Overview: Semisolid Foods

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1 Overview: Semisolid Foods

Foods can be classified into fluids, semisolids, and solids by their physical properties, such as rheological behavior and texture (Rao 2013). Fluid foods do not have the ability to support their own weight and retain their shape, but flow readily under an applied force, including gravitational forces. Solid foods, other the other hand, have the ability to retain their shape and do not flow under applied force. Rather, they tend to deform and fracture under sufficiently high forces. Semisolid foods share some properties with both fluid and solid foods, having the ability to retain their shape but flowing under pressure or force. Although semisolid foods can be recognized by determining whether they can hold their shape under an applied force, there is no specific measurable parameter (e.g. elasticity, viscosity, or yield stress) that can be used to quantitatively determine whether a material is semisolid. Typically, semisolid food materials exhibit both elastic and viscous behaviors, having higher viscosity than fluid materials and lower elasticity than solid materials. At the microscopic scale, semisolid food materials typically are amorphous solids, with disordered structure and randomly distributed molecules. Unlike many solid materials which have ionic bonding, semisolid materials are covalent substances, which have weaker bonds compared to ionic bonds. The microstructure of semisolid foods determines their flow behaviors and texture. Table 1 shows the wide variety of flow behaviors, textural attributes, and structuring components that can be present in semisolid foods.

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Table 1 Semisolid food examples and their flow behavior models, texture, and structuring components

Food	Viscosity range (Pa.s)	Flow behavior model	Important textural attributes	Structuring components	References
Mayonnaise	1.5–13.8	Herschel-Bulkley, Power law	Creaminess, cohesiveness, firmness, consistency, viscosity	Egg yolk lectin, fat droplet amount and size distribution	Maruyama et al. (2007); Ma and Barbosa-Cánovas (1995); Liu et al. (2007)
Yogurt	0.045–4.39	Power law, Casson, Herschel-Bulkley	Thickness, ropiness, smoothness, graininess	Casein network, fat globule amount and size distribution, gum	Karagül-Yüceer and Drake (2013); Benezech and Maingonnat (1994)
Butter spread	0.01–350	Herschel-Bulkley, Casson, Bingham	Creaminess, spreadability, firmness	Stabilizers, emulsifiers, fat crystal amount and size distribution	Taghizadeh and Razavi (2009); Singh et al. (2000); Totlani and Chinnan (2007)
Sauce	0.1–20.0	Power law, Casson, Herschel-Bulkley, Mizrahi-Berk	Smoothness, creaminess, thickness, viscosity	Stabilizers, emulsifiers, vegetable tissues	Rao et al. (1986); Sikora et al. (2007); Gamonpilas et al. (2011)
Ice cream	~1.0	Power law	Firmness, creaminess, coldness, coarseness	Ice and fat crystal size distribution, air bubble size distribution, overrun, stabilizers, emulsifiers	Bahramparvar et al. (2010)
Ice cream mix	0.01–0.1	Power law	Creaminess, firmness	Stabilizers and emulsifiers, fat crystals	Cottrell et al. (1980); Kuş et al. (2005)
Whipped cream	0.1–1.0	Cross model	Creaminess	Stabilizers and emulsifiers, fat crystals, air bubble size distribution, overrun, milk proteins	Camacho et al. (2005); Noda and Shiinoki (1986)
Salad dressing	0.5–2.5	Power law	Thickness, firmness, grittiness	Stabilizers, oil droplets	Ma et al. (2013); Lai and Lin (2004)

1.1 Typical Semisolid Food Behaviors

Although semisolid foods vary widely in their structural features, rheological behaviors, and texture attributes, they generally exhibit at least some degree of the behaviors described below. These behaviors can be used to qualitatively separate foods that are soft solids or high-viscosity fluids from foods that are semisolids.

1.1.1 Slumping

Semisolid foods can temporarily hold their shape. However, under external forces such as gravity, their shape may collapse. This phenomenon is called 'slumping' (Fig. 1). Slumping may be induced by phase transition. For example, at room temperature (20–25 °C), ice cream slumps when fat and water crystals partially or totally melt. Some semisolid foods, such as yogurt, salad dressing, and mayonnaise, may slump due to their supporting structure collapsing under its own weight.

Torsion, shear, and uniaxial compression can also make semisolid foods slump. Food gels, such as tofu, can dictate the failure mode of slumping and serum expulsion under compression force (Truong and Daubert 2000). Gellan gels (~1% w/w gellan gum) (Lelievre et al. 1992) and casein gels (Konstance et al. 1995) also slump under uniaxial compression and shear forces.

1.1.2 Spreading

Some semisolid foods, such as peanut butter and margarine, need to be spreadable at room temperature. Those foods require a certain amount of stress (yield stress) for adequate spreading and deformation (Daubert et al. 1998). Spreadability indicates how easily a food can be spread evenly over a surface and is one of the most essential features perceived by consumers (Glibowski et al. 2008). The spreadability of semisolid foods is the net result of a combination of rheological behaviors, of which viscosity is the most important. Increased viscosity typically decreases spreadability due to the increased resistance to flow. Additionally, increasing solid fat content in some lipid-based semisolid foods, such as spreads, margarine, cream cheese, and butter, can cause an increase in hardness and decrease spreadability.

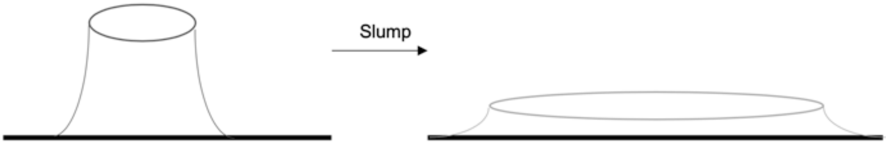


Fig. 1 Schematic of slumping

Typically, the consumer assesses the spreadability of semisolid foods using a knife. In a study by Kokini and Dickie (1982), the inverse of the torque needed to generate a given deformation was assessed as spreadability. The spreading action was then modeled by relating spreadability to the torque on a knife during application, which was used to estimate a transient, maximum shear stress.

1.1.3 Separation

Under some conditions, such as temperature variation, stirring or agitating, and pH change, semisolid foods can sperate into two or more phases. For example, peanut butter can show a visible oil layer on top and yogurt syneresis causes a layer of fluid whey to appear on the surface of the yogurt gel; neither of these separated products is appealing to consumers. These semisolid foods typically contain emulsions structures (see Sect. 2.1), and the separation is caused by the destabilization of the emulsion structure. The separation of an emulsion into its component phases is a two-step process. The first step is flocculation (aggregation, agglomeration, or coagulation), where the droplets clump together, forming aggregates or "flocs". The second step is coalescence, in which water/oil droplets coalesce together to form a continuous phase. This is an irreversible process that leads to a decrease in the number of water droplets and eventually to complete separation of the emulsion phases (Schramm 1992; Bobra 1990) (Fig. 2).

Syneresis is a phenomena during which liquid is expressed from a hydrogel. This phenomena can happen during yogurt storage and is considered as a defect. Syneresis can be induced by heat, external force, and pH, which can cause removal or break down of hydrophilic sites (Mizrahi 2010). Yogurt syneresis can be reduced by increasing the milk solids to ~15%, using stablizers (e.g. polysaccharides), or using exopolysaccharide (EPS)-producing starter cultures (Amatayakul et al. 2006).

Application of heat promotes the separation process of emulsions in semisolid food. Increased temperature can reduce the viscosity of the oil and the mobility of the water/oil droplets, promoting droplet collisions and favoring coalescence. Heat also weakens or ruptures the film on water/oil droplets because of water expansion and enhances film drainage and coalescence (Chen and Tao 2005).

