on the cone angle, W is the weight of the cone (g), p is the penetration depth raised to a fractional power $1.4 \leq n \leq 2$ as found empirically. The values of these empirical coefficients appear to depend on hardness and type of fat (Haighton, 1959; Tanaka, de Man, & Voisey, 1971) suggesting a complex relationship between the cone and yield value (e.g. for butter $n \approx 1.6$). The yield value may be affected by frictional forces between the fat and the tested material, though these are negligible for truncated cones (Wright et al., 2001). Since yield value and viscosity show some linear proportionality, measuring either of these parameters or a combination of both is necessary for defining the rheology of a system (Mulder, 1953). Using this relationship, yield values have been assigned to margarines and shortenings according to their usability (assessed by ‘thumb’ tests), though values are not universal but rather specific to product type and country (Haighton, 1959). Alternative definition of apparent yield stress (*AYS*) has been proposed (International Dairy Federation):

$$\mathrm{AYS} = \mathrm{P} / A_{proj} = gw / \pi d^2 tan^2 \left(\varepsilon\right) \tag{10.2}$$

where g is acceleration due to gravity, w is the weight of the cone, ε is the angle of the cone and d is the penetration depth (Wright et al., 2001). Penetration values can be also converted to hardness defined as force divided by penetration area (similar to *AYS* but divided by the impression area A_{imp}) (Wright et al., 2001). Alternatively, they can be converted to spreadability index (SI) using the following relation:

$$\mathrm{SI} = \mathrm{C_u} - 0.75\left(\mathrm{C_u} - \mathrm{C_w}\right) \tag{10.3}$$

where $\mathrm{C_u}$ and $\mathrm{C_w}$ refer to the yield values of unworked and worked fats, to determine the extent of work softening of margarine and butter (Haighton, 1965). Yield values have found good correlation with spreadability. Despite the advantage of cone penetrometry, some of the main arguments made against its use include poor reproducibility for firm butters compared to extrusion and ‘sectility’ tests, use of arbitrary testing conditions (e.g. penetration time), and ill-defined measures of yield value that deviate substantially from the ‘true’ yield stress (Atkins & Tabor, 1965). These assertions are supported by studies reporting the inability of cone penetrometry to differentiate among all textural differences of butter and correlations of yield values with spreadability (this property involves extensive shear and structural breakdown post yielding) (Haighton, 1959, 1965; Shama & Sherman, 1970). Van Aken and Visser (2000) estimated the firmness of milk fat (expressed as the yield value) during crystallization. Firmness decreased during kneading but it increased in between kneading periods and during storage. This behavior was attributed to softening of the fat due to rupture of inter-crystal bonds during kneading, reformation of new primary bonds in between kneading and recrystallization of fewer primary bonds (compared to unkneaded samples) during storage.

4.1.2 Extrusion Test

Extrusion has been used to a lesser extent to evaluate the texture of butter. Its main advantage is that it mimics the flow of butter during spreading (though in an empirical manner). It involves measuring the thrust of a piston required to extrude a soft material such as butter through an orifice or nozzle. In principle, it resembles a sectility test, in that in extrusion flow is confined to one side, whereas in cutting flow occurs past both sides of the cutting edges (Prentice, 1984a). Previous tests on butter have shown that the force of extrusion correlates well with spreadability as determined by subjective assessment (Prentice, 1993). The force of extrusion results from two major components: one associated with force to induce extrusion through the orifice, which is constant if properties and rate of extrusion remain constant; and the other with the force to overcome friction at the wall, which varies as the test progresses, e.g. frictional contribution diminishes as the barrel empties (Prentice, 1984a). Some criticisms to this test include time-consuming mounting of the sample and poor control of measuring temperature (Mortensen, 1983).

4.1.3 Wire Cutting Tests (Sectility)

Wire cutting consists of driving a standard wire through a block of sample and measuring the force required to cut the sample (at constant or variable speed) (Scott Blair, 1954). Their main advantage is that it is simple, accessible and reproducible and that the cutting force or 'sectility' is simply related to the diameter of the wire. Since wire cutting involves fracture, deformation, and friction in general, it offers a viable method to measure these properties using some simple assumptions described (Kamyab, Chakrabarti, & Williams, 1998) for cheese cutting. A schematic diagram of wire cutting perpendicularly through a surface is depicted in Fig. 10.3.

For a block of width B, cut by a wire of diameter d, where fractures are assumed to arise from elastic splitting and from yielding and friction, the fracture grows by length dx when the cutting force F moves dx, and F bears the fracture toughness G_c (for elastic splitting), yield stress σ_y and frictional force $\mu\sigma_y$:

$$Fdx = G_C Bdx \quad \left(\text{force associated with elastic splitting}\right) \tag{10.4}$$

$$F = 2B\int_0^{\pi/2} \frac{d}{2}\left(\sigma_y cos\theta + \mu\sigma_y sin\theta\right)d\theta\left(\text{force associated with yielding and friction}\right) \tag{10.5}$$

The total force is then

$$F = BG_C + B\left(1+\mu\right)\sigma_y d \qquad i.e., \quad \frac{F}{B} = G_C + \left(1+\mu\right)\sigma_y d \tag{10.6}$$

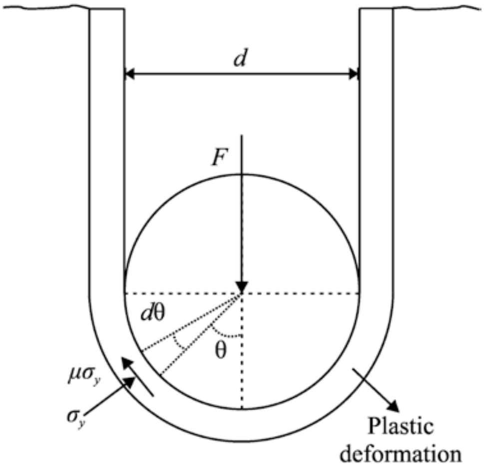


Fig. 10.3 Wire cutter of a block showing frictional and plastic deformation

This means that for steady-state cutting, *F/B* is proportional to *d* with slope of $(1+\mu)\sigma_y$ and intercept of G_c. A more elaborate equation than Eq. (10.6) has been proposed to account for plastic deformations (Kamyab et al., 1998). To the best of our knowledge, G_c has not been estimated for butter or milk fat blends but it should be somewhere around 10 J/m^2 as reported by (Kloek, van Vliet, & Walstra, 2005) using a more general analysis for hydrogenated palm oil-sunflower oil blends. Previous studies have shown excellent correlations of 'sectility' with firmness and viscosity of butter determined by compression of cylindrical specimens and with spreadability assessed subjectively (Scott Blair, 1954). A common argument made against the estimation of rheological properties with a wire cutter in butter is its anisotropic crystalline structure, which may lead to varying resistance in different cutting planes (e.g. for laminated structures, less resistance will be expected in the parallel direction to the lamination).

4.2 Fundamental Tests

4.2.1 Viscometry

Viscometric flows consists in applying steady shear to fluids or semifluid materials. These tests are typically performed with rotational viscometers or rheometers using Couette or cup-and-bob geometries. Results are commonly reported as steady shear viscosity η as a function of shear rate $\dot{\gamma}_0$. Much effort has been devoted to study the viscosity of cream given that it is the initial point of the manufacture of butter and it is a product by itself (Prentice, 1993). Cream is a structured fluid, an emulsion of milk fat in milk plasma (Huppertz & Kelly, 2006). Several factors influence its viscosity such as the volume fraction of fat globules and solid fat, their size and the rheology of continuous and dispersed phases, among others. These, in turn, are affected by origin, method of preparation and history of the cream. The rheology of cream is mainly non-Newtonian, i.e. pronounced shear thinning occurs. However, at

T ≈ 40–80 °C conceiving that all triglycerides contained within the fat globules are molten, it behaves nearly Newtonian and resembles somewhat the flow of milk, such as for creams containing ≤50% fat (or $\phi_{fat} \leq 0.4$) at approximate shear rates of $\dot{\gamma}_0 \geq 10\ \text{s}^{-1}$ (Phipps, 1969). For cream with similar fat content, a decrease of 3% of the apparent viscosity η_{app} (i.e. dependent on shear rate) per 1 °C rise of temperature has been estimated (Lyons & Pyne, 1933). In general, decreasing the fat content of the cream increases the encountering distance of the fat globules during shearing and thus reduces the resistance to mutual rotations (and thus of viscosity), whereas increasing the fat content, promotes the 'hindering' effect, partial coalescence during shear, which altogether increases viscous resistance. For example, η_{app} of cream with 54% fat compares to that of 48% fat only if the primer is subjected to a stress three times greater than the latter, to achieve the same flow rate.

