Rheological Innovations for Characterizing Food Material Properties

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Abstract

Rheological methods are continually evolving to encompass novel technologies and measurement methods. This review highlights novel techniques used to analyze the rheological properties of foods over the previous decade. Techniques reviewed include large amplitude oscillatory shear (LAOS) testing and rheological techniques coupled with other measurement methods, such as microscopy and nuclear magnetic resonance (NMR). Novel techniques are briefly overviewed and discussed in terms of advantages and disadvantages, previous use, and suggested future utilization.

INTRODUCTION

Linear viscoelastic region (LVR): the stress/strain region in which the sample exhibits a linear stress response to an applied strain; the complex, elastic, and viscous moduli are constant in this region

Small amplitude oscillatory shear (SAOS) testing: oscillatory shear testing within the linear viscoelastic region

Large amplitude oscillatory shear (LAOS) testing: oscillatory shear testing outside the linear viscoelastic region

Rheology is the study of the flow and deformation of matter. Rheological measurements are used in the food industry for scaleup and quality control as well as in the laboratory for scientific research. Although there are many possible tests, analyses of interest in food rheology may be grouped as either tensile, compressive, or shear testing. This review focuses on novel shear-testing techniques.

The validity and repeatability of the measurements gathered from shear testing depend on both instrumentation and methodology. For example, determination of rheological properties may be difficult when instrument sensitivity is below that needed to determine the property, or if the methodology used requires the sample to be altered (by mixing with a solvent, heating, cooling, shearing, etc.) or contains assumptions that may not hold true for the sample. Additionally, certain foods such as foams, foods with high lipid content, and foods containing hydrocolloids can be difficult to analyze, as these foods can be extremely shear sensitive and exhibit phenomena such as slip or problems associated with significant normal stress differences. Traditional rheological tests are inherently disruptive to the sample, applying sufficient force to the sample to induce a deformation. This force may damage sensitive structures, altering the rheological properties of the sample. It is often necessary to develop protocol that is minimally disruptive to the sample. Depending on the desired measurement, it may also be necessary to couple rheological equipment with other analytical tools such as microscopy or magnetic resonance equipment. In particular, methodology that couples microscopy with traditional rheological techniques, or microrheology, has evolved significantly over the past decade. Although microrheological measurements are not directly relatable to traditional rheological measurements, microrheology is able to overcome several limitations of traditional shear rheology. Additionally, methodology that can account for nonideal behavior or behavior beyond the linear viscoelastic region (LVR) may prove useful when measuring rheological properties of foods, given that foods are ultimately subjected to stresses outside the linear elastic domain. The objective of this paper is to highlight the rheological techniques that have been novel to food science over the past decade. Rather than providing in-depth explanations, a general overview of each technique is provided, and recent advances and potential applications in food science are discussed.

LARGE AMPLITUDE OSCILLATORY SHEAR

Oscillatory shear testing of materials may be broken down into small amplitude oscillatory shear (SAOS) and large amplitude oscillatory shear (LAOS). Both SAOS and LAOS testing may be performed on a standard stress- or strain-controlled rheometer, as both instruments involve a rheological tool (bob, cone, vane, etc.) imparting an oscillating stress or deformation to the sample. The major difference between the two testing methods is that SAOS testing is restricted to the LVR, whereas LAOS testing occurs beyond linearity. Although LAOS testing has been used to study various polymers and polymer melts for over 40 years (Debbaut & Burhin 2002), it is not widely used in the food industry. Most studies use SAOS testing as a means to quantify rheological properties of foods. Keeping the material tested in the LVR results in material responses independent of the magnitude of applied stress or strain, or the rate of strain application. However, many processes involving foods, such as chewing and swallowing, require very large deformations, occurring well outside the LVR (Steffe 1996). Using LAOS to quantify material responses under large deformations allows for the study of rheological properties during common food processes (Song et al. 2006, Brenner et al. 2009).

When a sample is sheared, it often undergoes microstructural changes such as polymer chain alignment with the flow field, increased chain interaction, and network formation or disruption

(Sim et al. 2003). Because of sensitivity to microstructural changes, LAOS is often used to determine rheological properties of polymers (Hyun et al. 2002, Carotenuto et al. 2008). This sensitivity is a useful analytical tool for classifying polymers based on general microstructural changes during large strain application (Hyun et al. 2002). Hyun et al. (2002) tested several polymer melts as well as a xanthan gum solution under LAOS at constant frequency (1 rad s^{-1}) and varied strain (3% to 1000%). The resulting data indicated that polymers could be divided into four categories based on their behavior during LAOS: strain softening (both G', the storage modulus, and G'', the shear loss modulus, decrease), strain hardening (both G' and G'' increase), weak strain overshoot (G' decreases and G'' initially increases, then decreases), and strong strain overshoot (both G' and G'' initially increase, then decrease). Strain hardening was defined as a decrease in deformation rate with increasing strain, whereas strain softening was defined as an increase in deformation rate with increasing strain (Hyun et al. 2002). Although calculation of G' and G'' requires a linear relationship between stress and calculations involving these parameters outside of the LVR should be invalid, Hyun et al. (2002) performed strain and measurements beyond the region of linearity and analyzed stress responses via Fourier transform, and concluded that the deviation from linearity was not significant. Sim et al. (2003) created a nonlinear network model of the stress tensor matrix created by application of LAOS on various types of polymers. Although simplistic, the model was found to have good agreement with the results of Hyun et al. (2002) (Sim et al. 2003). Sim et al. (2003) hypothesized that the model could be useful in explaining polymer behavior in terms of microstructural changes.

There has been an increased interest in Fourier analysis to examine LAOS data. Fourier analysis is more precise and modern computing technology can readily perform the necessary calculations (Debbaut & Burhin 2002, Sim et al. 2003). In oscillatory testing, strain is applied according to a sinusoidal function. The shear rate at any time may be found by differentiating the applied strain function with respect to time. Using Fourier analysis, the absolute value of the shear rate expression is converted to a sum of different harmonic contributions (Wilhelm 2002), enabling LAOS data to be analyzed for the contribution of different harmonics. Although the stress response from SAOS may be described by the first harmonic alone, stress responses from LAOS include higher-order harmonics (Debbaut & Burhin 2002). The contribution from the higher-order harmonics becomes significant in the nonlinear region due to the dependency of apparent viscosity on applied strain rate: Strain rate varies sinusoidally, so apparent viscosity will also vary sinusoidally. This sinusoidal variation in apparent viscosity can be used to explain differences among viscoelastic samples: Samples with the same apparent viscosity may have significantly different higher-order harmonic intensities and thus different flow behavior (Wilhelm 2002). Fourier transforms are also useful for increasing the signal-to-noise ratio, the measure of signal strength to random fluctuations for improved sensitivity (Wilhelm 2002). In addition to analysis of shear stress, strain, and phase angle data, Fourier transforms have also been used to examine normal stress during LAOS (Nam et al. 2008), linear to nonlinear material behavioral transitions (Wilhelm 2002), polymer morphology (Wilhelm 2002, Carotenuto et al. 2008), accuracy of predictive rheological models (Debbaut & Burhin 2002, Wilhelm 2002), and characterization of polymer dispersions (Wilhelm 2002).