In some cases, agitating or stirring increase the stability of emulsions. High speed agitating or stirring can causes violent mixing of oil and water and leads to smaller

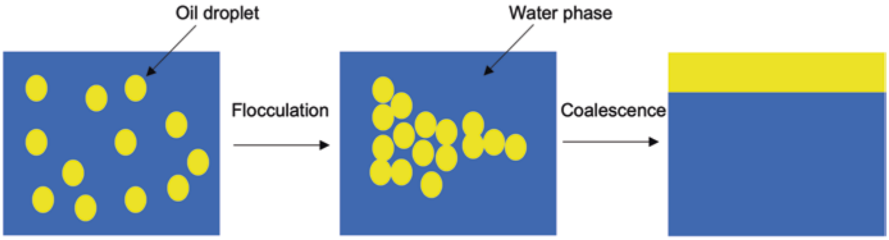


Fig. 2 Destabilization of an o/w emulsion

droplet sizes, which are relatively more stable than larger droplets (Floury et al. 2003). In some cases, such as butter churning, the stability of emulsions is affected adversely by agitation due to high speed collisions between droplets (Buldo et al. 2013).

2 Structural Variety in Semisolid Foods

Semisolids foods typically consist of two or more immiscible components such as water, oil, and fibers. The stabilization of their structure is achieved by processing methods such as homogenization, thermal treatment, and acidification to form stable structures. Emulsions and protein–polysaccharide networks are two common structures of semisolid foods. Both of these structures play an important role in sustaining stability (Dickinson 2009), delivering desirable sensory attributes (Chen 2014), and maintaining flavors (Mao et al. 2017). Several comprehensive reviews on food emulsions (Muschiolik 2007; Dalgleish 2010) and protein–polysaccharide networks (Lam and Nickerson 2013) have been published; these topics are covered in more detail in these reviews.

2.1 Emulsions

Emulsions are colloidal systems containing either water dispersed in oil (w/o) or oil dispersed in water (o/w). Water and oil are mixed in a way that droplets of one fluid are dispersed within another (Fig. 3) (Dickinson 2010). These droplets may vary in size from the micro-to the nanometer scale. Therefore, while there are still two different phases in the material, properly stabilized emulsions look homogeneous on a macroscopic scale. Emulsions may be stabilized by emulsifiers, which have a polar, hydrophilic section and a nonpolar, hydrophobic section. Due to these amphiphilic properties, emulsifiers are able to coat the emulsion droplets, aligning their polar and nonpolar regions with the water and oil phases, respectively. This reduced the

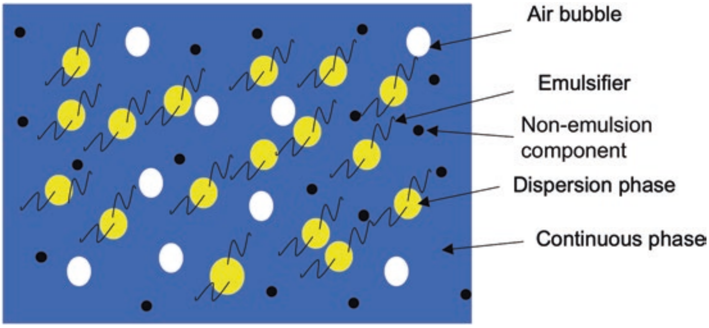


Fig. 3 Schematic of a stabilized emulsion

likelihood of the emulsion droplets to flocculate or coalesce (Dickinson 1987). Many semisolid foods, including salad dressing, yogurt, whipped cream, frozen desserts, and margarine, are stabilized emulsions.

2.1.1 Oil-in-Water Emulsions

Oil-in-water (o/w) emulsions are common in semisolid foods. For example, the crema in espresso is an unstable oil-in-water emulsion, in which the milkfat is the oil phase and the coffee is the water phase. Mayonnaise is an o/w emulsion with a high oil volume fraction (70–80%), which provides its high viscosity (Nikzade et al. 2012). Because the oil volume fraction is so high, mayonnaise must be stabilized with egg yolk lecithin or other stabilizers or it will separate during storage. Salad dressing is vegetable oil droplets dispersed in water (vinegar); other ingredients, such as vegetable pices and spices, may be suspsended in the water phase as well. Ice cream mix is a stabilized o/w emulsion that is converted into a foam when air is incorporated during production. The stability of the ice cream emulsion controls its texture: poorly stabilized ice cream may have a coarse texture due to formation of large fat crystals and improper incorporation of air.

2.1.2 Water-in-Oil Emulsions

Water-in-oil (w/o) emulsions are less common in foods, but still exist. For example, butter is an emulsion of water droplets dispersed in milkfat. Solid margarines are also a w/o emulsion with tiny water droplets disperse in a fat phase that is in a stable crystalline form. Margarine and butter have similar fat content (≥80% fat). However, margarine consists not only of a relatively wide range of triacylglycerols but also contains different ingredients in the aqueous phase, such as emulsifiers and preservatives. Conversely, the composition of butter is relatively consistent: in the US, butter is not legally permitted to contain any ingredients but Grade A milk, salt, and colorants. The only compositional changes result from milk composition variation due to the breed of cow, the type of feed provided to the cow, and stage of lactation (Juriaanse and Heertje 1988).

2.1.3 Emulsion Destabilization

Destabilization of emulsions happens when the driving force for coalescence promotes flocculation of small droplets, which subsequently form large droplets, and eventually form a continuous phase of the formerly dispersed fluid. Destabilization typically is not desirable for semisolid foods (Syrbe et al. 1998). For example, oil separation in peanut butter and salad dressing is not palatable to consumers. To prevent emulsion destabilization, hydrocolloids (emulsifiers) can be used to provide physical barriers to prevent droplets from coming together. Reducing the driving force between droplets by reducing the thermodynamic energy level of the system through changing pH or ionic strength can also help prevent destabilization (Dalgleish 2006). Furhtermore, reducing oil droplet size can help stabilize emulsions, as this increases the time needed for coaleascence based on Stokes' Law (see Chapter "Introduction: Measuring Rheological Properties of Foods").

2.2 Protein and Polysaccharide Networks

Some semisolids foods are structured by aggregated proteins with trapped or attached polysaccharide molecules. For example, yogurts have protein networks formed by aggregated casein micelle chains or clusters when the pH of heat-treated milk drop to the isoelectric point of casein (pH 4.6) (Lee and Lucey 2010). Polysaccharides, including gums, starches, pectin, and dietary fibers, are often used to modify the structure by attaching and embedding to the protein networks (Fig. 4). Adding functional ingredients to yogurt or using different processing strategies or treatments can change the microstructure of yogurts, influencing their physicochemical properties and texture.

2.3 Crystallization of Triacylglycerols

Solid or partially solid lipds can also serve as structuring materials. The specific structure of the lipid depends on its origin. For example, shortening is composed of fluid oil and fat crystals; it is structured by a network of fat crystals (Heertje et al. 1987). Margarine has a fat crystal network that similar to shortening. The main difference in structure is the presence of water droplets in margarine, which disrupts the continuous fat phase (Juriaanse and Heertje 1988). Ice cream has a complex microstructure consisting of ice crystals, air bubbles, and partially coalesced and aggregated fat globules, all of which are surrounded by a continuous matrix of sugars, proteins, salts, polysaccharides, and water (Clarke 2015).