4.2.2 Pressure-Driven Flow: Capillary Rheometry (Orifice Die Extrusion)

Orifice die extrusion flows are useful for determining viscosities at controlled shear rates closed to those encountered during manufacturing and usability of pastes such as butter (e.g. during spreading $\dot{\gamma} \approx 300\ \text{s}^{-1}$ and cutting $\dot{\gamma} \approx 16\ \text{s}^{-1}$) (Castro, Giles, Macosko, & Moaddel, 2010; Prentice, 1993). They can also be used for the determination of yield stress. For this, a capillary rheometer consists in driving a tool (e.g. a piston, ram) at a linear speed S to force material through a barrel with diameter D_0 and a die of diameter D and length L (see Fig. 10.4) (Macosko, 1994).

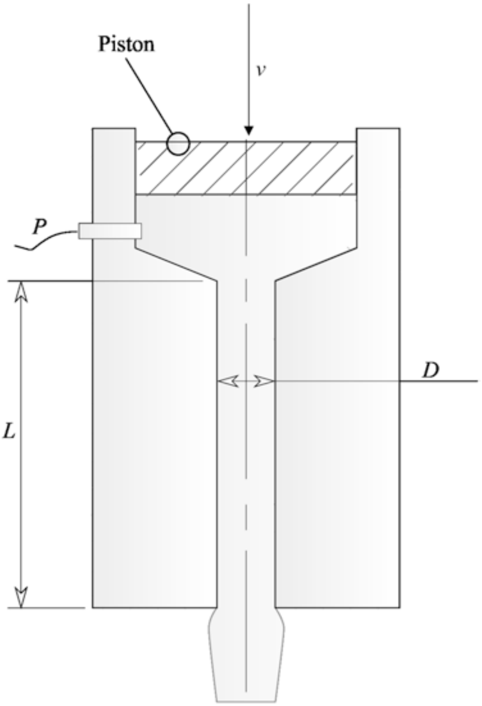


Fig. 10.4 Schematic view of a material being extruded through an orifice die with diameter D and length L in a capillary rheometer. Pressure P is applied by a piston with velocity v, and measured during the test

During this operation, the total pressure drops (P_{tot}) are measured which are made up of two major contributions: pressured drops at the entrance (P_{en}), associated with extensional viscosities μ, and shear pressure drops at the capillary wall (P_{shear}), associated with shear viscosities η. To interpret the results, common corrections that need to be applied include Rabinowitch, Bagley, Mooney and wall slip corrections to account for non-Newtonian behavior, entrance pressure losses, and wall slip at the die wall respectively. The shear stress at the wall (σ_w) and the corrected non-Newtonian shear rate ($\dot{\gamma}_w$) at the wall are calculated with standard formulas to determine apparent viscosities (η_{app}):

$$\sigma_w = \frac{(P_{tot}) \cdot D}{4L} \tag{10.7}$$

$$\dot{\gamma}_w = \frac{8D_0^2 \cdot S}{D^3}\left(\frac{3}{4} + \frac{1}{4}\frac{d\,lnQ}{d\ln\sigma_w}\right) \tag{10.8}$$

and

$$\eta_{app} = \frac{\sigma_w}{\dot{\gamma}_w} \tag{10.9}$$

where Q is the flow rate. The term in the parenthesis corresponds to the Rabinowitch correction. To calculate true shear stress σ, P_{en} can be calculated using the Bagley correction and substracted from P_{tot} in Eq. (10.7). The correction consists in obtaining pressures drops typically at two shear rates (using capillaries with the same D_0 but different D/L) and extrapolation to a die of zero length. To determine true shear rate (and thus true viscosity), wall slip is corrected using the Mooney relation to extrapolate to infinite diameter (Macosko, 1994). The entrance pressure can also be used to estimate μ. Moreover, pressure drops can be utilized to calculate yield stress of pasty materials (Castro et al., 2010). The yield stress σ_{y} using capillary extrusion can also be calculated using the analysis developed by Benbow and Bridgewater (1993). Considering constant volume, zero-length orifice die, plastic behavior and rate-dependence of pressure, the following relationship was proposed:

$$P = 2\left(\sigma_0 + \alpha V^n\right)\ln\frac{D_0}{D} \tag{10.10}$$

where P denotes the pressure to deform a material from its original diameter D_0 to a final diameter D, σ_0, α, and n can be considered material constants independent of die geometry and extrusion rate. The extensional yield stress σ_0 can be converted into a shear stress according to Von Mises yield criterion:

$$\sigma_0 = \frac{\sigma_y}{\sqrt{3}} \tag{10.11}$$

Castro et al. (2010) recently applied this method to the characterization of the yield stress of soft solids and found good correlation with results obtained from rotational steady shear measurements. Pressure drops and rheological properties of butter such as yield stress σ_y and apparent viscosity η_{app} have been reported as a function of measuring temperature, storage temperature and time ('ageing') using various relations such as the Hagen-Poiseuille (assuming Newtonian flow), Casson and power-law equations have been used to describe yield stress (Hanck & Wall, 1966), estimated as $\sigma_y \approx 2\text{–}12$ kPa at $T = 5\text{–}15$ °C (Kawanari, Hamann, Swartzel, & Hansen, 1981). Values of σ_y and η_{app} were affected by test temperature and 'ageing' temperature, although the latter factor had little effect on properties determined by empirical compression and penetrometry suggesting capillary extrusion was more sensitive to such changes. Temperature is inversely correlated to apparent viscosity (i.e. higher temperature, less resistance to flow). This effect is less pronounced for butter containing high melting triglycerides possibly due to a greater degree of crystallinity leading to firmer products (Shukla, Rizvi, & Bartsch, 1995). Flow behavior of cream has also been studied but with a capillary 'consistometer', in which the material is forced by compressed air at known pressure through a series of standard glass capillary tubes (Scott Blair, Hening, & Wagstaff, 1939). Flow of natural, homogenized and reconstituted cream revealed five types of characteristic behavior: (1) truly fluid; constant viscosity, (2) viscosity is dependent of stress and independent of dimensions of the capillary—in most cases viscosity falls with increasing stress (structural viscosity), (3) viscosity is independent of stress but dependent of capillary dimensions—in the majority of cases narrower or longer capillaries show lower viscosity (structural breakdown), and (4) viscosity dependent on stress and dimensions of capillary. Such complex behavior might be attributed to the fat content of the cream and varying amount of crystalline fat within the globules. A major instrumental concern when conducting capillary rheometry at high shear rates is the likelihood of wall slippage, especially due to the self-lubricating nature of butter, milk fat and dairy fat blends. Thus, it is customary practice to correct for wall slip as shown above. Other corrections and equation (such as those described above) to get reliable estimation of material properties can make the tests laborious.