A method to simultaneously quantify both viscous and elastic nonlinear behavior using LAOS was recently developed by Ewoldt et al. (2008). In this method, the general stress response is broken down into elastic (σ') and viscous stress (σ'') responses. The elastic and viscous stresses are plotted against the strain (γ) and strain rate ($\dot{\gamma}$) input functions, and Chebyshev polynomials (first kind) are fit to the plots

$$\sigma'\left(\frac{\gamma}{\gamma_o}\right) = \gamma_o \sum_{n:odd} e_n(\omega, \gamma_o) T_n\left(\frac{\gamma}{\gamma_o}\right) \tag{1}$$

and

$$\sigma''\left(\frac{\dot{\gamma}}{\dot{\gamma}_o}\right) = \dot{\gamma}_o \sum_{n:odd} \upsilon_n(\omega, \dot{\gamma}_o) T_n\left(\frac{\dot{\gamma}}{\dot{\gamma}_o}\right), \tag{2}$$

where γ_o is the strain amplitude, $\dot{\gamma}_o$ is the strain rate amplitude, $e_n(\omega, \gamma_o)$ and $\upsilon_n(\omega, \dot{\gamma}_o)$ are the elastic and viscous Chebyshev coefficients, respectively, and $T_n(\frac{\gamma}{\gamma_o})$ and $T_n(\frac{\dot{\gamma}}{\dot{\gamma}_o})$ are n$^{\text{th}}$ order Chebyshev polynomials of the first kind. A general form of the Chebyshev polynomials of the first kind is given by

$$T_n(x) = 2xT_{n-1}(x) - T_{n-2}(x). \tag{3}$$

The Chebyshev polynomials were chosen for fitting the data because these polynomials consist of orthogonal terms, have odd symmetry around $\frac{\gamma}{\gamma_o} = 0$, and have a bounded range for higher-order coefficients. The third-order Chebyshev coefficients (e_3 and υ_3) may then be used to determine material behavior (Ewoldt et al. 2008). Ewoldt et al. (2008) grouped materials into four main categories: strain hardening ($e_3 > 0$), strain softening ($e_3 < 0$), shear thickening ($\upsilon_3 > 0$), and shear thinning ($\upsilon_3 < 0$). The third-order Chebyshev coefficients may also be calculated from the third-order Fourier coefficients,

$$e_3 = -|G_3^*| \cos \delta_3 \tag{4}$$

and

$$\upsilon_3 = \frac{|G_3^*|}{\omega} \sin \delta_3, \tag{5}$$

where δ_3 is the initial value of the third-order harmonic contribution and varies between 0 and 2π. These coefficients give a physical interpretation to the Fourier coefficients (Ewoldt et al. 2008).

Ewoldt et al. (2008) also developed a new interpretation of viscoelastic moduli in the nonlinear region. Previously, it was not possible to calculate storage or loss moduli in the nonlinear region, as the assumptions for the equations were violated, and the results had no physical meaning (Steffe 1996, Hyun et al. 2002, Cho et al. 2005). Many of the studies using LAOS to investigate the nonlinear region attempted to develop a method to extend the validity of the calculations for stress and shear rate used in the linear region to the nonlinear region rather than develop new interpretations of the data. However, Ewoldt et al. (2008) were able to derive viscous and elastic behavior from the first- and third-order Chebyshev coefficients. The elastic modulus was broken down into a minimum strain modulus, G'_M (the tangent modulus measured at zero strain), and large strain modulus, G''_L (the secant modulus measured at maximum strain), that took higher harmonic contributions into account. These two moduli may be seen in a Lissajous plot of shear stress versus applied strain (**Figure 1**). The dynamic viscosity was broken down into the instantaneous viscosity at minimum shear rate, η'_M, and the instantaneous viscosity at maximum shear rate, η'_L. As with the newly defined elastic moduli, the instantaneous viscosities took higher harmonic contributions into account. These instantaneous viscosities may be seen in a Lissajous plot of shear stress versus applied strain rate (**Figure 1**). The elastic moduli and instantaneous viscosities were used to calculate the strain-hardening and shear-thickening ratios, respectively (Ewoldt et al. 2008). Ewoldt et al. (2008, 2009) used this method to determine the properties of gastropod pedal mucus, a 0.2% xanthan gum solution, and cetylpyridinium chloride and sodium salicylate in brine. The method may also be used for food and pharmaceutical products, yielding valuable information about nonlinear rheological behavior. LAOS testing has been used in many studies on suspension and polymer behavior (Debbaut & Burhin 2002, Joshi 2005, Narumi et al. 2005, Hyun et al. 2006, Sugimoto et al. 2006, Grosso & Maffettone 2007, Ravindranath & Wang 2008) to examine rheological behavior of various solutions exposed to large deformations. A few studies have examined food ingredients, including oil in water emulsions (Knudsen et al.

2008), gluten gels (Ng & McKinley 2008), fish protein isolate gels (Brenner et al. 2009), skim milk gels (Knudsen et al. 2006), and hydrocolloid solutions (Song et al. 2006, Klein et al. 2008). This technique shows great potential for application in the food industry: most food processing as well as oral processing occurs in a region well outside the LVR and a general means to characterize food behavior in such processes is not currently in use.

RHEOLOGY COUPLED WITH OTHER MEASUREMENT TECHNIQUES

Over the past decade, there has been growing interest in using rheology coupled with various other techniques such as microscopy, ultrasound, and magnetic resonance. These techniques allow for the observation of material structure on both a macroscopic and microscopic level (Nicolas et al. 2003b, Squires & Brady 2005), as well as material behavior under process conditions (Nicolas et al. 2003b, Barnes et al. 2006, Wiklund et al. 2007). Combining rheology with other measurement methods allows limitations of traditional shear rheometry, such as the need for relatively large sample sizes (Squires & Brady 2005, Cicuta & Donald 2007), sample disruption (Barnes et al. 2006), limitations on stress and frequency ranges tested (Cicuta & Donald 2007), and inability to precisely replicate process conditions (Wiklund et al. 2007).