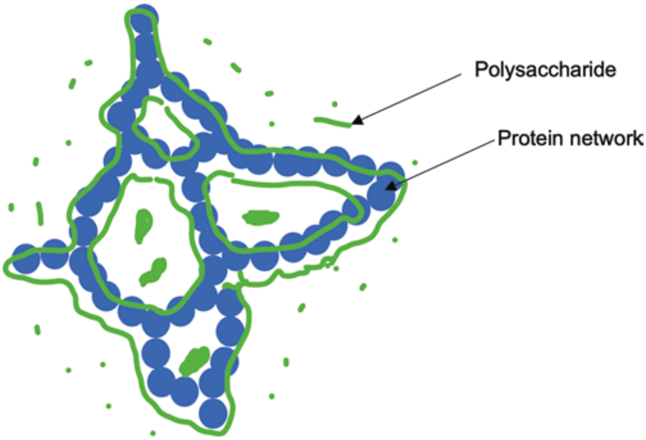


Fig. 4 Typical yogurt microstructure

Fat droplets in food may coalesce or aggregate upon whipping or freezing, which results in large particle sizes and a more heterogeneous particle size distribution. In ice cream, decreased fat cystal size can reduce the storage modulus and increase metling time (Granger et al. 2005). Particle size of fat crystals also contributes to the sensory attributes of ice cream. For example, particle sizes between 0.1 and 2 um provide a creamy sensation; however, particles >3 um can result in a gritty or powdery mouthfeel (Ohmes et al. 2010).

3 Rheological Behaviors of Semisolid Food

3.1 Viscosity

Viscosity measures the ability of a materials to resist flow and gradual deformation by shear stress or tensile stress (Vocaldo 2007). For semisolid foods, viscosity typically refers to dynamic viscosity or apparent viscosity, which is calculated by:

$$\eta = \frac{\sigma}{\left(\frac{\Delta u}{\Delta x}\right)} \tag{1}$$

where η is apparent viscosity (Pa.s), σ is shear stress (Pa), and $\frac{\Delta u}{\Delta x}$ is the velocity gradient (1/s). Depending on the geometry used for viscosity measurement, the velocity gradient can be represented by shear rate ($\dot{\gamma}$), e.g. when parallel plates are used. A demonstration of a setup used to measure dynamic viscosity is shown in Fig. 5. In viscosity measurements, a shear rate or shear rate sample is applied to a material and the resulting shear stress measured. Viscosity is then calculated using Eq. 1. Measuring viscosity over a range of shear rates allows a flow profile of the material to be generated. This flow profile can be used to predict the material's viscosity and flow behaviors under a range of industrial and oral processing conditions.

There are several types of viscosity aside from apparent viscosity. Kinematic viscosity can be obtained by dividing apparent (dynamic) viscosity by density. Bulk viscosity (volume viscosity) measures the internal friction resistance to flow when a compressible fluid or semisolid is compressed or expanded evenly by sound or shock waves. It can be used to explain the loss of energy in sound and shock waves

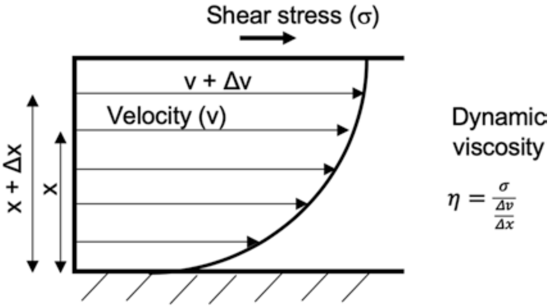


Fig. 5 Diagram of dynamic viscosity

Table 2 Apparent viscosity of liquid and semisolid materials

Food	Temperature (°C)	Viscosity range (Pa.s)	Physical state	Reference
Water	25	0.001	Liquid	Kestin et al. (1978)
Honey	25	3–24	Liquid	Yanniotis et al. (2006)
Corn syrup	25	1.3806	Liquid	Lide (2003)
Milk	25	0.002–0.06	Liquid	Bakshi and Smith (1984)
Seed oil	26	0.032–0.057	Liquid	Diamante and Lan (2014)
Mayonnaise	25	13.8–1.5	Semisolid	Maruyama et al. (2007)
Stirred yogurt	25	0.045–0.057	Semisolid	Ramaswamy and Basak (1991)
Set yogurt	20	2.28–4.39	Semisolid	Paseephol et al. (2008)
Goat milk yogurt	5	0.5–2	Semisolid	Li and Guo (2006)
Nonfat yogurt	10	5.38–120	Semisolid	Teles and Flôres (2007)

described by Stokes' law of sound attenuation (Hirai and Eyring 1958). Note that this is not the same Stokes' Law used for determining the rate of suspension creaming or settling, although G. G. Stokes did publish both laws.

The viscosity ranges of selected typical fluids and semisolids at certain temperatures are listed in Table 2. Fluid foods typically have low viscosity; for example, seed oil has viscosity of 2–60 mPa.s. Semisolid materials, however, have much higher viscosity than fluid materials; for example, mayonnaise has a viscosity of 1.5–13.8 Pa.s, a threefold increase in order of magnitude compared to many fluids. Viscosity of many semisolid and fluid foods are temperature-dependent. Generally, higher temperatures promote lower viscosities because the increased thermal energy allows the molecules in the material to more more freely. However, the viscosity changes in some foods due to temperature fluctuations can change the physical state of the food or food components, significantly increasing or decreasing the viscosity. These changes may be reversible or irreversible. For example, fluid egg becomes solid at temperatures >60 °C due to protein denaturation and gelation (Icier and Bozkurt 2011); hard candies become semisolid below their glass transition temperature (Tan and Kerr 2017); food polymer solutions (whey protein, carrageenan, and casein) transform from fluid to a solid gel at temperatures >80 °C due to increased entanglements, structural rearrangement, and gelation (Tan and Joyner 2018); and milk (fluid) turns into to yogurt (semisolid) due to the heat and acidification during yogurt production, which causes whey proteins to denature and casein proteins to aggregate, forming a gel (Lee and Lucey 2010). An example of how tomato salad dressing viscosity changes as a function of temperature and shear rate is shown in Fig. 6. These changes may cause noticeable differences in processing ability and texture perception.

3.1.1 Newtonian Behavior

Newtonian behavior is a flow behavior with a simple linear relation between shear stress and shear rate (Fig. 7). This relation is known as Newton's law of viscosity, in which shear stress is equal to the product of of viscosity and shear rate. Because shear

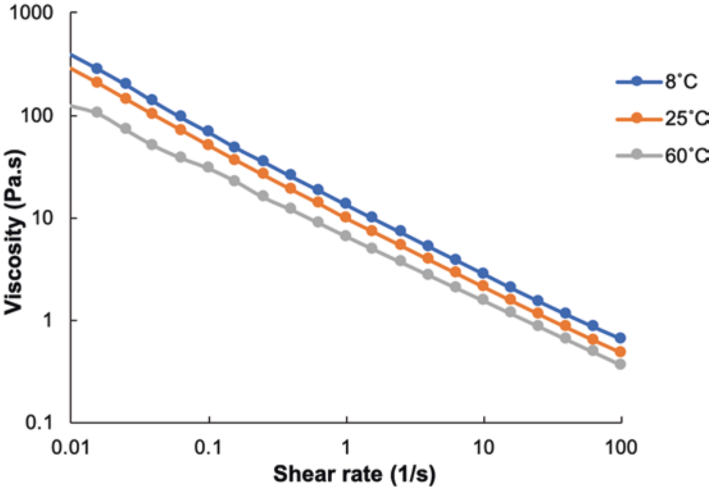
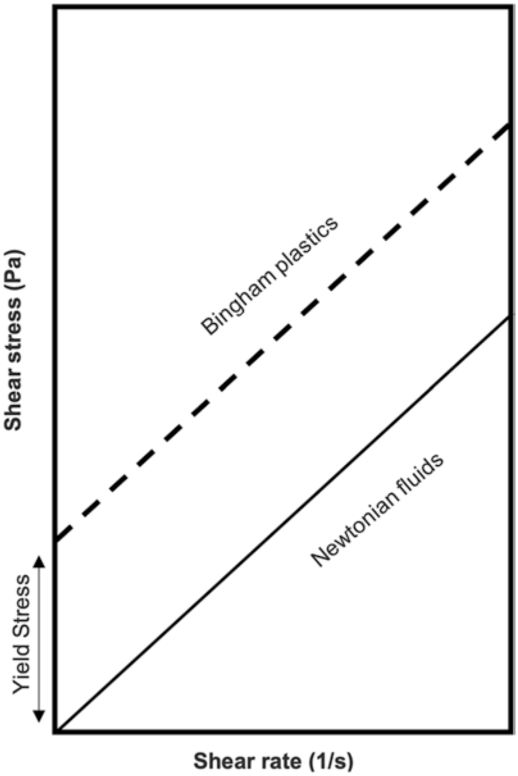


Fig. 6 Viscosity of tomato salad dressing as a function of shear rate at different temperatures

Fig. 7 Shear stress of Newtonian and Bingham plastic fluids as a function of shear rate



stress scales linearly with shear rate, the viscosity of Newtonian fluids is constant over all shear rates. Newtonian fluids typically comprise small isotropic molecules, which can easily orient to the direction of flow (Walters 1962). Some example of Newtonian fluids are water, honey, milk, mineral oil, and organic solvents. Some large anisotropic molecules in dilute solutions, such as protein or polysaccharides, can also exhibit Newtonian behavior (Hemar et al. 2001). However, higher concentrations of these polymers result in non-Newtonian behaviors, which can manifest in a variety of ways.