4.2.3 Compression

Compression tests are one of the most popular tests for determining fundamental rheological, fracture properties and empirical textural attributes due to their practicability and easiness of interpretation. They involve deforming a specimen of known dimensions (typically a cylinder) at constant force (creep) or at constant crosshead speed (uniaxial compression if only the upper plate is mobile) for a standardized time. For creep compression, deformation is measured as a function of time, whereas for the latter, force is recorded as a function of time. Davis (1937) and DeMan, Gupta, Kloek, and Timbers (1985) conducted compressive creep (force loading) and recovery (force unloading) on cylindrical samples of butter. Davis (1937) determined modulus of elasticity G for the recovered deformations and viscosity defined as the ratio of the compressive stress to the strain rate ($\eta = \sigma / \dot{\gamma}$) from the plastic non-recovered deformations, whereas DeMan et al. (1985) differentiated among instantaneous elasticity and retarded elasticity. Accounts on how to calculate similar materials measures albeit obtained from creep shear are given subsequently. A combination of apparent shear modulus G and viscosities η provided a measure of 'firmness' (the resistance to creep deformation typically measured over long time), and a ratio of viscosity to elasticity η/G offered a measure of 'springiness' (i.e. the extent of instantaneous recovered strain evaluated at short times), though not justification of such relationships were provided (Davis, 1937). Recently, clear relationships between such properties have been developed for shear creep and recovery compliance (Faber, Jaishankar, & McKinley, 2017b). Increases in loading time, magnitude of force, work softening and temperature all lowered elastic and viscous properties (DeMan et al., 1985; Scott Blair, 1938). Scott Blair conducted successive loading experiments similar to those by Davis (1937) but measured the time required for achieving a strain deformation of 50% to estimate a pseudo-viscosity which he linked with spreadability. For uniaxial compression, force-time curves are reported or converted into normal stress σ_n versus Hencky strain $\in$ or strain rate $\dot{\epsilon}$. Previous studies on butter and milkfat have also interpreted firmness or hardness as the maximum load of the force-time curve, and other textural attributes have been determined by double compression imitative tests referred as to "Texture Analysis". To convert force-time curves, treating butter or milk fat as an incompressible material, the following equations have been applied (Kloek et al., 2005):

$$\sigma_n = F / A \tag{10.12}$$

$$\epsilon_h = \ln\left(h_t / h_0\right) \tag{10.13}$$

$$\dot{\epsilon} = \left(d\epsilon / dt\right) = \dot{h} / h \tag{10.14}$$

where A is the circular area of a cylinder with diameter D, h_0 and h_t are the specimen heights at the beginning and during the test. Apparent rheological measures (i.e. measures that vary according specimen height) of the Young's modulus E_{app} (measured as $d\sigma_n/d\in$ where $\in \to 0$), yield point $\sigma_{\mathrm{y\_app}}$ (defined as the maximum stress) and viscosity η_{app} (determined from the slope $d\sigma_n/d$). Some limitations of compressive test include their limited range of accuracy, e.g. true elastic modulus cannot be measured for yield strains below ≈2% (paradoxically this falls somewhat within the yielding region of fats), manifestation of cracks or shear bands (regions of 'strain localization') due to large strains, e.g. in firm and brittle butters compressed at low temperature, buckling or bulging (cylindrical sample becomes barrel-shaped) and strong frictional effects at the boundary of the sample. Adequate specimen sizes ($h_0/D < 1.5$ but not too low to avoid friction) and lubricated plates (e.g. coated with oil or Teflon) can be used to circumvent the last two effects (Vliet, 2013).

4.2.4 Squeeze Flow

Squeeze flow are relatively simple to implement and allow a wide range of shear rates. These flows are encountered namely during rolling compression. Squeeze flows entails compressing a highly viscous or soft solid typically between two parallel circular plates to squeeze it out radially. The use of lubricated sample-wall interfaces can lead to principal planes (of vanishing shear stress) that achieve frictionless or perfect slip, so pure elongational strain (or biextensional flow) occurs during compression (see Fig. 10.5).

Note that unlike other rheometric tests where slip makes measurements more intricate and lengthy, the attainment of perfect slip rather simplifies the calculations involved in this test. Calculations are based on initial theory developed by (Chatraei, Macosko, & Winter, 1981) for homogeneous deformation (perfect slip) under constant compressive deformation (creep), and adapted to constant displacement rate experiments (Campanella & Peleg, 2002). Assuming a perfect slip boundary condition, for a material being squeezed for a time *t* between circular plates of radius *R*, the relationship of the squeezing force *F*(t) and time dependent sample thickness is given by:

$$F(t) = \frac{3\pi\eta_b R^2}{h(t)} \dot{h}(t) \tag{10.15}$$

where η_b is the biaxial extensional viscosity, and $\dot{h}$ is the steady squeeze rate [or $-\mathrm{d}h(t)/\mathrm{d}t$ or $-\mathrm{d}H(t)/\mathrm{d}t$]. Depending on the type of experiment, *F*(t) or $\dot{h}(t)$ remains constant. For this relationship to hold, experiments must be conducted at large aspect ratios $h \ll R$ ($h/R \approx$ 10–30) to reduce end effects and increase signal (this latter aspect is applicable to semi-fluids). The first aspect imposes some limitation in the consistency of the measured sample, e.g. preparing pristine solid-like butter disks with appropriate *h/R* is somewhat difficult (ratios of $h/R \approx$ 2–4 have been used previously in the literature of butter). Researchers have conducted squeeze flow of butter with constant area (i.e. sample fills entirely the plates). Assuming perfect slip for butter (based on its self-lubrication), steady (at $\dot{\gamma}_0 \approx 10^{-3}\ \mathrm{s}^{-1}$) and non-steady (not stress nor shear rate were constant) viscosities of butter have been estimated as $\eta_b \approx 10^8$ Pa s at 15–17 °C. Butters made of high melting triglycerides have shown higher η_b (~1 log order higher at 17 °C) than those formulated with anhydrous milk

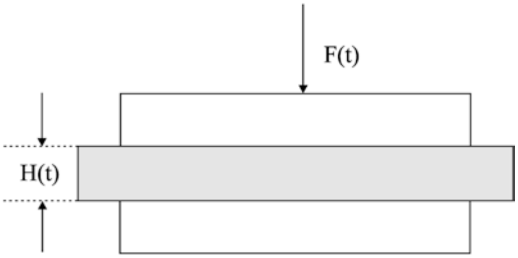


Fig. 10.5 Schematic view of a material moving radially outward during lubricated squeeze flow between parallel plates

fat, and their viscosity increases for both types of butter during storage. These findings support that solid-like high melting triglycerides increase resistance of crystal aggregates to flow and that sintering occurs during storage. Some disadvantages of squeeze flow include that at very large Hencky strains ($\in \approx 3$) the lubricated condition may be violated. In such a case, complex flow fields occur where both slip and shear boundaries coexist, something that is not always easy to detect experimentally and requires more elaborate analysis of the data.

4.2.5 Drag Flow: Oscillatory Shear

Shear rheometry can be performed at small or large strains or stress with rotational rheometers. In this respect, oscillatory shear is the most popular fundamental test employed in butter, milk fat and dairy spreads. Oscillatory shear consists of applying a sinusoidal input function (strain or stress) and measuring the associated response comprising in-phase (stored energy or elastic modulus) and out-of-phase (loss energy or loss modulus) components with respect to the input function. Depending on the amplitude of the input function, oscillatory shear can be divided into two regimes: small amplitude and large amplitude, which probe linear and nonlinear viscoelastic regions, respectively (Hyun et al., 2011). An intermediate regime between small and large amplitude has been referred as to the medium amplitude regime where the nonlinear response grows asymptotically. We do not make a distinction of such regime, and any deformation beyond the linear viscoelastic region is considered large amplitude or nonlinear. Two types of geometries: cone and plate and parallel plate geometries are commonly used for oscillatory shear. In cone and plate, geometries are brought together slowly to minimize sample breakdown or residual stresses affecting the measurement. In parallel plates, loading of stiffer preformed samples is performed with sufficient normal force to allow full contact with the geometry and prevent slippage during measurements but not too high to disturb the sample. Parallel plates appear more satisfactory to reduce damage to the microstructure although this cannot be completely eliminated (Macias-Rodriguez & Marangoni, 2016; Prentice, 1984a). Compared to other fundamental tests, oscillatory shear allows simultaneous characterization of elastic and viscous properties in a broad spectrum of flow conditions (defined by stress or strain and oscillatory frequency) and provides more controlled flow (i.e. gradual increase of deformations). A shortcoming of this test is that it is prone to edge fracture and wall slippage, though the latter artifact can be circumvented using modified surfaces (e.g. covered with sandblasted paper or filter paper to enhance adhesion to the plates).