Many of the methods that couple rheological techniques with other measurement techniques fall under the definition of microrheology (Nicolas et al. 2003b, Cicuta & Donald 2007). The term microrheology has several definitions, although the general definition is a method that links local properties to bulk rheological behavior (Nicolas et al. 2003b, Mizuno et al. 2008, Kimura 2009). Microrheology may also be defined as rheology from mutual interactions of microparticles or rheology using microliter sample sizes (Nicolas et al. 2003b, Mizuno et al. 2008). Rheology coupled with nuclear magnetic resonance (NMR) (Nicolas et al. 2003b), magnetic resonance imaging (MRI), confocal scanning laser microscopy (CSLM) (Nicolas et al. 2003b, Filip et al. 2006), atomic force microscopy (AFM) (Filip et al. 2006), and diffusing wave spectroscopy (DWS) (Harden & Viasnoff 2001) are all examples of microrheological techniques and are discussed further in the next sections.

Nuclear magnetic resonance (NMR): a spectroscopy technique that uses the spin properties of certain nuclei to determine the sample composition

Magnetic resonance imaging (MRI): a technique that uses multiple nuclear magnetic resonance images to create a three-dimensional map of the sample

Confocal scanning laser microscopy (CSLM): a microscopy technique that uses a scanning laser to create a three-dimensional image of the sample

Atomic force microscopy (AFM): a microscopy technique that uses a tip attached to a cantilever to scan and create a contour map of the sample surface

Diffusing wave spectroscopy (DWS): a spectroscopy technique that correlates the light scattering pattern to sample properties

Rheology and Ultrasound

Ultrasound is defined as mechanical wavelengths ranging from 0.001 to 1.0 mm in length. The methodology for using ultrasound to measure the rheological properties of materials was developed in the late 1990s (Ouriev et al. 2000) and has become widely used for characterizing rheological properties of foods during the past decade. Ultrasound has been used to characterize many different foods, including carrageenan gels (Wang et al. 2005), protein gels (Wang et al. 2007), dairy products (Dukhin et al. 2005, Eskelinen et al. 2007), chocolate (Ouriev et al. 2004), cake batter (Gómez et al. 2008), flour doughs (Ross et al. 2004, Garcia-Alvarez et al. 2006, Álava et al. 2007), honey (Kulmyrzaev & McClements 2000), tomato concentrate (Choi et al. 2006), and tofu (Ting et al. 2009). Ultrasound may be used to measure the rheological properties of either stationary samples or fluids flowing in a pipe. Both methodologies use frequencies ranging from 1 to 100 Hz (Ouriev et al. 2000, Dukhin et al. 2005).

The methodology of ultrasonic measurements in a stationary sample involves two transducers placed on either side of a sample chamber containing the material to be measured (**Figure 2**). One transducer (T_1) converts an input electrical impulse into a sonic pulse at a preset frequency and directs the pulse at the sample. The sound waves travel through the sample and are detected by the second transducer. The second transducer (T_2) converts the waves back to an electrical impulse and sends the electrical pulse to a computer for comparison to the input pulse for signal

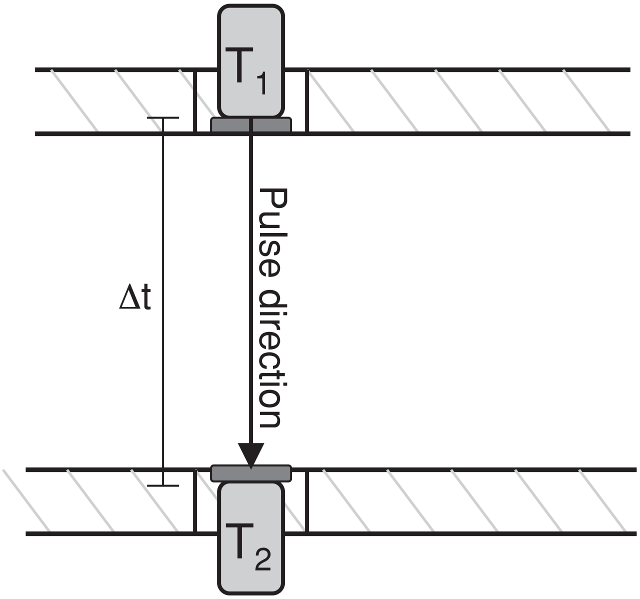

Figure 2

Two-transducer ultrasound instrumentation setup for static sample.

loss due to attenuation and time delay (Dukhin et al. 2005). Various properties of the material, such as storage and loss modulus, and size of suspended particles, can then be calculated from the velocity and time data (Dukhin et al. 2005). A second method using ultrasound to calculate shear properties of materials was developed by Kulmyrzaev & McClements (2000). This method uses an ultrasonic shear transducer with a delay line. The transducer fires an ultrasonic pulse along the delay line at the sample interface, which reflects the pulse, and the same transducer detects the reflected pulse. The phase and magnitude as a function of frequency are then analyzed by Fourier transform. Complex shear modulus, phase angle, and dynamic viscosity may be calculated from the Fourier transform of the data (Kulmyrzaev & McClements 2000). Ting et al. (2009) used a similar method to examine changes in viscoelasticity of tofu during gelation.

Although static measurements of materials using ultrasound yield valuable rheological information, there are several disadvantages to this method. Measurement rate is slow and generally provides data at a single shear rate (Dogan et al. 2005, Pfund et al. 2006, Wiklund et al. 2007). It is also difficult to properly replicate process conditions in a laboratory (Dogan et al. 2005, Wiklund et al. 2007), so the properties or the velocity profiles of the material measured in the lab may not be the same as those of the material in the process (Dogan et al. 2005, Young et al. 2008). In addition, calculating rheological properties from available process information (temperature, pressure, etc.) is extremely difficult (Ouriev et al. 2004). Therefore, it is necessary to measure rheological properties of the material during processing using an in-line technique. Many studies have been done over the past decade to develop such techniques that utilize ultrasound (Ouriev et al. 2000, Ouriev & Windhab 2002, Dogan et al. 2005, Wiklund et al. 2007).