3.1.2 Non-Newtonian Behavior: Yield Stress

Fluids and semisolids may require an external force to initiate flow. This force is called yield stress. Materials that require a yield stress to flow but show Newtonian behavior upon the initiation of flow are called Bingham plastics (Bingham 1916). It is also possible for these materials to show non-Newtonian flow behaviors; these behaviors are discussed further in subsequent sections. Typical Bingham plastic foods include mayonnaise and tomato paste. The following equation, known as the Bingham model, describes the relationship between the shear stress and shear rate of a Bingham plastic material. Figure 7 shows the viscosity of Bingham plastics as a function of shear rate compares to Newtonian fluids.

$$\sigma = \sigma_o + \mu_{pl}\dot{\gamma} \tag{2}$$

Here, σ_o is the yield stress (Pa.s) and μ_{pl} is the plastic viscosity (Pa.s).

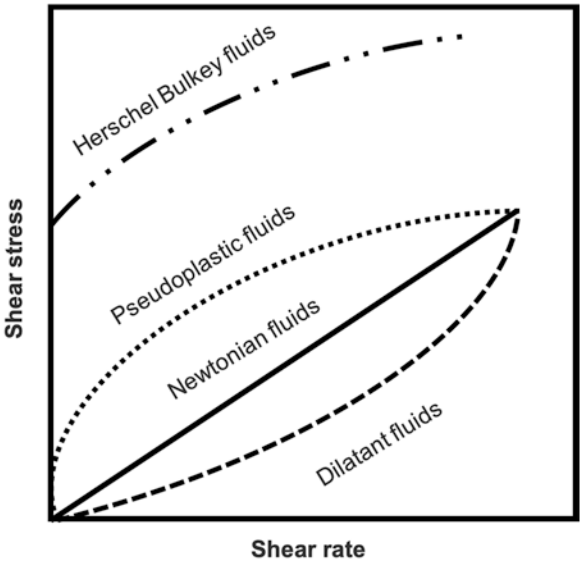
Materials that exhibit a yield stress are considered to have a structural network extending throughout the entire volume of the system. The strength of this network is dependent on the strength and type of interactions between the molecules comprising the network as well as the structure of the dispersed phase and the strength and type of its interactions with the network. Typically, after the yield stress is reached, the viscosity is relatively low; however, before the applied force reaches the yield stress, the strong interactions among the structural components can cause the material to behave like a solid, deforming instrad of flowing (Larson 1999).

3.1.3 Non-Newtonian Behavior: Shear-Dependency

Most semisolid foods are non-Newtonian, which means their viscosity is dependent on shear rate. Unlike Newtonian fluids, non-Newtonian materials do not have a linear relationship between shear stress and shear rate. The ratio of the two parameters, which is viscosity, increases (dilatant fluids) or decreases (pseudoplastic fluids) as shear rate increases (Fig. 8).

The viscosity of pseudoplastic fluids decreases with the rate of shear; therefore, another term for this behavior is shear-thinning. A dilatant or shear-thickening material is one in which viscosity increases with shear rate. This behavior is typically observed in suspensions or colloids instead of homogeneous materials. While

Fig. 8 Shear rate dependency of Herschel-Bulkley, pseudoplastic, Newtonian, and dilatant fluids



there are not many shear-thickening food materials, a classic example is a suspension of cornstarch and water. Many semisolid foods, such as yogurt, hydrocolloid solutions, cheese sauces, and chocolate milk show shear-thinning behavior. It is hypothesized that shear-thinning behaviors are due to large molecular chains that tumble at random, and the large hydrodynamic radius can significantly affect the resistance to flow of fluids under low shear. Under increasing shear rates, these large molecular chains gradually align themselves in the direction of the shear force, which allows them to slip past each other and decreases the resistance of flow (Saramito 2016). In the case of case of full fat yogurt, the large molecules that align with applied force incldue caseins, fat globules, and whey proteins.

The power law equation is often sufficient for describing shear-dependent behaviors:

$$\sigma = K\left(\dot{\gamma}\right)^{n} \tag{3}$$

where K is the flow consistency index (Pa.s^n) and n is the flow behavior index (unitless). n typically falls between 0 and 1 for pseudoplastic materials. If n is >1, the flow behavior is dilatant, and if n is equal to 1, the flow behavior is Newtonian, and the equation collapses to the equation for Newtonian fluids.

Many shear-dependent materials also have a yield stress. A general model for these materials, the Herschel-Bulkley model, is established by adding a yield stress term to the power law model:

$$\sigma = \sigma_0 + K\left(\dot{\gamma}\right)^{n} \tag{4}$$

Herschel-Bulkley flow behavior is shown in Fig. 8. Note that the example of Herschel-Bulkley flow in this figure is of a material that shows pseudoplastic behavior after intiation of flow. It is possible for the material to exhibit dilatant behavior after flow initiation, but this is not common in food products.

One disadvantage of the power law and Herschel-Bulkley models is that they do not fit many materials well in the low-shear and high-shear ranges. Because zero-shear viscosity is important for characterizing the stability of many foods, models that account for zero-shear viscosity are needed for proper modeling of these food systems. Moreover, for a relatively highly viscoelastic gelled food material, e.g. Greek yogurt, a certain amount of force or stress (yield stress) is needed before it starts to flow. Thus, more comprehensive models that include zero-shear viscosty, infinite-shear viscosity, or both are needed for better describing certain semisolid food materials. Examples of these models are shown in the equations below. For additional models and a more detailed explanation of the models presented here, the reader is encouraged to review Metzger's The Rheology Handbook (Mezger 2014).

Casson model:

$$\sigma^{\frac{1}{2}} = \sigma_C^{\frac{1}{2}} + \left(\eta_C \dot{\gamma}\right)^{\frac{1}{2}} \tag{5}$$

Cross model (simplified version):

$$\frac{\eta\left(\dot{\gamma}\right)}{\eta_0} = \frac{1}{1+\left(C\dot{\gamma}\right)^{p}} \tag{6}$$

Carreau model (simplified version):

$$\frac{\eta\left(\dot{\gamma}\right)}{\eta_0} = \frac{1}{\left(1+\left(C_1\dot{\gamma}\right)^{2}\right)^{P_c}} \tag{7}$$

In the equations above, σ_C is the Casson yield stress; η_C is Casson viscosity (Pa), C is the Cross constant (s), P is the Cross exponent, η_0 is zero-shear viscosity (Pa.s), C_1 (s) is the Carreau constant (s), and P_c is the Carreau exponent.