Small amplitude oscillatory shear (SAOS). Small amplitude oscillatory shear (SAOS) tests are useful to measure viscoelastic properties of the underlying microstructure. SAOS imposes relatively small strains or stresses in the linear viscoelastic region (LVR) typical of materials interacting via short-range van der Waals forces such as butter and edible fats in general (van den Tempel, 1961). As mentioned, to avoid disturbance of the original network, careful loading (preferably with normal force control) must be performed (Macias-Rodriguez & Marangoni, 2016; Thareja et al., 2011). During SAOS tests, strain and stress maintain their linear proportionality and the crystal network exhibits viscoelastic solid-like behavior ($G' > G''$) characterized by high modulus and weak frequency (ω) dependence (van den Tempel, 1961; Narine & Marangoni, 1999b; Macias-Rodriguez & Marangoni, 2016; Rohm & Weidinger, 1993; Thareja et al., 2013). For a sinusoidal strain excitation $\gamma(t) = \gamma_0 \sin(\omega t)$, a sinusoidal stress response $\sigma(t) = \gamma_0 \sin(\omega t + \delta)$ is obtained at the same input frequency ω, and with phase angle δ. The response can be decomposed as

$$\sigma(t) = \gamma_0 G'(\omega)\sin(\omega t) + \gamma_0 G''(\omega)\cos(\omega t) \tag{10.16}$$

in which G', the in-phase elastic modulus or stored energy represents the real component, and G'', the out-of-phase viscous modulus or dissipated energy represents the imaginary component of the complex modulus G^* at a given frequency (ω) (Ferry, 1980; Macosko, 1994; Tschoegl, 1989). A Fourier analysis (which converts the time function into frequency domain) of the stress response reveals in the LVR region, only the first or fundamental harmonic ($n = 1$) associated with ω occurs. Figure 10.6 depicts a frequency sweep and strain amplitude sweep of butter illustrating its weak frequency dependence and values of viscoelastic moduli of $G' \approx 10^6$ Pa and $G'' \approx 10^6$ Pa. This is in good agreement with previous studies on butter obtained from high-melting triglyceride (HMT) and anhydrous milk fat (AMF) (Rohm & Weidinger, 1993; Shukla & Rizvi, 1995).

Values of elastic modulus, complex viscosities and critical strains of $G' \approx 10^6$–10^7 Pa, $\eta^* \approx 10^5$ Pa s and $\gamma_c \approx 10^{-4}$–10^{-3} at T = 15–17 °C respectively were reported (Rohm & Weidinger, 1993; Shukla & Rizvi, 1995). HMT butter showed less temperature dependence and higher magnitudes of the rheological functions due to higher solid fat content and arguably due to microstructure. Both butters have shown increases of G' during storage attribute to 'setting' (increased in firmness due to continuous crystallization). From a practical perspective, the elastic modulus G' correlates well with material hardness (Suresh & Marangoni, 2001).

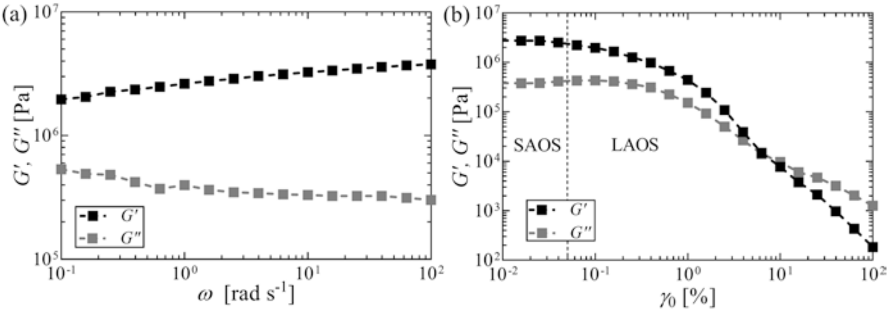


Fig. 10.6 Storage G' and loss G'' moduli of butter (T = 18 °C) measured during (**a**) frequency sweep ($\gamma_0 = 0.01\%$) and (**b**) strain amplitude sweep ($\omega = 3$ rad/s). Dotted line in (**b**) indicates approximate transition from linear (SAOS) to nonlinear regime (LAOS)

Large amplitude oscillatory shear (LAOS). Above a critical strain or critical stress, the material plastically deforms as it starts to yield and 'flow'. As alluded to previously, the yield stress σ_y is an important property that correlates with the usability and sensory perceptions of butter. Despite much controversy about the existence of a 'true' yield stress, the past notion that flow occurs at extremely long timescales below a critical value can be considered negligible at the timescales of applications of most materials (Coussot, 2007). In butter, the confusion rather arose due to the absence of a stress overshoot in steady shear experiments. Nevertheless, this is a common feature of other yield stress materials (Dinkgreve, Paredes, Denn, & Bonn, 2016). From oscillatory experiments, σ_y can be best defined in two main ways: the first requires intersecting stress and strain curves using power law equations to obtain a dynamic yield stress, and the second determining the stress at the intersection of G' and G'' curves as a function of strain to estimate a static yield stress. The primer gives the lowest value of σ_y and γ_y, whereas the latter provides the highest values of σ_y and γ_y since the material have already experience some yielding. Dinkgreve et al. (2016) concluded that for thixotropic materials, both static and dynamic yield stresses must be considered. At large amplitudes (LAOS), complex and nonlinear responses arise in viscoelastic materials such as butter and milk fat. LAOS offers many advantages over more traditional nonlinear rheological methods (e.g. steady shear, capillary rheometry) such as simultaneous and full viscoelastic characterization in deformation and timescale domains, controlled flow (i.e. gradual increase of oscillatory shear minimizes slip) ample operational window (i.e. deformations go well beyond the LVR and thus it can differentiate among microstructures insensitive to SAOS), superior sensitivity (Hyun et al., 2011). LAOS allows independent variation of two parameters: loading strain amplitude γ_0 (for strain-control tests) and frequency ω deformation, yielding viscoelastic responses in a 2D regime map termed the Pipkin space (Pipkin, 1972). In this, nonlinear viscoelastic measures $G'(\omega, \gamma_0)$ and $G''(\omega, \gamma_0)$ are seamlessly linked with linear viscoelastic moduli $G'(\omega)$ and $G''(\omega)$, and with the steady flow viscosity $\eta(\dot{\gamma})$ (Dealy & Wissbrun, 1999; Ewoldt & Bharadwaj, 2013). For a strain input test, the stress material response is in the LAOS or nonlinear regime when the viscoelastic moduli are either variant to changes in γ_0, e.g. $G'(\omega, \gamma_0)$ or $G''(\omega, \gamma_0)$ or the stress response is no longer sinusoidal. As seen in Fig. 10.6, the onset of nonlinear behavior occurs at $\gamma_y \approx 0.06\%$ ($\sigma_y \approx 1360$ Pa). There are several approaches to analyze the nonlinear LAOS data, which include investigating the behavior of the first-harmonic moduli, time-domain raw waveforms τ(t) or two-coordinate axes figures referred as to Lissajous-Bowditch curves and analyzing the raw waveforms via FT rheology, Chebyshev stress decomposition, time dependent moduli, etc. The first-harmonic or average viscoelastic moduli G' and G'' (normally the output of a strain sweep in commercial rheometers) denote the global ('full' or 'intercycle') stress response in the nonlinear behavior. In Fig. 10.6, it can be seen that butter (and fats in general) undergoes average elastic softening coupled with increase dissipation or thinning due to disruption of the crystal network as strain increases. Time-domain raw signals σ(t) and Lissajous-Bowditch curves qualitatively distinguish among material response and capture the onset of nonlinear behavior. Lissajous-Bowditch curves are closed loop plots of γ_0 on the abscissa and σ(t) on the ordinate (elastic representation) or $\dot{\gamma}_0$ on the abscissa and σ(t) on the ordinate (viscous representation). Figure 10.7 shows raw elastic Lissajous-Bowditch plots of butter within and outside the LVR for butter at T = 18 °C.