Techniques using ultrasound to measure properties of fluids flowing in a pipe take advantage of the Doppler effect (Ouriev et al. 2000, Ouriev & Windhab 2002). A transducer is mounted at a set angle of inclination in a flow adapter cell in the pipe in which measurements will be taken (**Figure 3*a***). The transducer fires short pulses of ultrasonic waves into the fluid as it flows through the pipe. The pulses are separated by a set time period. The waves are reflected by the fluid

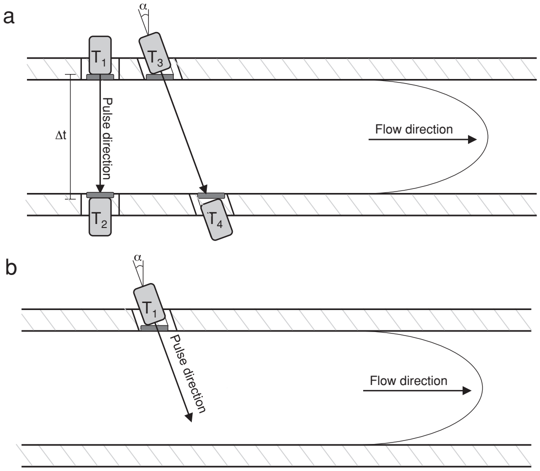

Figure 3

(*a*) Two pair transducer ultrasound instrumentation setup used for pipe flow. (*b*) Single transducer ultrasound instrumentation setup used for pipe flow.

and received either by the same transmitter, which is switched into receiving mode when not transmitting ultrasonic pulses, or a second transducer in receiving mode (Young et al. 2008, Wiklund et al. 2007). The returned pulses are shifted slightly in frequency owing to the Doppler effect (Wiklund et al. 2007). A Fourier transform of the received waves may be used to calculate the Doppler shift frequency spectrum at each radial position in the pipe (Dogan et al. 2005). Frequency shift and time interval between transmitted and received pulses are then used to calculate the velocity profile of the fluid (Wiklund et al. 2007). Wiklund et al. (2007) developed algorithms using fast Fourier transforms to improve the signal-to-noise ratio for estimating velocity profiles.

A second method of measuring properties of flowing fluids using ultrasound involves two pairs of transducers (**Figure 3*b***), one pair (T_1 and T_2) set perpendicular to the pipe wall and a second pair (T_3 and T_4) set at an angle (α) to the pipe wall. The first pair of transducers is used to measure the velocity of the fluid from time-of-flight measurements. The second pair of transducers is used to determine the velocity profile of the fluid. This setup allows simultaneous measurement of acoustic properties of the fluid and the flow profile of the fluid (Wiklund & Stading 2006).

Velocity profile measurements derived from the ultrasonic measurements are often combined with measurements of pressure drop in the fluid, resulting in a technique known as ultrasonic pulsed echo Doppler-pressure difference (UVP-PD) (Ouriev & Windhab 2002). UVP-PD may be used to measure flow profiles, viscosity over a range of shear rates, wall slip behavior, yield stress behavior, volumetric flow rate (Ouriev & Windhab 2002), and physical changes in process material (Ouriev et al. 2004, Dogan et al. 2005, Wiklund & Stading 2006).

Ultrasound may be used to measure various properties of foods such as gelling behavior (Wang et al. 2005, 2007; Ting et al. 2009), fat content (Dukhin et al. 2005), particle size (Dukhin et al. 2005), molecular relaxation (Wang et al. 2007), shear properties (Kulmyrzaev & McClements 2000, Dukhin et al. 2005, Ting et al. 2009), and viscosity (Wang et al. 2007). Ultrasound has also been used for quality control (Álava et al. 2007, Eskelinen et al. 2007). Advantages of ultrasound include nondestructive measurement of samples (Dukhin & Goetz 2002, Eskelinen et al. 2007), precise and rapid measurements (Dukhin & Goetz 2002, Eskelinen et al. 2007), propagation of waves through opaque materials and pipe walls (Ouriev & Windhab 2002), relatively low cost compared to other imaging techniques (Dogan et al. 2005, Eskelinen et al. 2007), and ability to characterize volumetric viscosity (Dukhin & Goetz 2002). However, the sensitivity and accuracy of ultrasound measurements depend upon the penetration depth of the sound waves. Too small a penetration depth decreases the signal-to-noise ratio of the measurements, decreasing measurement accuracy (Eskelinen et al. 2007). Penetration depth depends on the food and is highly frequency dependent (Dukhin et al. 2005). In addition, air bubbles in the sample can increase attenuation at low frequencies (Dukhin et al. 2005). Measurement sensitivity of in-line Doppler measurements is dependent on the spatial resolution of the ultrasound measurements, which is impacted by pulse width, beam width, and demodulation filter bandwidth (Pfund et al. 2006). Finally, velocity measurements are very temperature sensitive, requiring temperature control to 0.1°C for accurate measurement (Dukhin et al. 2005).

Rheology and Nuclear Magnetic Resonance

NMR, an analytical technique traditionally used to determine material components and molecular structure, has been used in food science since the 1970s to study the structure and dynamics of solid systems (Bertocchi & Paci 2008, Mariette 2009). Because NMR can differentiate between different structural orientations and arrangements, it is commonly used as a fingerprinting method for various foods and food components, such as carbohydrate, proteins, and lipids (Bertocchi & Paci 2008). Over the last decade, the use of NMR in food science has begun to shift from a fingerprinting tool to a rheological tool. Several advances in NMR technology have allowed rheological properties to be determined from NMR output. In particular, NMR velocity profiling, diffusometry, and relaxometry have been particularly useful in determining rheological properties of foods (Thybo et al. 2004, Callaghan 2006). NMR velocity profiling involves the use of MRI (Götz et al. 2001, Barnes et al. 2006, Callaghan 2006) and will be discussed in the next section.

NMR diffusometry examines the translational motion of molecules and particles (Nydén & Holmberg 2009) and has been widely used in the investigation of colloidal and emulsion behavior (Hollingsworth & Johns 2004, Gabriele et al. 2009, Nydén & Holmberg 2009, Voda & van Duynhoven 2009). Pulsed field gradient (PFG) NMR (**Figure 4**) is the most common type of NMR method used in this type of study, as it is most capable of quantitatively measuring droplet size distribution (Voda & van Duynhoven 2009). Knowing the droplet size distribution is critical to understanding emulsion rheology and functionality (Johns & Hollingsworth 2007, Johns 2009, Voda & van Duynhoven 2009). In PFG NMR, the sample is placed in a chamber surrounded by a radio frequency (RF) coil. Two sweep coils are located on either side of the sample. A transmitter fires two gradient pulses of the same magnitude and duration through the RF coil into the sample. Because PFG NMR works on the basis of spin echo, a 180° pulse is fired into the sample between the two gradient pulses. The first gradient pulse dephases proton precession frequency, whereas the second gradient pulse rephrases the frequencies. Particle diffusion causes a phase shift in proton frequency, leading to signal loss in the second pulse (Johns 2009, Voda & van Duynhoven 2009). The self-diffusion coefficient may be calculated from the phase shift and the gradient pulse parameters (Johns 2009). Droplet size distribution may also be calculated, as the phase shift is a distribution rather than a single value (Johns & Hollingsworth 2007, Voda & van Duynhoven 2009). This technique has been used by many researchers to study the behavior of various food and pharmaceutical colloids and emulsions (Hollingsworth & Johns 2004, Johns & Hollingsworth 2007, Gabriele et al. 2009, Johns 2009, Nydén & Holmberg 2009, Voda & van Duynhoven 2009), as well as gelatin (Brand et al. 2006).