Like other semisolid foods, the viscosity and shear-dependent behavior of yogurt can be modified. Many factors including fat and whey protein content, heating temperature and time, and microbial cultures used for fermentation can impact the rheological properties of yogurts. Temperature and duration influence yogurt viscosity by changing the aggregate size of whey proteins, which in turn is influenced by covalent (disulfide) interactions arising from denaturation of globular whey proteins (Shaker et al. 2000). Formulation can have a dramatic impact on yogurt flow behaviors. Decreased fat content in yogurt can also result in low viscosity due to the decrease in total milk solids. Fat content also has a significant influence on the firmness of yogurt gels (Shaker et al. 2000). Higher whey protein concentration can result in higher yield stress and viscosity in yogurt by forming more dense and intense network (Damin et al. 2009). Adding dietary fibers to yogurt can either increase or decrease the apparent viscosity of yogurt depending on the source of fiber and its interaction with the other yogurt ingredients. Previous work has indicated that adding apple fiber can significantly increase yogurt apparent viscosity; however, addition of bamboo, wheat, and inulin fibers slightly decreased its apparent viscosity (Dello Staffolo et al. 2004). Addition of other food polymers such as pectin also contributes to an increase of apparent viscosity and flow behavior index (reduced shear shinning) (Basak and Ramaswamy 1994). Calcium-fortified fruit yogurt has less shear-thinning behavior and higher apparent viscosity than non-fortified yogurt due to the increased number of colloidal calcium phosphate (CCP) linkages between casein micelles and hence, a stronger yogurt gel network (Singh and Muthukumarappan 2008). Figure 9 shows the mechanism of how CCP strengthens the casein network in yogurt.

Figure 10 shows diagrams of the mechanism of shear-thickening behaviors in a colloidal system. Here, repulsion forces (van der Waals forces) keep the suspended particles from aggregating with other particles. When shear force become dominant, the particles begin to flocculate, forming bigger particles. This disrupts the suspension system, resulting in a viscosity increase (Morrison and Ross 2002).

3.1.4 Non-Newtonian Behavior: Time Dependency

The viscosity of some semisolid food materials changes over time due to continually applied shear. Thixotropic materials show a decrease in viscosity over time, while rheopectic materials show an increase in viscosity over time (Fig. 11). After the applied shear is removed or at least lowered to minimal shear, the material may return to its original viscosity over time. Thixotropy is observed when shear forces disrupt the microstructure of materials; this structure may partially or totally recover when the material is quiescent. The driving force for thixotropic behavior is the

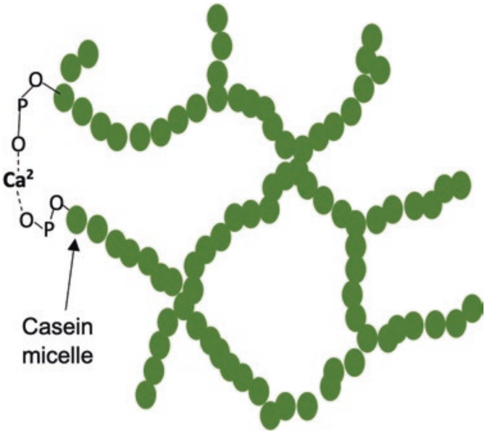


Fig. 9 Colloidal calcium phosphate (CCP) in a casein network

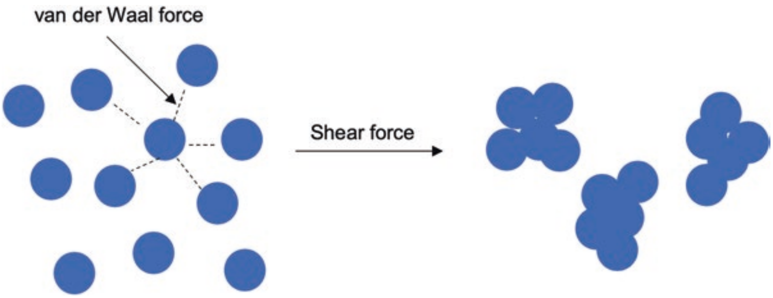
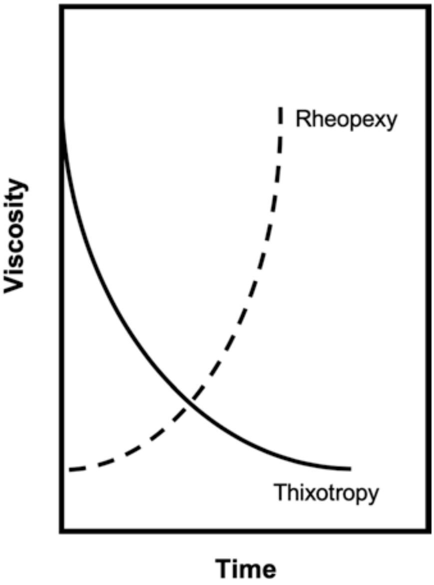


Fig. 10 Microstructural changes in a shearing-thinning material under shear

Fig. 11 Thixotropic and rheopectic fluid behaviors



competition between structural breakdown due to applied force and structural buildup due to in-flow collisions and Brownian motion (Barnes 1997). Foods with time-dependent behavior typically show thixotropy. While some foods appear to be rheopectic, the increase in viscosity is actually due to a change in their composition or a fundamental, permanent change in the configuration of individual molecules, not a shear-induced arrangement of molecules over time, as is the case in true rheopexy. For example, whipped cream is not rheopectic even though it can be sheared until it forms a relatively stiff material. This increase in viscosity and rigidity is due to the incorporation of air and the subsequent unfolding of proteins at the air–water interface. Thus, this is a compositional and microstructural change. Similarly, the churning of cream into butter is not rheopexy because buttermilk is removed from the final butter mass (compositional change) and there is a fundamental shift in structure that is more than just simple molecular jamming: the o/w emulsion in cream shifts to a w/o emulsion in butter.

Exponential models are typically used to characterize thixotropic behavior:

$$\sigma\left(t\right)=\sigma_0 e^{-kt} \tag{8}$$

$$\sigma\left(t\right)=\sigma_\infty+\left(\sigma_0-\sigma_\infty\right)e^{-kt} \tag{9}$$

where σ_0 is the stress at the onset of shearing (yield stress, Pa), σ_∞ is the equilibrium stress after shearing for infinite time (Pa), and k is the consistency coefficient (1/s). $\sigma_0 > \sigma_\infty$ due to the fact that the microstructure of a material is intact at the beginning stage of shearing and thus has more resistance to shearing than after the original microstructure begins to collapse.

As previously mentioned, the sturcutre of thixotropic semisolid foods such as yogurt can partially or totally rebuild after the removal of shear, resulting in an increase in viscosity up to the orginal viscosity if the material is left at rest. The exponential model for characterizing this rebuilding behavior is:

$$\sigma\left(t\right)=\sigma_0-\left(\sigma_0-\sigma_\infty\right)e^{-kt} \tag{10}$$

The thixotropic behaviors of many food materials can be modified by altering their formulations. For example, calcium-fortified yogurt sheared at a constant rate had significantly less decrease in apparent viscosity over time as compared to non-fortified yogurt. In addition, after long-time quiescence, less reduction in initial apparent viscosity was observed in calcium-fortified yogurt than non-fortified yogurt (Singh and Muthukumarappan 2008). This was due to an increased number of CCP linkages between casein micelles in calcium-fortified yogurt, so an increased force was required to break those bonds, and formation of more CCP linkages was promoted after shearing ended. Similarly, addition of hydrocolloids to yogurt, such as pectin and fiber, also decreased viscosity reduction from shearing and increased viscosity recovery after the shear force was removed (Basak and Ramaswamy 1994). This result may have been due to greater heterogeneity among large particles (pectin, fiber, and caseins), requiring higher shear force to align all particles to the direction of flow (Fig. 12).