Within the LVR region ($\gamma_0 < 0.01\%$), the plots mirror nearly 'perfect' ellipses where the tangent slope corresponds to G' and the area enclosed by the ellipse represents G''. Beyond LVR at amplitudes where yield stress is exceeded ($\gamma_0 > 0.01\%$), the plot become gradually distorted and acquire square-like shapes enclosing increasingly larger areas (Ewoldt, Hosoi, & McKinley, 2008; Hyun et al., 2011). Typical features, e.g. global strain softening, and additional local features, e.g. intracycle stiffening, masked by the average viscoelastic moduli can be visualized. Global or average elastic softening, is manifested as inter-cycle clockwise rotation in the slope of the stress-strain curve at strain minima $\gamma_0 = 0$ (i.e. at the 'origin' where strain rate $\dot{\gamma}$ is at maxima) toward the strain-axis. Local strain stiffening is clearly visible as the intracycle upturn of the shear stress at strain maxima $\gamma_0 = \max$ (i.e. at the 'extreme' where $\dot{\gamma} = 0$). Stress overshoots, akin to those observed during in start-up shear, appear in the upper left quadrant of the Lissajous-Bowditch and indicate yielding. Such a stress overshoot is rather 'smooth' (where the tangent to the nearly flat part of the curve cuts the stress axis) for butter and is closely related (though lower) to the stress associated with spreading (Prentice, 1984a). The reversibility of the observed behavior during flow reversal evokes microstructure "healing" or thixotropy (Renou, Stellbrink, & Petekidis, 2010; Kim, Merger, Wilhelm, & Helgeson, 2014; Ewoldt & McKinley, 2010) as previously reported for butter (Sone, 1961; Macias-Rodriguez & Marangoni, 2016). A similar analysis was early described by Elliot and Ganz (1971) and Prentice (1984b) to compare yielding during steady shear with that of oscillatory shear for butter. Application of oscillatory strain amplitude exceeding the yield stress resulted in similar behavior to start-up shear, as demonstrated by nearly square waves similar to those depicted in Fig. 10.7 at $\gamma_0 = 40\%$. Prentice also suggested that Lissajous-Bowditch curves of

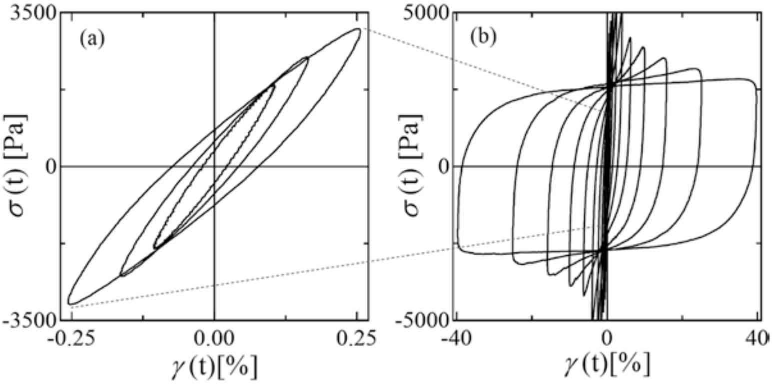


Fig. 10.7 Raw Lissajous-Bowditch plots (elastic perspective) of butter (T = 18 °C) obtained from an oscillatory shear test (ω = 3.6 rad/s) (**a**) linear to mildly nonlinear transition (SAOS to LAOS), (**b**) fully nonlinear response (LAOS)

cream reflected a type of ‘fugitive elasticity’ (or fluid viscosity) established under the action of shearing forces but rapidly relaxed as shearing ceases (Prentice, 1984c). As mentioned earlier, the first-harmonic viscoelastic moduli are the common output of most rheometers, whereas the locally defined measures should be calculated using any of the frameworks proposed to analyze the nonlinear response such as FT, Chebyshev stress decomposition method. The FT analysis, converts time-domain periodic signals into frequency-domain signals that make up a spectrum encompassing the fundamental frequency and its higher order odd integers ($n = 1, 3, 5\ldots$) in the case of nonlinear response. The leading higher-order harmonic (i.e. the third harmonic) signals the onset of nonlinear behavior. Despite its utility, this “elegant” approach provides little if any physical insight into the nonlinear response. Therefore, other frameworks that overcome this weakness have been proposed such as the Chebyshev stress decomposition. According this, the stress response can be decomposed into elastic and viscous stresses, described by Chebyshev polynomial series of the first kind, which are interrelated to the Fourier series. Similar to the third order Fourier harmonic, Chebyshev coefficients indicate departure from linearity. Some of the metrics developed to capture the nonlinear response, verbatim (Ewoldt et al., 2008):

$$G_M' \equiv \frac{d\tau}{d\gamma} = \sum_{n:odd} nG_n' = e_1 - 3e_3 + \ldots, \tag{10.17}$$

$$G_L' \equiv \frac{\tau}{\gamma} = \sum_{n:odd} G_n' \left(-1\right)^{(n-1)/2} = e_1 + e_3 + \ldots, \tag{10.18}$$

$$\eta_M' \equiv \frac{d\tau}{d\dot{\gamma}} = \frac{1}{\omega} \sum_{n:odd} nG_n'' \left(-1\right)^{\frac{n-1}{2}} = \upsilon_1 - 3e_3 + \ldots, \tag{10.19}$$

$$\eta_L' \equiv \frac{\tau}{\dot{\gamma}} = \frac{1}{\omega} \sum_{n:odd} G_n'' = \upsilon_1 + \upsilon_3 + \ldots, \tag{10.20}$$

where G_M' is the minimum-strain or tangent modulus at $\gamma(\mathrm{t}) = 0$ and and G_L' is the large-strain or secant modulus at $\gamma(\mathrm{t}) = \gamma_{\max}$. Likewise, η_M' is the minimum-rate viscosity and η_L' is the large-rate viscosity. The letters e_n and v_n refer to elastic and viscous Chebyshev coefficients of n order fitting the data, and chosen as they allow. All these material functions reduce to G' and G'' ($\eta' = G''/\omega$) in the LVR region. For the sake of simplicity, we only provided a general overview of the framework. For the interested readers, Ewoldt et al. (2008) and Ewoldt and Bharadwaj (2013) cover the fundamentals of LAOS rheology and its applications to lipid-based systems are reviewed in Macias-Rodriguez and Marangoni (2017). Another protocol has been developed by Rogers (2012), which consists in calculating instantaneous time-dependent moduli $R'(t)$ and $R''(t)$ as projections of binomial vectors of 3D Lissajous-Bowditch plot (stress vs. strain vs. strain rate) onto the strain-stress and shear rate-stress plane. This analysis provides a ‘complete’ picture of yielding that is not revealed by the stress-decomposition Chebyshev framework or any measures at ‘fixed’ points. It must be noted that this area of research is ongoing progress and so far there is not a definite answer as to whether a protocol is more suitable or appropriate than the other. Each protocol has its own merits and weaknesses that shall be considered prior to their implementation.