NMR offers several advantages over other techniques used to study emulsions. Being noninvasive, it may be used for opaque emulsions, emulsions contaminated with gas or suspended solids, and highly concentrated emulsions (Gabriele et al. 2009, Johns 2009). NMR also allows the

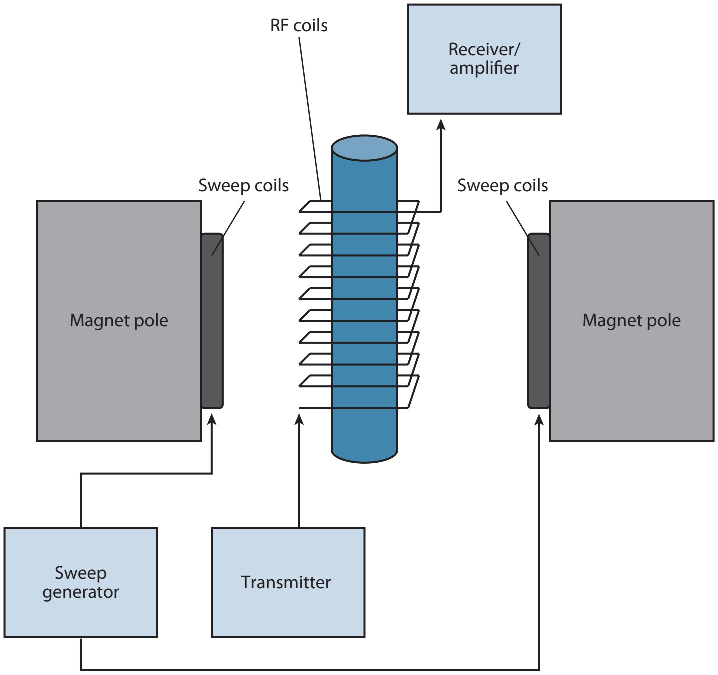

Figure 4

Nuclear magnetic resonance instrumentation setup.

identification and analysis of the behavior of each component in the sample from a single measurement (Occhipinti & Griffiths 2008). However, the sensitivity of NMR in this application is limited by the restricted molecular diffusion. A rule of thumb given by Johns (2009) for sufficient sensitivity is that the mean molecular diffusion length should be approximately equivalent to the droplet radius. Sensitivity is also limited by the instrument: Benchtop NMR instruments usually have relatively low magnetic field homogeneity and strength. The lower-quality magnetic field results in decreased measurement sensitivity reproducibility. However, recent technological advances, as discussed by Voda & van Duynhoven (2009), have been shown to improve measurement sensitivity. In addition, the sample must contain a spin-active nucleus (Occhipinti & Griffiths 2008). Hydrogen (^{1}H) is typically used when studying foods because it is the most sensitive probe for water (Zhou & Li 2007), which is generally present in large quantities in food products.

NMR relaxometry measures the spin-lattice and the spin-spin relaxation of particles in a material. Spin-lattice relaxation refers to the interaction of a spin and the environment, whereas spin-spin relaxation refers to the mobility of interacting spins (Baranowska et al. 2008). In relaxation, energy is exchanged between a spin and the environment (spin-lattice) and among spins (spin-spin) (Kim et al. 2008) to bring the material to an equilibrium state. It is possible to relate the spin-lattice and the spin-spin relaxation of a particle to the molecule containing the particle (Ahmad et al. 2005, Callaghan 2006, Baranowska et al. 2008). In food systems, the most common spin-active molecule used in this technique is ^{1}H. By measuring the spin-lattice and spin-spin relaxation time of a food component such as water, it is possible to determine the mobility of water in the food. It is also possible to determine the mobility of components (polymers, etc.) in the water by examining the chemical exchange of ^{1}H between the water and the second component (Ahmad et al. 2005). This information may be used to determine phase behavior, such as the transition from liquid to solid state (Goh et al. 2009). For these reasons, NMR relaxometry has been used to examine gelling behavior of egg white protein (Goh et al. 2009), fish proteins (Ahmed et al. 2005), gelatin (Zandi et al. 2007), starches (Karim et al. 2007), various hydrocolloids (Baranowska et al. 2008), and pectins (Dobies et al. 2008). Additionally, it has been used to study the gelatinization behavior of starch (Dona et al. 2007, Ritota et al. 2008), dough behavior (Assifaoui et al. 2006a,b; Lopez-da-Silva et al. 2007), addition of starch to imitation cheeses (Noronha et al. 2008), fat content and crystallization (Mariette 2009), and melting behavior of sugar solutions with added hydrocolloids (Herrera et al. 2007). Many of these studies showed good correlation between traditional rheometry and NMR data.

Rheology and Magnetic Resonance Imaging

MRI, an analytical technique that forms images from NMR data, is generally associated with the medical field as a diagnostic tool, but it can be used for many other purposes. Recently, it has been used to measure many different parameters in many branches of science (d'Avila et al. 2005, Bonn et al. 2008), including food science and rheology. An MRI apparatus generally consists of three parts: a magnet, an RF coil, and gradient coils (**Figure 5**). The magnet creates a constant, homogenous magnetic field in the sample, and the RF coil both sends out and detects pulses in the sample (d'Avila et al. 2005, Bonn et al. 2008). The gradient coils detect motion in the sample, allowing the motion to be resolved spatially (Deka et al. 2006, Bonn et al. 2008). This spatial resolution allows parameters such as proton density, spin-lattice relaxation, spin-spin relaxation, and diffusion properties, as well as a general profile of the sample, to be mapped (Thybo et al.

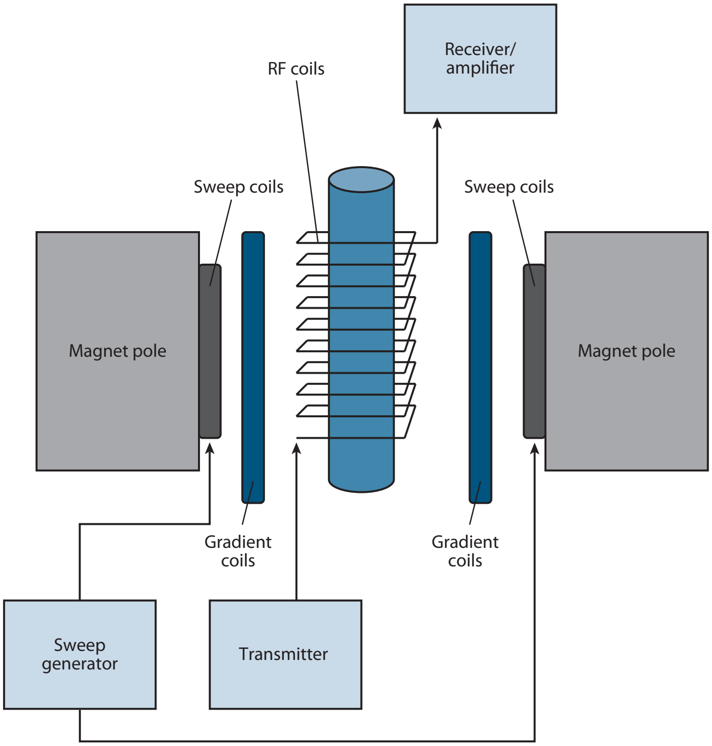

Figure 5

Magnetic resonance imaging instrumentation setup.