Yogurt fermented by different cultures may also influence thixotropic behavior. For example, dairy lactic acid bacteria, such as *Lactobacillus delbrueckii ssp. bulgaricus* is able to produce exopolysaccharides, which are long polymer chains that can attach to casein micelles and decrease viscosity reduction during shearing (Rawson and Marshall 1997). This is in agreement with studies on the effects of added hydrocolloids on yogurt viscosity (Basak and Ramaswamy 1994).

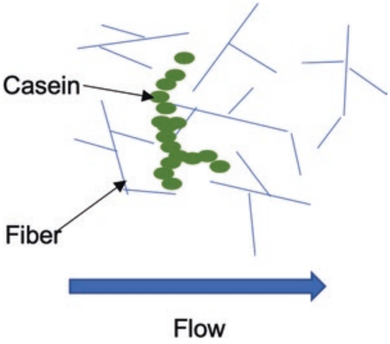


Fig. 12 Microstructure of fiber-enriched yogurt under shear

3.2 *Viscoelastic Behaviors*

3.2.1 Viscoelasticity

Viscoelastic materials exhibit both elastic and viscous behaviors. Viscous behaviors manifest as the dissipation of imparted energy by flow and viscous heating (Stachurski 2009). Models for flow behaviors are discussed in Sect. 3.1. Elastic behavior is the ability to store deformational energy when an external force is applied (Stachurski 2009), then return to its initial shape and size after the force is removed (Timoshenko and Goodier 1986). Multiple parameters can be used to quantify elastic behavior, including Young's modulus, shear modulus, and bulk modulus. The principal differences among these moduli are the direction of applied force (Fig. 13). For Young's modulus, the applied force is perpendicular to the surface of a material. Shear modulus measures elastic behavior when the direction of force is parallel to the interacting surface. Bulk modulus is measured when pressure is applied to all surfaces of a material, resulting in a change in volume.

Many semisolid foods, such as cheeses, butters, yogurts, doughs, gels, and ketchup show viscoelastic behaviors. The viscoelastic properties of semisolid materials are typically determined by geometries that provide an oscillating torque (stress) to a material at a given amplitude and frequency, and measure the resulting deformation (strain), or vice versa (Zhong and Daubert 2013). Viscoelastic moduli and phase angle can be derived from the oscillatory shear data. For a detailed description of viscoelastic parameters and the measurements used for evaluating viscoelastic behaviors, please refer to Chapters "Introduction: Measuring Rheological Properties of Foods" and "Rheological Testing for Semisolid Foods: Traditional Rheometry".

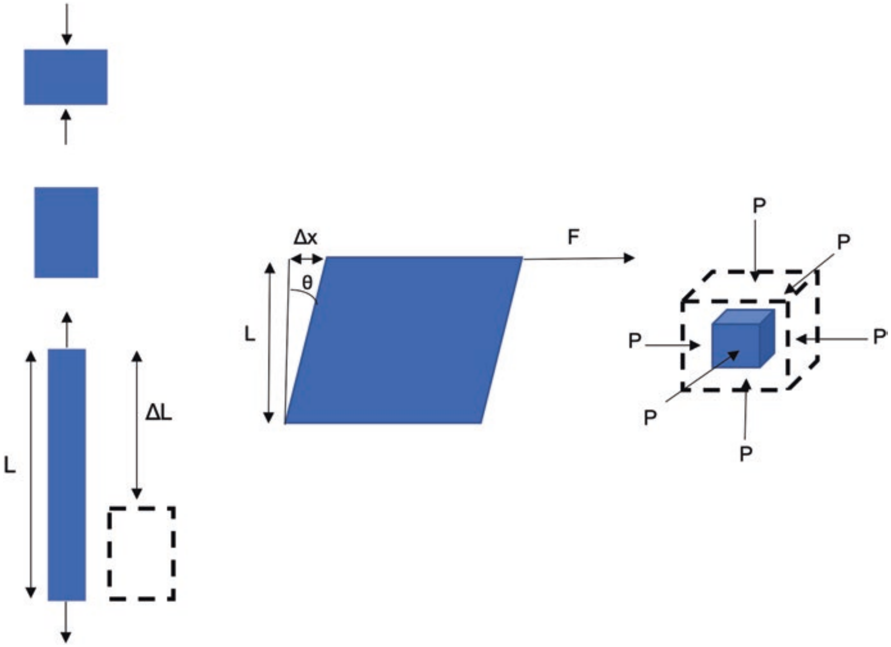


Fig. 13 Diagram of mechanical moduli: Young’s modulus, shear modulus, and bulk modulus (left to right)

3.3 *Modification of Viscoelastic Properties*

The viscoelastic properties of semisolid foods can be modified by either formula or physical treatments. For example, studies have reported that adding dietary fibers, such as orange fiber with a particle size range from 0.4 to 1.0 mm, resulted in increased yogurt viscoelastic moduli with increased fiber addition (0.2–1.0% w/w), while maintaining a relatively constant phase angle(~0.3 rad) (Sendra et al. 2010). These results indicated that addition of orange fibers promoted a more rigid yogurt gel but did not alter its ratio of elastic to viscous behavior. Similarly, addition of gelatin to yogurts can also increase viscoelastic moduli values (Supavititpatana et al. 2008). However, adding inulin, a dietary fiber containing fructans, decreased storage modulus values while loss modulus values remained relatively unchanged. Thus, addition of inulin promoted a weaker, more fluid yogurt gel (Paseephol et al. 2008).

Viscoelastic properties of yogurt can be starter culture-dependent. ‘Ropy’ and ‘non-ropy’ starter cultures are used for the manufacture of stirred and set types of yogurt, respectively (Hassan et al. 2002). Ropy cultures include *Streptococcus salivarius ssp. thermophilus* and *Lactobacillus delbrueckii ssp. bulgaricus,* which can produce extracellular polysaccharides during fermentation (Vlahopoulou and Bell 1993). These polysaccharides provide a long, stringy texture to the yogurt and can increase both the yogurt viscosity and its extent of fluid-like behavior. Yogurts fermented by ropy cultures were found to have increased viscous and decreased elastic behavior than yogurt fermented with non-ropy cultures. The extracellular polysaccharides added to the yogurt gels did not help to build the yogurt structural network; however, they did increase yogurt viscosity (Vlahopoulou and Bell 1993).

Homogenization of skim milk or whey protein concentrate solutions during yogurt manufacture can also significantly increase yogurt storage modulus values. Homogenization at 10–20 MPa reduces the size of milk fat globules to 0.1–1 um; smaller milk fat globules more readily facilitate the incorporation of fat into the protein network during yogurt manufacture due to their increased surface area to volume ratio (Chandan 2007). The increased surface area favors interactions among fat and milk proteins, casein, and denatured whey during acidification, promoting gel formation (Cano-Ruiz and Richter 1997).

3.4 Creep-Recovery Behavior

Creep-recovery tests are conducted by applying a constant force (uniaxial stress or shear stress) to a material and recording the strain as a function of time during the time of force application and after the force is removed (Fig. 14). For semisolid foods, recovery is usually incomplete and requires a significant amount of time. Creep-recovery testing can provide important parameters, such as zero shear viscosity (η_0) and creep compliance (J), or the ratio of strain to stress during creep or recovery, for characterizing rheological behaviors of food. For example, cookie doughs which had nearly the same viscosities showed significant differences in compliance and elastic recoil, which are important for predicting the shape of the dough after extruding to avoid variations in product size (Franck 2005).