4.2.6 Drag Flow: Step Shear Stress (Creep) and Step Shear Strain (Stress Relaxation)

Creep tests consist in applying constant step load (small or large stresses σ_0) for some extended time and measuring displacement (strain) before and after removal (recovery) of the load. The time dependence of creep tests makes them particularly suitable for evaluating mechanical responses both for a short time (material compliance and firmness) and for long times (such as creeping of stacked butter in-store). The load and the duration of the time period should be high and long enough respectively, to induce sufficient creep motion and quantify the Newtonian viscosity, but not too high or long to trigger formation of cracks or induce irreversible plastic deformations as observed in butter (DeMan et al., 1985). Another use of creep tests is for the determination of the yield stress σ_y, where for $\sigma_0 < \sigma_y$ results in γ(t) curves characterized by an increase in strain and then a plateau or saturation (a hallmark of the solid regime of pastes), and $\sigma_0 > \sigma_y$ the same curves tend to a straight line with slope 1 in logarithmic scale, indicating infinite deformation at constant rate (a hallmark of the liquid regime of pastes) (Coussot, Tabuteau, Chateau, Tocquer, & Ovarlez, 2006). Experimentally, for stresses $\sigma_0 < \sigma_y$, creep compliance curves overlap or nearly overlap onto each other, whereas for stresses $\sigma_0 > \sigma_y$, deviations from this behavior occur and indicate the onset of nonlinear behavior. However, calculation of σ_y by this method may prove inefficient in stiff pastes (e.g. butter at low temperature) due to heterogeneous flow imposed by sudden stress jumps and higher sensitivity of this method to structural changes over long periods at constant stress (Dinkgreve et al., 2016). For stress inputs $\sigma_0 < \sigma_y$, the rheological behavior of butter and milk fat bears some resemblance with a Burgers body (see Fig. 10.8a), comprising a Maxwell model (spring and dashpot in series) coupled to a Kelvin-Voigt model (spring and dashpot in parallel) (Steffe, 1996) (Fig. 10.8b).

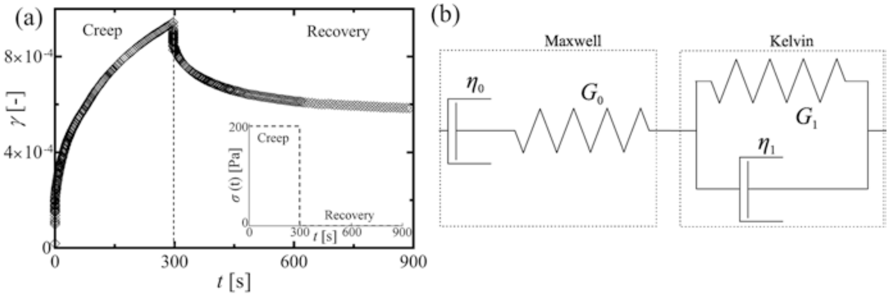


Fig. 10.8 (**a**) Strain deformation of butter (T = 18 °C) measured during (**a**) creep (σ_0 = 200 Pa) and recovery (σ_0 = 00 Pa). (**b**) Burgers model comprising Maxwell and Kelvin elements in series

The compliance function $J(t) = \gamma(t)/\sigma_0$ during the creep (a) and recovery (b) is described by the following equations:

$$J(t) = \frac{t_c}{\eta_0} + \frac{1}{G_0} + \frac{1}{G_1}\left[1 - \exp\left(-\frac{t_c}{\lambda_1}\right)\right]\text{Creep} \tag{10.21}$$

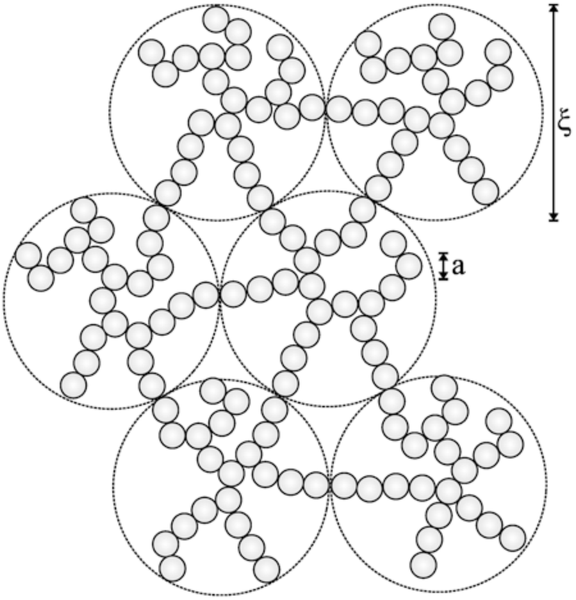
$$J(t) = \frac{t_c}{\eta_0} + \frac{1}{G_1}\left[1 - \exp\left(-\frac{t_c}{\lambda_1}\right)\right]\exp\left(-\frac{t_r - t_c}{\lambda_1}\right); t_r > t_c \text{ Recovery} \tag{10.22}$$

where t_c and t_r are the creep and recovery times, respectively, G_0 and μ_0 are the elastic modulus and viscosity of the Maxwell element, G_1 and μ_1 are similar parametersin the Kelvin-Voigt element and $\lambda_1 = \frac{\eta_1}{G_1}$ is the characteristic retardation time. Notethat G_0 and G_1 are equivalent to instantaneous J_0 and retarded compliances J_1 as $J = 1/G$ in the LVR. Increase the number of linear elements (e.g. adding an extra Kelvin body in series) is customary to describe the complex relaxation behavior, this, however, increases the phenomenology of the model (Scott Blair & Burnett, 1959). It has been suggested that firmness is a time-dependent texture attribute related to the time shear creep compliance $J(t)$:

$$F(t) = \frac{1}{J(t)} \tag{10.23}$$

Previous studies have shown that $J(t)$ can differentiate between soft and firm materials (e.g. cheese) (Brown, Foegeding, Daubert, Drake, & Gumpertz, 2003; Ewoldt, 2014). Figure 10.9 shows an illustration of a creep and recovery compliance obtained for butter T = 18 °C. At first glance, butter shares some resemblance with a Burgers body; however, materials properties calculated from the creep phase are not necessarily the same with those obtained from the recovery phase even for stress inputs within the LVR. Scott Blair and Burnett (1959) attributed this behavior to marked thixotropic behavior at the beginning of straining and recovery of renneted milk gels, and offered some additions to the Burgers model. Past literature on butter investigating their viscoelastic properties as a function of temperature and expectedly reported decrease of all material functions as temperature rises (DeMan et al., 1985; Shama & Sherman, 1970; Vithanage, Grimson, Smith, & Wills, 2011). During work softening, butter loses less of its instantaneous elasticity, recovers more of its elasticity during and less of Newtonian viscosity compared to margarine, suggesting less irreversible bonds and better network reformation for butter. An alternative approach is to conduct a stress relaxation test, i.e. input a step strain deformation and monitor stress decay over time as measured by the relaxation modulus $G(t)$. This is important to determine stress dissipation with the timescale of material usage, e.g. lowering the temperature of butter from 17 °C to 8 °C promotes faster stress relaxation.

Fig. 10.9 Putative microstructure of a fractal aggregate in a fat crystal network. Particles of size *a* aggregate in flocs with limits ξ represented by dotted lines, which form a close packing



5 Microscopic Modeling: Structure and Rheology Relationships

5.1 Cream

Some attempts have been made to provide some quantitative relationships between solid fat content and steady state viscosity of cream. For Newtonian flow, e.g. in creams containing ≤50% fat at T = 40–80 °C, hydrodynamic interaction determines the viscosity of the cream η as a function of volume fraction of dispersed particles ϕ, as described by Euler's equation:

$$\eta = \eta_0 \left(1 + \frac{1.25\phi}{1 - \phi / \phi_{\max}} \right)^2 \tag{10.24}$$

where η_0 is the viscosity of the continuous phase and $\phi_{\max}$ is the maximum volume fraction depending on shape and size distribution of the dispersed particles (spherical for cream). For a correct description of the data, ϕ must take into account the sum of volume fraction of fat globules, casein micelles, protein molecules and lactose molecules, and $\eta_0 \approx 1.02\eta_{\text{water}}$ (considering the continuous phase is roughly a 1% solution of salts) and $\phi_{\max} \approx 0.9$. This relationship holds for $\eta/\eta_0 > 10$ at $\dot{\gamma}_0 \leq 10\ \text{s}^{-1}$. For non-Newtonian shear-thinning behavior, e.g. in creams containing 60% fat at T = 15–80 °C, η_{app} has been described using a power law equation of the following type:

$$\eta'_{app} = \eta'_1 \dot{\gamma}^{-\beta} \tag{10.25}$$

where η'_1 is the viscosity at unit shear rate and β is a constant having a finite value for non-Newtonian flow (and equal to 0 for Newtonian flow). The power law holds over a very wide range of shear rates, including at very low shear rates ($\dot{\gamma}_0 \approx 10^{-4}\ \mathrm{s}^{-1}$) though such measurements are impractical due to the biological nature of milk which undergo gradual changes over time. A major weakness of this equation is that it does not account for the dependence of η_{app} on $\dot{\gamma}_0$. In this regard, it has been suggested that η_{app} may be interpreted as originating from disruption of linkages amongst dispersed liquid droplets, caused by stress σ and shear rate $\dot{\gamma}_0$ (Blair, 1965). On one side, σ tends to break the linkages, on the other $\dot{\gamma}_0$ hinders droplets to become in close contact. The number of linkages n per unit volume is linearly proportional to the logarithmic of both σ and $\dot{\gamma}_0$, yielding the following relationship:

$$\ln \dot{\gamma} = \frac{a}{b} ln\tau + C \tag{10.26}$$

where a and b are constants related to σ and $\dot{\gamma}_0$ ($a > b$ for shear-thinning fluids such as cream) and C is an integration constant. The Eq. (10.26) holds in a wider range of $\dot{\gamma}_0$ though it fails at very high shear rates at which all linkages may be broken (Blair, 1965). The picture of physical linkages appears more suitable for partially-coalesced high-fat creams displaying 'network-like' formation; otherwise such concept can be envisaged as averages in time and space of the forces acting on the globules (Prentice, 1993; van Vliet & Walstra, 1979).

5.2 *Butter, Milk Fat and Dairy Spreads*

Constitutive equations have been proposed to model the rheology of butter, milk fat and dairy spreads. Some of these efforts include the visco-plastic model (Tanaka et al., 1971), the modified Bingham model (Elliot & Green, 1972) and the viscous Maxwell-Bingham model (Diener & Heldman, 1968). Tanaka et al. (1971) proposed to express stress (obtained from penetration) as the sum of stress caused by plastic and viscous deformations where the primer is associated with yield value and the latter with apparent viscosities post yielding. Elliot and Green (1972) proposed the use of a modified Bingham model after observation of the stress response of butter subjected to steady shear and dynamic oscillations. The model consisted of a viscous element and yield stress element comprising static and dynamic yield stresses, and an elastic element of modulus connected in series. Diener and Heldman (1968) assigned the Maxwell element of his model to the fat globule theorized as being purely viscous internally and elastic externally or at the boundaries, the yield element to the failure of crystal grain boundary and viscous elements of the free fat in the crystal granules. Despite the utility of these models as "visual aids" to describe empirical equations, the use of spring and dashpots do not represent the actual structure being subjected to deformations. Therefore, we will turn our attention to mesoscopic models that aim to establish structure-rheology relationships, particularly those applicable to fat crystals networks present in milk fat and dairy spreads. Several microscopic models to link the structure and rheology of fat crystal networks have been proposed starting from the early proposed linear chain model (van den Tempel, 1979) to the fractal model (Marangoni & Rousseau, 1996; Narine & Marangoni, 1999c; Tang & Marangoni, 2007; Vreeker, Hoekstra, den Boer, & Agterof, 1992). The discussion presented here will be restricted to latter given its relevance and sound basis. The fractal model operates under the assumption that fat particles (crystalline nanoplatelets) assemble into fractal (self-similar) flocs or clusters (Fig. 10.9). Above a critical particle fraction ($\phi_c \approx 0.05$–0.10), flocs grow enough and overlap ('gelation' occurs) forming a continuous microscopic crystal network with solid-like or elastic behavior.

The elasticity of the system scales as a function of particle fraction ($\phi = \mathrm{SFC}/100$), according to which two discrete regimes may be distinguished (Marangoni & Rousseau, 1996; Narine & Marangoni, 1999b). At low particle concentration ($\phi < 0.1$), the strong-link regime occurs, i.e. individual clusters grow large and their elasticity (not that of the cluster links) dictates the elastic modulus G' of the system, where each aggregate has a backbone which bears the force applied to it:

$$G' \sim \phi^{\left[(d+x)/(d-D)\right]} \tag{10.27}$$

where d is the Euclidean dimension of the embedding space (usually 3), D is the fractal dimension, which describes spatial distribution and morphology of the network, x is the backbone fractal dimension (~1 to 1.3). The fractal dimension also provides information on the aggregation mechanism of the network, e.g. $D = 1.75$ for DLCA and $D = 2.1$ for RLCA. At high particle concentration ($\phi > 0.1$ such as in most model and complex fat systems), the weak-link regime occurs, i.e. small clusters behave as rigid springs and the links among clusters or microstructures govern the elasticity of the system:

$$G' \sim \phi^{1/(d-D)} \tag{10.28}$$

An additional pre-exponential term $\dfrac{A}{\pi a \gamma d_0^2}$ (for crystal aggregates with spherical-like morphology) added to the weak-link relationship helps to discern among crystal networks showing similar D and ϕ but different G' (Marangoni, 2000). In the pre-exponential term, A corresponds to the Hamaker's constant, a to the size of the primary crystal unit and d_0 to the intercluster distance (Narine & Marangoni, 1999b). A modified fractal model has also been proposed for less "ideal" systems that do not obey exact power law dependence, due to highly heterogeneous crystal networks.

In such systems, stress localization happens in a small fraction of the interconnected network which serves as "weakest bonds" (Tang & Marangoni, 2007). The separate effects of the network microstructure, stress distribution and interconnectivity are determined as follows:

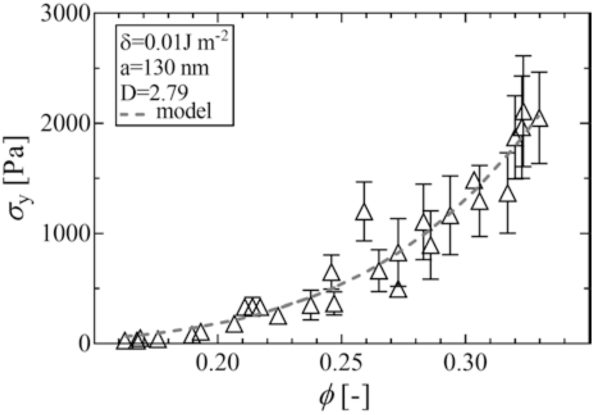


Fig. 10.10 Yield stress σ_y as a function of volume fraction ϕ for blends of milk fat with canola oil. Samples were crystallized statically from 40 to 5 °C at a cooling rate of 1 °C/min, and annealed at 5 °C for 2 h. Symbols represent the average and standard deviation of 2–6 samples fitted to the model in Eq. (10.30). Estimates of the model parameters are indicated. The surface free energy δ was fixed as a constant

$$G' \sim \phi_e^{1/(d-D)} \tag{10.29}$$

where the effective volume fraction of solids responsible for stress-bearing is $\phi_e = 1 - e^{-k\phi^b}$ and k and b are constants. Furthermore, a rough estimation of σ_y of milk fat crystal networks (Fig. 10.10) can be obtained applying thermodynamic considerations as follows:

$$\sigma_y \sim \frac{6\delta}{a}\phi^{1/(d-D)} \tag{10.30}$$

where δ is equivalent to the crystal-melt interfacial tension ($\delta \approx 0.01$ J m^{-2}). Dividing both sides by γ_y yields an estimation of the Young modulus $\in$:

$$\in = \frac{\sigma_y}{\gamma_y} \sim \frac{6\delta}{a\varepsilon^*}\phi^{1/d-D} \tag{10.31}$$

where the shear modulus G can be estimated from $\in$ assuming a Poisson ratio $\mu = 0.5$ for incompressible viscoelastic materials, through the following relation:

$$\epsilon = 2(1+\mu)G \tag{10.32}$$

Overall, despite the elegance of these approaches, there still seems to be some degree of uncertainty on the estimation of G', since milk fat or butter set relatively slowly compared to other type of fats due to its highly heterogeneous composition that hinders crystal packing. The exact variation of G' as a function of ϕ, and pre-exponential affecting G' also requires accurate estimation of Hamaker's constant for two interacting crystal nanoplatelets and structural information of both nano and microstructure. Obtaining such information is by no means trivial. For a comprehensive description of network mesoscopic models, the readers are referred to (Narine & Marangoni, 1999a; Tang & Marangoni, 2007).