2004). A sequence of these mapped parameters over time yields valuable information on material behavior, e.g., the interaction of water with other compounds in the sample and the relative amounts of water and lipid present (Thybo et al. 2004). Studies examining foams (Stevenson et al. 2007), emulsions (Johns & Hollingsworth 2007), oil migration in confectionary products (Deka et al. 2006), pasta drying (Xing et al. 2007), structural changes in bread during baking (Wagner et al. 2008), changes in foods during storage (Zhou & Li 2007, Lodi et al. 2007), and gelation of meat systems (Herrero et al. 2009) have taken advantage of this ability, revealing new insights on these food processes. MRI has advantages and disadvantages similar to NMR: It is a nondestructive technique that can be used on opaque samples (Uludag et al. 2001, d'Avila et al. 2005, Elkins & Alley 2007), but its sensitivity is limited by the strength and homogeneity of the magnetic field (Metz & Mäder 2008).

Rheo-NMR: the use of MRI to map a material's velocity profile, allowing calculation of flow properties

One novel application of MRI that is of particular interest in rheology is MRI velocity profiling, also called rheo-NMR. This has been done in both a cup and bob apparatus and in pipe flow. The principle for either experiment remains the same. The velocity of the material in the apparatus is measured by using the time-of-flight, spin-tagging, or phase-shift method (Bonn et al. 2008), with time-of flight and phase-shift being the most common methods (Uludag et al. 2001, d'Avila et al. 2005). The time-of-flight method is the oldest method of velocity measurement and tracks the NMR excitation of a predetermined part of the sample. The displacement of that part of the sample is tracked over time, allowing calculation of the velocity. This technique is relatively simple to perform and gives accurate results at steady-state flow but cannot be used for multidirectional flow and is not sensitive enough to measure low velocities (less than 1 mm s^{-1}) (d'Avila et al. 2005). The spin-tagging method is similar to this method but looks at the magnetic pattern over the whole sample, allowing flow in the entire sample to be mapped (Bonn et al. 2008). The phase-shift method is more accurate than time-of-flight and spin-tagging. This technique maps the NMR signal in the sample and compares the measured phase of each pixel with the phase of that pixel in a flow-compensated reference map (Bonn et al. 2008).

Determination of the velocity profile of the material allows the calculation of flow properties such as viscosity (Uludag et al. 2001), yield stress behavior during flow (Raynaud et al. 2002, Barnes et al. 2006), thixotropic behavior (Raynaud et al. 2002), and shear stress and shear rate (Bonn et al. 2008). MRI velocity profiling can also be used to study complex flow (Elkins & Alley 2007, Bonn et al. 2008), shear banding phenomena (Callaghan 2006, Bonn et al. 2008), wall slip (Cullen et al. 2000, Yoon & McCarthy 2002), and crystallization behavior (Mazzanti et al. 2008). Because most foods are complex, viscoelastic, non-Newtonian, or a combination thereof, this technique is highly useful in studying flow behavior of foods, although few foods have been studied in this manner. Foods studied in a Coutette-type apparatus using MRI velocity imaging include lipids (Mazzanti et al. 2008) and food emulsions (Hollingsworth & Johns 2004, d'Avila et al. 2005, Gabriele et al. 2009). MRI velocity profiling data had similar results to traditional rheometry data (Hollingsworth & Johns 2004, Gabriele et al. 2009). MRI velocity imaging of foods has also been studied in pipe flow of hydrocolloids (Goloshevsky et al. 2005), yogurt (Yoon & McCarthy 2002, Henningsson et al. 2006), and biscuit dough (Barnes et al. 2006).

Advantages of MRI velocity imaging include the ability to measure opaque materials and to measure velocity without the need for flow markers or optical access, as well as noninvasive measurements (Cullen et al. 2000, Götz et al. 2001, Barnes et al. 2006, Elkins & Alley 2007). It also has the ability to measure materials during processing, yielding valuable information on food behavior under processing conditions (Uludag et al. 2001, Barnes et al. 2006). Disadvantages include possible image blurring at high velocities, the need for large sample sizes with time-of-flight methods to improve signal strength (Callaghan 2006), and the inability to use the Couette cell with certain materials such as pastes (Götz et al. 2001). However, these disadvantages are

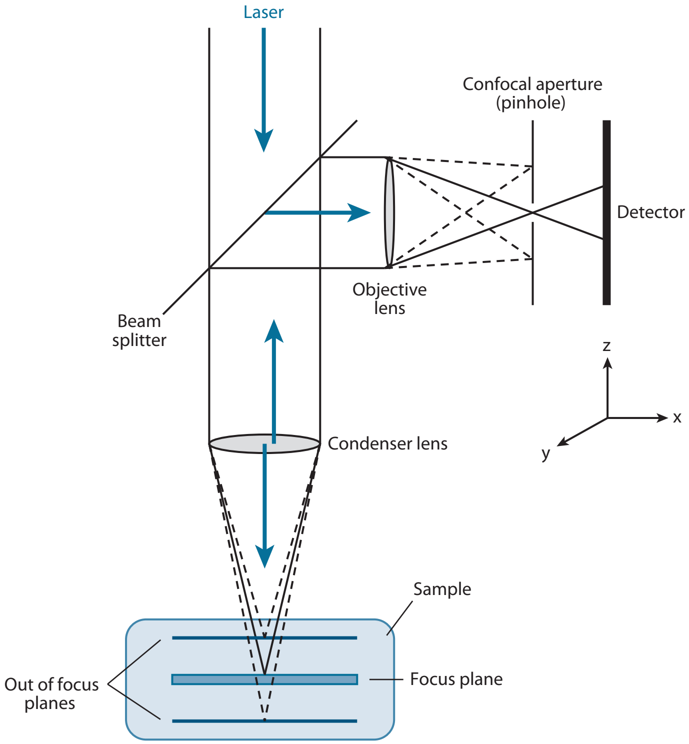

Figure 6

Confocal scanning laser microscopy instrumentation setup.

mitigated by several recent advances, such as rapid imaging techniques (Sederman et al. 2003, 2004; Callaghan 2006) and the use of Fourier transforms (Callaghan 2006).