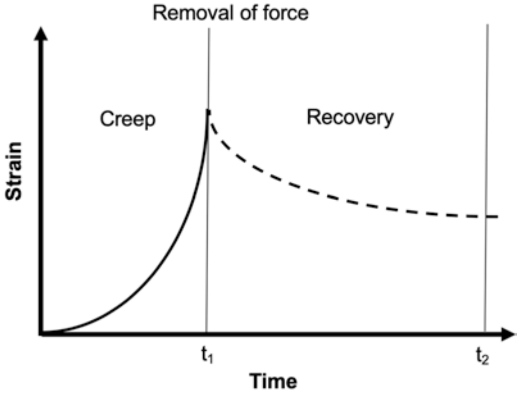


Fig. 14 Creep-recovery behaviors after applying and removing force

3.4.1 Creep-Recovery Model

Due to the complexity of creep-recovery behaviors of semisolid materials, it is common to characterize them by combining damper and spring elements, which represent pure viscous and elastic behavior, respectively. These models usually contain some arrangement of a certain number of Maxwell and Kelvin models (Fig. 15). Maxwell and Kelvin models are used to represent different types of viscoelastic behavior. In the Maxwell model, the material is represented by a purely viscous damper element and a purely elastic spring element connected in series (Eu 1985). Whena Maxwell materials are subjected to a stress, the spring compresses first, followed by the damper depressing. In other words, the material stores energy from the imparted stress over short time periods, but dissipates the energy (relaxes) over long time periods. Conversely, the Kelvin model consists of a damper element and a spring element is in parallel. If a sudden constant stress is applied to a Kelvin material, the spring and the damper act simulatenously, meaning that the material both stores energy and relaxes (dissipates energy) at the same time.

One common model for creep compliance of semisolid materials as a function of time is the Burgers model, which consisits a Kelvin model acting in series with a Maxwell model (Fig. 16, Eqn. 11):

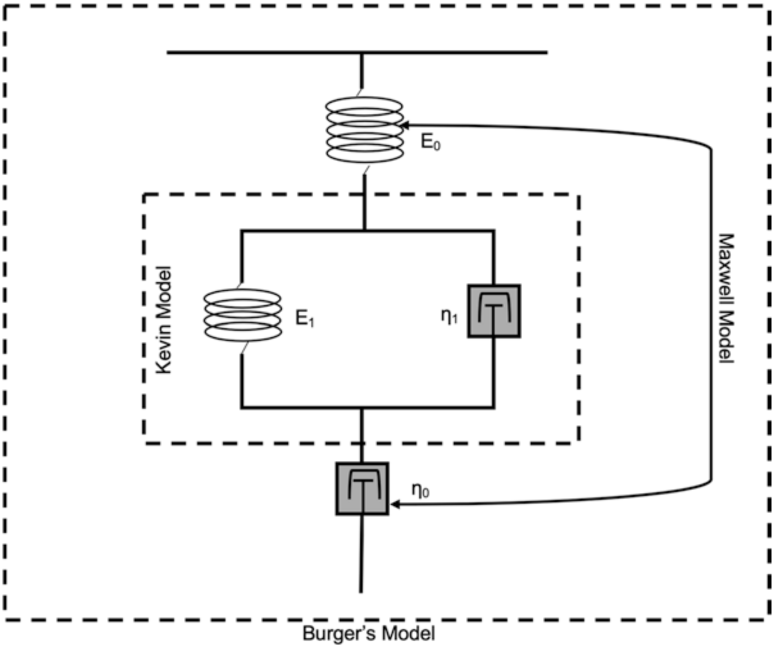


Fig. 15 Diagram of Maxwell, Kelvin, and Burgers models

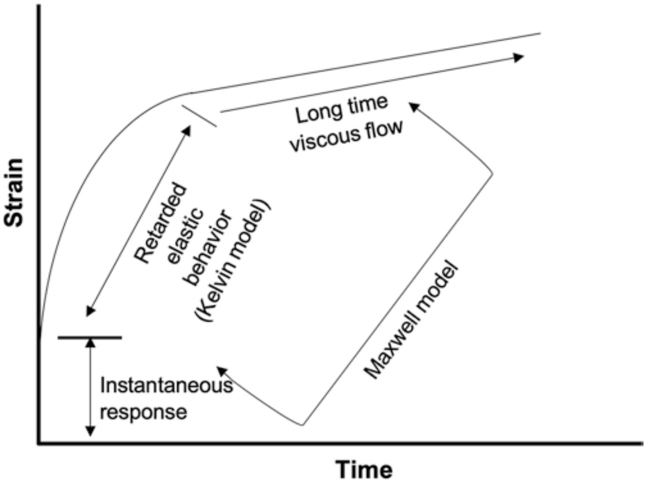


Fig. 16 Creep behavior characterized by the Burgers model

$$J(t) = J_0 + J_1\left(1 - e^{-\frac{t}{\lambda_{\text{ret}}}}\right) + \frac{t}{\eta_0} \tag{11}$$

where J_0 is the instantaneous compliance, which is the reciprocal of elastic modulus, E (1/Pa), or strain over stress; J_1 is the retarded compliance defined as $1/E_1$, or the reciprocal of the elastic modulus of the compound spring (1/Pa); t is time (s), λ_{ret} is the retardation time (s), or the time needed for the compliance needed to reach 63.2% of its final value; and η_0 is the Newtonian viscosity of the free dashpot (Pa.s).

3.4.2 Modification of Creep-Recovery Behaviors

Because creep and recovery are linked to visoelastic behaviors, creep-recovery behaviors of semisolid foods can be modified by both formula and physical treatments in the same manner as viscoelastic behaviors. In full-fat yogurt, casein is the main milk protein used to form an uninterrupted network composed of protein chains and clusters (Kalab 1979). Fat globules can interact with the gel casein matrix as binders, providing a strong elastic structure (Lucey et al. 1988). Previous studies indicated that whey protein isolate incorporated into skim milk (10.5 g whey protein/L) combined with heat treatment at 80 °C for 10 min can make non-fat yogurt, in which whey protein provides structure, had smaller values of J_0 and λ_{ret} than full-fat yogurt, which implied that the elasticity of whey protein-fortified yogurt was higher than that of full-fat yogurt, so less time was needed to recover from sudden stress application. Other studies showed that incorporation of whey protein in reduced-fat yogurt tended to form chains of casein micelles (protein particles linked in chains) rather than clusters (large protein aggregates), with whey proteins occupying the spaces between the casein chains and increasing the yogurt gel strength (Puvanenthiran et al. 2002; Lobato-Calleros et al. 2004). However, adding microparticulated whey protein to yogurt (particle size 1–2 um) can significantly increase J_0 and J_1, indicating a greater degree of deformation, lower recovery ability, and a predominatly viscous nature of the protein network. It was hypothesized that addition of microparticulated whey protein to yogurt gels reinforced the gel microstructure by forming a secondary network in the interstices between casein chains, interrupting the casein micelles clusters and chains (Sandoval-Castilla et al. 2004), which was in agreement with the other aforementioned studies.

4 Texture and Oral Processing Features of Semisolid Foods

Consumer acceptability is key to success of a food product. For semisolid foods, in addition to price, consumer acceptability is determined by food sensory attributes including flavor, texture/mouthfeel, and food and packaging appearance. Although rheological properties cannot be used to completely replace food texture measurements conducted by sensory panels, many studies have related semisolid food rheological behaviors to texture attributes such firmness, creaminess, smoothness, graininess, thickness, stickiness, and coarseness (Nishinari 2004). Additionally, changes in rheological behaviors may be reflected in modification of multiple texture attributes.

4.1 Sensory Attributes of Semisolid Foods

The texture characteristics of semisolid foods can be grouped into six categories: (1) viscosity-related attributes, e.g. non-oral and oral viscosity; (2) surface texture attributes, e.g. smoothness; (3) attributes related to bulk homogeneity or heterogeneity, e.g. smooth; (4) attributes related to adhesion or cohesion, e.g. stickiness; (5) attributes related to sensations of wetness and dryness; and (6) attributes associated with fat sensations, e.g. creaminess (Weenen et al. 2003). Six important sensory attributes of semisolid foods will be introduced in the next six subsections.