6 Comparison Among Methods for Rheological and Texture Characterization

Direct comparisons amongst different methods and research reports cannot be drawn prior to careful assessment of the measuring principles of the test, testing conditions and relationships between load, time, deformation during measurement. Such relationships are strictly defined in fundamental tests (e.g. shear oscillatory, shear creep, etc) for homogeneous deformations. For heterogeneous deformations, rheological functions become variant to testing conditions and thus become apparent. In empirical tests, flows are poorly defined, properties depend on measuring specifications and comparisons among tests are made at the practitioner's own risk. While correlations among empirical tests such as penetrometry, indentation, empirical extrusion tests have been widely found, these do not warrant that similar properties had been measured as suggested in the literature. Strong correlations have been found between quite different properties, e.g. yield value and viscosity (using cone penetrometry). Dolby found excellent agreement between his 'sectility' measurements and Scott Blair's apparent viscosities determined by Scott Blair's parallel plate plastometer, and conceptualized that similar properties may have been measured (Scott Blair, 1954). Scott Blair's viscosities were determined at arbitrary conditions and thus comparisons appear somewhat dubious (Mulder, 1953). Drawing correlations between yield value and viscosity seems strictly dependent on the specific rheology of the butter and measurement conditions (e.g. extent of deformation). For example, a firm and plastic butter may show a high yield stress to initiate "flow" and high viscosities due to 'gradual' yielding (i.e. proportionality between yield stress and viscosity holds true). A firm and brittle butter will not follow the same trend, yield stress may be high but viscosity post-yielding will drop substantially as it breaks catastrophically. Some experimental techniques such as oscillatory shear will be more sensitive to capture such differences than empirical instruments such as cone penetrometry. Several authors have correctly asserted that penetration cannot discriminate among all butter or fat blends rheology. Direct comparison of small deformation and large deformation tests seem troublesome since the primer are attributed with viscoelastic properties of the pristine butter or milk fat microstructure, whereas the latter with the same properties or viscoelastic textural attributes of the 'broken' microstructure. In some cases, sensory correlation with instrumental parameters or material properties (e.g. viscosity) is remarkably successful (Scott Blair, 1958).

7 Properties and Attributes of Most Interest

The main fundamental properties of interest in butter, milk fat and milk fat blends include their elastic and viscous properties, yield stress and thixotropy. These influence widely measured attributes of butter such as firmness, spreadability, ‘setting’, ‘work softening’. In general, the elastic modulus is large not major differences among butters may be expected provided they are formulated, processed and stored at similar conditions. Butters do not show marked elasticity (i.e. they have a narrow linear regime) and yield stress differences are typically marginal. This does not imply that elastic properties are unimportant since they contribute to solid-like behavior and provide “a vivid appearance” (Mulder, 1953). On the other hand, viscous properties determine whether the material displays a brittle-like behavior or a ductile-like behavior. In butter and milk fat the yield stress refers as the critical value beyond which the material transitions from purely elastic deformations to plastic deformations. The estimation of this value appears to be obtained by oscillatory shear experiments in butter and milk fat despite certain limitations. Firmness and butter are two major important viscoelastic texture attributes affecting the acceptability of butter, which are inversely related. Firmness is a time-dependent attribute and as earlier mentioned, it can be best estimated by the shear creep time compliance. Spreadability involves large shear deformations such as those obtained by extrusion experiment. Thus, apparent viscosities at arbitrary shear rates determined by extrusion seems to provide a fair assessment of this property. It has been argued that viscosity and spreadability are inversely related (Davis, 1937), i.e. spreadability is directly related to the extent of shear-thinning of butter. ‘Setting’ refers to the increase of firmness over storage time due to continuous crystallization and crystal aggregation, which causes an increase in the viscoelastic moduli during storage. On the opposite case, ‘work softening’ has been used to describe a decrease in the consistency of butter when worked or kneaded (Van Aken & Visser, 2000). This decrease is due to strong strain softening of the elastic modulus and shear thinning of the viscosity and thus these more general terms appear more appropriate. After application of shear, the modulus and viscosity increase partially or fully during ‘rest’ as network restructuring occurs, a property referred as to thixotropy. A distinction must be made between the decrease and subsequent recovery of viscoelastic properties or textural attributes (i.e. viscoelastic moduli, firmness) that occur from the action of strong shear (e.g. butter working) and those from ‘mild’ shear (e.g. spreading) (Prentice, 1993; Sone, 1961). In the first case, mechanical behavior results mainly from melting and re-crystallization of the network, whereas in the second case, it arises due to thixotropic behavior.

8 Control of Rheological Properties of Milk Fat and Butter

There are several formulation and processing schemes aimed to tailor the rheology of milk fat, butter and dairy fat blends. Here, we briefly cover those approaches which have been extensively reviewed (Wright et al., 2001). Original FA and TAG composition of milk fat varies according source, season, animal breed, feed, among other factors. This can be altered using various processes including blending, fractionation and interesterification. In addition to composition, pretreatment of milk cream and crystallization conditions such as cooling, shear or mechanical working all affect crystallization and formation of mesoscopic crystal networks that determine rheological properties.

A commonly used approach to modify the original composition of milk fat is to modify the feed of the cows such as with the addition of vegetable or fish oils high in unsaturation or whole oilseeds (e.g. canola seeds). This typically increases oleic acid content while reducing saturated fatty acids content and leading to softer butters. Supplementation of the feed with sufficiently high levels of stearic acid can also promote desaturation of the mammary gland and improve butter spreadability.

Blending with vegetables oil increases the level of unsaturation of milk fat and affects crystallization as observed in melting profiles and hardness index (Rousseau, Hill, & Marangoni, 1996). This operation needs to comply with standards of identity for butter and dairy fat blends. Fractionation separates milk fat into various fractions with distinct TAG chemical makeup and physical properties, which are recombined in various proportion to improve the spreadability of butter. For example, very high melting fractions melt at $T_m > 50$ °C and provide structural integrity, while low melting fraction melt at $T = 10$–25 °C and reduce hardness, of recombined butters (Wright & Marangoni, 2006). Interesterification randomizes FAs along the TAG backbone, altering crystallization and thus physical properties. Chemical and enzymatic interesterification improve cold spreadability of butter though this comes to reduction of butter flavor (Wright & Marangoni, 2006).

Aging or ripening of cream involves holding it at specific temperatures typically overnight to alter crystallization of the fat contained within the globules. This cost-effective and successful approach has been a widespread practice to reduce firmness and increase spreadability of butter. Churning of cream induces partial phase inversion, i.e. rupture of fat globule and release of fat crystal for their further aggregation and crystallization. Depending on the process, butters with varying rheology can be obtained. For example, continuously-churned butter is firmer than batch-churned butter, since in the primer fat globules are fully destroyed and hence more crystals are available to form the mesoscopic network. Mechanical treatment can also be applied during manufacture of butter, e.g. continuous agitation and shearing during crystallization enhances secondary nucleation, removal of heat of crystallization, which lead to creation of discrete crystal aggregates, whereas batch crystallization promotes formation of larger crystals. Crystal morphology affects the texture of butter, e.g. adequate mechanical working and cooling during crystallization leads to firm yet spreadable butter, whereas excessive working and poor heat dissipation, causes melting that leads ‘sticky’ butter. Storage conditions influence ‘setting’ of butters and their final texture, e.g. mild increases in storage temperature can double the firmness of butter (Mortensen & Danmark, 1981).

9 Conclusions

Major developments on the rheology and texture of butter, milk fat and dairy spreads took place in the past as the subfield of food rheology emerged. Early studies were mainly empirical and consisted largely of the measurement of attributes such as firmness and spreadability. With the advent of modern rheometric techniques, more fundamental methods have been introduced to characterize rheological properties of these products. With increasing consumption of dairy products forecasted for the upcoming years, rheology and texture will continue to provide valuable insights into the quality, usability and consumer acceptability of butter and dairy spreads.

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