Rheology and Confocal Scanning Laser Microscopy

CSLM has been used to investigate the microstructure of foods since the 1980s. CSLM works on the same principle as confocal microscopy (**Figure 6**). A point light source (a laser) is shone through an objective lens, which focuses the beam at a certain depth on a very small region of the sample. The optical system focuses the reflected, scattered, or fluoresced light from the sample at that point through a pinhole in front of a detector. The pinhole is situated in such a manner that only the light backscattered from the laser is in focus, enabling it to pass through, yielding one image point. Confocal scanning laser microscopes are able to scan along the *x* and *y* axes (perpendicular to the direction of the beam), forming a two-dimensional image of the sample at the focal depth. Scanning along the *z*-axis (parallel to the direction of the beam) forms a stack of two-dimensional images, allowing a three-dimensional image to be constructed (Branzan et al. 2007).

Advantages of using CSLM for imaging include viewing of several different compounds at one time by use of different stains (Nicolas et al. 2003b, Puppo et al. 2008), ability of three-dimensional imaging (Nicolas et al. 2003b), no image blurring (Nicolas et al. 2003b, Nicolas & Paques 2003), and relatively little sample preparation as compared to other microscopy techniques (Nagano et al. 2008, Guggisberg et al. 2009). CSLM has the disadvantage of the penetration depth of the beam ranging only from a few micrometers to a few millimeters. In addition, the optical spatial resolution is limited to the submicron level, the penetration depth is a property of the sample examined (Nicolas et al. 2003b), the acquisition rate of points is inversely proportional to the desired spatial resolution (Nicolas et al. 2003b, Nicolas & Paques 2003), and the images collected may become distorted under dynamic conditions (Ko & Gunasekaran 2007). However, recent developments in high-speed cameras have enabled collection of images with resolution in the millisecond range (Kimura 2009), and various algorithms have been developed to mitigate several errors in CSLM image collection and assembly (Ko & Gunasekaran 2007).

It is not often possible to validate a hypothesis about material behavior from rheological data alone. By using CSLM to view the microstrucure of foods, the rheological properties of the food under different conditions may be investigated in an in-depth manner. Over the past decade, CSLM has been used in conjunction with various rheological tests to investigate the properties of emulsions (Puppo et al. 2008), hydrocolloid gels (Nunes et al. 2006, Nagano et al. 2008, Savary et al. 2008, Firoozmand et al. 2009), dairy proteins (Dubert-Ferrandon et al. 2006, Bertrand & Turgeon 2007, Lutz et al. 2009, Ye & Hewitt 2009), yogurt (Guggisberg et al. 2009), starches (Noisuwan et al. 2008, Vallons & Aredt 2009), bread dough (Mariotti et al. 2009), meat products (Chattong et al. 2007), and bread (Renzetti & Arendt 2009, Renzetti et al. 2008). In general, the CSLM images in these studies supported and provided insights into rheological data. Common uses of CSLM in conjunction with rheology include determination of starch gelatinization behavior and gels under various conditions.

Recently, CSLM and rheology have been used to examine the properties of more specialized products, such as gluten-free dough and bread structure (Mariotti et al. 2009, Renzetti & Arendt 2009, Renzetti et al. 2008). There has also been some study on using CSLM and rheology in the nonlinear region using colloidal probes that were pulled through the sample with an optical tweezer, or a focused laser beam used to move particles via optical gradient forces (Dufresne & Grier 1998). The theory used ignored hydrodynamic interactions, so could only be used for shear-thinning fluids in dilute solutions. It was suggested that the addition of hydrodynamic effects would allow the method to be used for shear-thickening fluids as well (Squires & Brady 2005). Suggested further work included the use of multiple probes and the investigation of microstructural deformations in nonequilibrium conditions (Squires & Brady 2005). Another study by Nicolas & Paques (2003) used CSLM and rheology to study fish protein gels in compression. Nicolas & Paques (2003) noted that these techniques were useful for studying behavior of food structure during oral processing and manufacturing conditions.

Rheology and Atomic Force Microscopy

A second microscopy technique recently coupled with rheology is AFM. AFM enables study of both individual molecules and the interaction between molecules, such as network formation and aggregation (Funami et al. 2009), as well as film surface topography (Bonaccurso et al. 2008, Handojo et al. 2009). This technique enables a relationship between physical, chemical, and structural behavior to be formed (Noda et al. 2008). AFM provides a high-resolution image of the sample surface by scanning it with a pointed tip attached to a cantilever (**Figure 7**) (Bonaccurso et al. 2008, Handojo et al. 2009).

The sample is scanned in the x, y, and z directions. Depending on the instrumentation used, the sample may be placed on a platform that shifts the sample in the x, y, and z directions as it is scanned by a stationary cantilever (**Figure 7*a***), or the cantilever may be moved in the x, y, and z directions as it scans a stationary sample (**Figure 7*b***). There are two main operational modes in which AFM may be used: contact mode and tapping mode (Handojo et al. 2009). Contact mode is sometimes called scratching mode (Handojo et al. 2009). In this mode, the tip is in continuous contact with the sample surface, and the force placed on the sample by the tip may be changed by adjusting the cantilever parameters. As the sample is scanned in the x and y directions, the deflection of the

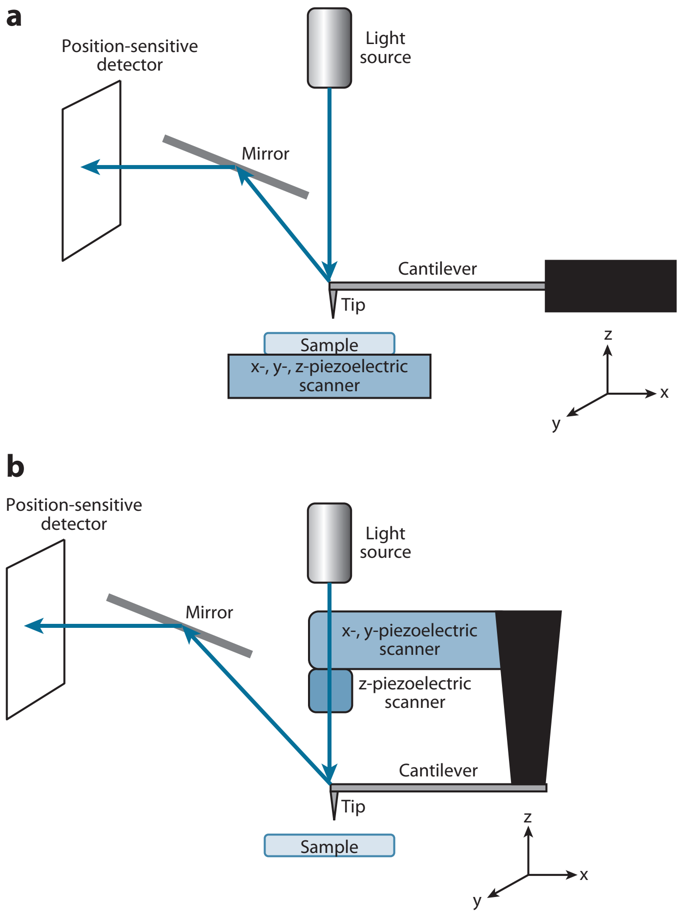

Figure 7

(*a*) Atomic force microscopy (AFM) instrumentation setup for a moving sample. (*b*) AFM instrumentation setup for a stationary sample.