4.1.1 Firmness

Firmness, or the resistance of the food to deformation under an applied force, is one of the most researched texture attributes for a wide variety of foods. It can be determined either by human senses using touch or sight or instrumentally measured by rheometers (Faber et al. 2017). Firmness of yogurt and ice cream were reported positively correlated to complex modulus; however, firmness was negatively correlated to syneresis (Folkenberg et al. 2006; Akalin and Erişir 2008). The magnitude of expected and preferred firmess is product-specific; for example, Greek yogurt is expected to be significantly firmer than stirred yogurt.

4.1.2 Ropiness

Ropiness is an important sensory attribute for semisolid foods, especially yogurts. It describes the degree to which a strand (rope) will form when a spoon is dipped into the product and slowly pulled out (Drake et al. 2000). Determination of ropiness can be achieved by evaluating the amount of threads or drops that form when introducing the spoon vertically into the sample and raising it vertically from the sample (Ares et al. 2007). Viscosity hysteresis loop area has been found to have a power law relationship with yogurt ropiness (Folkenberg et al. 2006):

4.1.3 Creaminess

Creaminess is a descriptor that is often used to describe the sensory properties of lipid-based foods. Altough it is difficult to define—some sensory scientists consider it to be a consumer term and do not use it in descriptive sensory analysis—it is an important indicator of consumper perception of product richness and high quality (Kilcast and Clegg 2002). Previous study indicated that granularity or grittiness decreases creaminess sensation, and creamy-textured soups should have a very smooth mouthfeel, with complete absence of a powdery sensation when consumed (Wood 1974). Thickness, smoothness, and in some cases, slipperiness have been empiricaly found to relate to creaminess through a power law replationship (Kokini et al. 1977). While the sensations of thickness, smoothness, and slipperiness contribute to the sensation of creaminess, they do not completely describe it.

Some previous studies (Daget et al. 1987; Daget and Joerg 1991) found correlations between creaminess and instrumentally measured viscosity and flow behavior index in caramel creams and soups. Creaminess has also been determined by measuring the time needed to dissolve or mix a sample with saliva. Using this measurement method, creaminess was positively correlated to instrumentally measured yield stress, consistency coefficient, and hysteresis in the viscosity curve; it was negatively correlated to syneresis and flow behavior index (Ares et al. 2007). These results indicated that creamier samples were thicker, more pseudoplastic, and broke down more easily under shear, but were more stable during storage.

4.1.4 Viscosity

Both spoon viscosity and oral viscosity are frequently used to evaluate and differentiate semisolid foods. Spoon viscosity refers to the resistance of the sample to be stirred with a spoon (Ares et al. 2007). Oral viscosity refer to the perceived thickness of the food in the mouth during consumption (Skriver et al. 1999). Previous studies have shown that yogurt spoon viscosity was corrected to both complex modulus measured by dynamic oscillatory measurements and viscosity obtained from a viscometer operating at 5 rpm (Skriver et al. 1999). Oral viscosity was reported to be correlated with dynamic viscosity (Richardson et al. 1989; Houska et al. 1998). However, non-oral viscosity (obtained by stirring with a spoon) did not correlate well with oral viscosity (Stanley and Taylor 1993; Rohm and Kovac 1994).

4.1.5 Thickness

Thickness is a key textural attribute of semisolid foods, including yogurt, ice cream, mayonnaise, and salad dressing. It can be perceived by visual observation of flow behavior during spreading or pouring and by oral mouthfeel. It can also be determined instrumentally by measuring dynamic viscosity (Borwankar 1992). Evaluation of yogurt thickness has been performed by evaluating the residual mouthcoat, or the perception of the layer of residual food that covers the palate and tongue after swallowing the sample. These thickness measurements were positively correlated to viscosity measured at high shear rates (Skriver et al. 1999). Additionally, thickness has been correlated to the shear stress on the tongue during oral processing (Dickie and Kokini 1983):

4.1.6 Smoothness

Smoothness has been described as the sensation a material produces on soft tissues (Szczesniak 1979). To assess smoothness, the tongue is moved lightly across the food product, and the perception of the sensations between the food, the tongue, and the roof of the mouth are recorded. Smoothness has been inversely related to the friction force required to have skin slip across skin or food (Kokini 1987). Typically, smoothness is a desirable trait in semisolid foods, including yogurt, pudding, custard, sour cream, and dairy spreads.

4.2 Texture Modification

Similar to modification of semisolid food rheological behaviors, modification of semisolid food textural attributes can be achieved by altering its formulation or processing parameters. This is because semisolid food microstructural features can influence both rheological and texture characteristics. This topic is discussed in further detail in Chapters "Structuring Semisolid Foods" and "Relationships Among Semisolid Food Microstructures, Rheological Behaviors, and Sensory Attributes"; a brief overview of methods for texture modification are described in the following sections.

4.2.1 Storage Time

The influence of storage time on semisolid food texture is mainly due to time-dependent destabilization of emulsions in the foods or syneresis. For example, oil droplets in peanut butter can coalesce to form a continuous oil phase that forms a surface layer, resulting in a decrease in sensory quality (Gills and Resurreccion 2000). Yogurt after 14 days of storage had lower thickness and graininess compared to yogurt after 1 day of storage time. These textural differences were reflected by significantly increased viscosity and storage modulus (Biliaderis et al. 1992). In a different study, chewiness and iciness of ice cream increased with increased storage time (Schaller-Povolny and Smith 1999).

4.2.2 Solid Content

The impact of altering solid content on semisolid food sensory quality varies based on both the total solids contant and the solids used in the product. For example, stirred yogurt with small amounts of added whey protein (<4.2%) showed a lower score in smoothness compared to yogurt with a larger amount of whey protein (6.0%) (Janhøj et al. 2006). Both creaminess and smoothness have shown dependency on viscosity and dynamic moduli, so increasing viscosoity and viscoelastic moduli by increasing the solids content of the product would increase creaminess and therefore increase sensory quality. On the other hand, changing solids content may not have any relationship to the measured sensory attributes. For example, while stirred yogurt yield stresses varied with different fat content and whey protein addition, their yield streses were not correlated to any sensory attributes (Janhøj et al. 2006).

4.2.3 Fat Content

The fat content of semisolid foods has significant influence on their texture, namely on creaminess and smoothness. It was reported that the creaminess and smoothness of a group of semisolid foods composed of mayonnaises, low-fat yogurt (fat content <1%), custards, and white sauces, which had a broad range of fat content (0–80%), were positively correlated to fat content (Kilcast and Clegg 2002; de Wijk et al. 2006). In general, foods that are higher in fat tend to be perceived as thicker, smoother, and creamier, with a higher degree of mouthcoat.

4.2.4 Polysaccharide and Calcium

Polysaccharides are commonly used in semisolid foods as texture modifiers. Similarly, calcium can be used as a texture modifier in dairy products because it has a notable influence on casein–casein interactions. For example, addition of xanthan gum and guar gum to salad dressing (Tanaka and Fukuda 1976), mayonnaise (Su et al. 2010), and cream (Cottrell et al. 1979), can significantly increase the thickness by increasing the viscosity of the foods. In dairy products, addition of dietary fiber from wheat, bamboo, and inulin improved yogurt texture scores and slightly decreased their viscosity (Dello Staffolo et al. 2004). Calcium-fortified yogurt with up to 40% more calcium than a traditional yogurt had slightly decreased appearance and texture scores; however, its viscosity was significantly increased (Singh and Muthukumarappan 2008).

5 Conclusion

The physiochemical properties and texutre of semisolid foods are a result of the intra- and intermolecular connections among the polymers, e.g. lipids, polysaccharide, and proteins; and small molecules, e.g. water and ions, that comprise their formulation. These structures, including emulsions protein-polysaccharide networks, and fat or ice crystal networks, give semisolids unique rheological behaviors, product stability, texture, flavor, and appearance. Thus, the use of appropriate stablizers, processing methods, and formula is critical to control the quality of semisolid foods.

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