cantilever in the z direction indicates the force between the tip and the sample. Plotting cantilever deflection versus tip position on the sample creates a topographic image of the sample surface (Bonaccurso et al. 2008). However, this method may damage the sample or tip when large loading forces are applied (Sahin et al. 2007). Because of this potential issue, tapping mode, which is much less likely to cause tip or sample damage, is generally used. In tapping mode, the cantilever vibrates at its resonance frequency as it is brought in contact with the sample. Contact with the sample changes the phase and amplitude with which the cantilever vibrates. Changes in the vibrations, used to create a topography map, are monitored by a feedback system (Sahin et al. 2007).

An issue with AFM in rheology is hydrodynamic drag on the cantilever due to friction between the tip and the sample, especially in soft samples (Alcaraz et al. 2002). This drag force may be estimated and taken into account during contact force measurement, although it is difficult to determine precisely and is often underestimated. A study by Alcaraz et al. (2002) investigated hydrodynamic drag in soft samples and developed correction factors for drag based on cantilever height, tip velocity, and oscillation frequency. Alcaraz et al. (2002) noted that drag force could be accurately estimated by the extrapolation of drag force data from measurements taken at varying heights above the sample, allowing an increase in scanning velocity and velocity range.

AFM may be used to examine heterogeneous samples, as it is able to differentiate between the length, diameter, and conformation of molecules in the sample. Because AFM scanning involves vertical movements of either the sample or the probe, the image generated also contains quantitative information on sample surface topography (Ikeda 2003). Other advantages of AFM include nanoscale resolution, small sample size requirements, little sample damage in preparation, ability to view molecular interactions (gel structures, aggregations, etc.), and ability to examine interfacial behavior (Sriamornsak et al. 2008, Funami et al. 2009). Although AFM is able to resolve individual molecules, it may not be able to resolve some subdomain structures. In these cases, spectroscopy is required for further study (Ikeda 2003). Furthermore, artifacts may be present in the sample after preparation of more fragile samples (Noda et al. 2008).

AFM is typically used in the study of surface structure and topography but can also be used to measure local viscoelasticity (Kimura 2009). AFM has been used in combinations with rheological techniques to examine various material properties such as gelling behavior under various conditions (Ikeda 2003; Funami et al. 2007, 2008, 2009; Noda et al. 2008), interfacial behavior (Patino et al. 2007, Gromer et al. 2009), behavior in aqueous solutions (Yang et al. 2008), and film behavior (León et al. 2009). Foods tested with this technique include hydrocolloid gels and solutions (Funami et al. 2008, 2009; Noda et al. 2008; Shimoni 2008; Yang et al. 2008; Gromer et al. 2009; León et al. 2009) and dairy proteins (Ikeda 2003, Shimoni 2008). As with CSLM, AFM has supported and provided insights into rheological data. A study by Boskovic et al. (2002) showed that AFM and AFM cantilevers may also be used to measure density and viscosity in liquids and gases, including turbid and opalescent samples. The method developed was also able to measure sample properties in situ (Boskovic et al. 2002).

One study by Filip et al. (2006) combined AFM and CSLM to study local rheological properties of gelled emulsions (**Figure 8**). Filip et al. (2006) showed that AFM was able to provide a

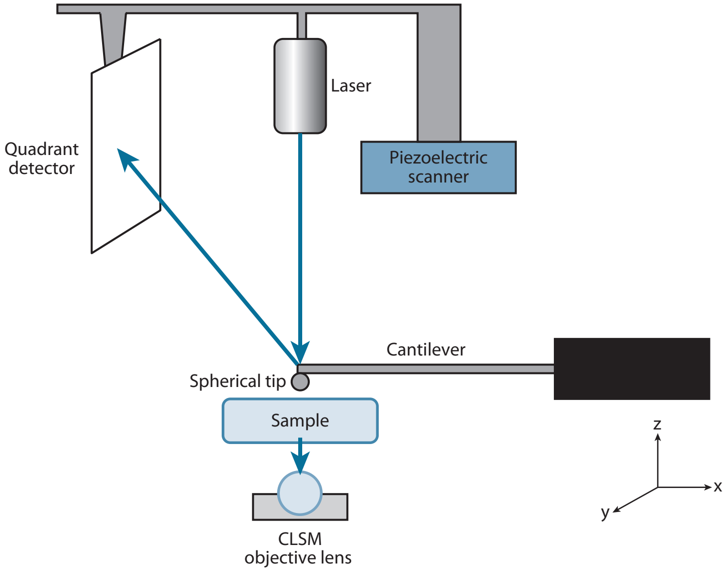

Figure 8

Combined atomic force microscopy–confocal scanning laser microscopy instrumentation setup.

mechanical fingerprint of the emulsion that gave information on stress relaxation, force hysteresis, and material stiffness, whereas CSLM showed how the emulsion was affected by the AFM probe. These measurements were taken simultaneously at several time points, allowing the effects of aging on the sample to be studied. It was found that the combined AFM-CSLM method was able to differentiate between elastic and plastic behavior of the sample and detail how the sample changed over time, as well as semiquantitatively provide surface deformation information. Filip et al. (2006) noted that multiple measurements on the same sample were possible, allowing more accurate measurements on materials that have behavior dependent on mechanical history. It should be noted, however, that the measurements of the AFM-CSLM technique were not directly relatable to traditional rheometry measurements. Samples with structures that are heterogeneous at length scales greater than that of the length of the AFM probe show different behavior based on where the sample is measured. These heterogeneous samples should either be measured with a larger probe (provided that the cantilever is able to operate properly with the larger probe) or be measured in several locations and the force curves averaged to give a general material response to the probe (Filip et al. 2006). Overall, this technique may be useful for the study of food emulsions, gels, and foams, but further work must be done to correlate the microrheological measurements to traditional rheometry measurements.

Rheology and Diffusing Wave Spectroscopy

DWS is a light-scattering technique with a frequency range of up to 1 MHz that uses particle movements to determine material viscoelastic properties (Nicolas et al. 2003a, Waigh 2005, Cicuta & Donald 2007, Kimura 2009). Unlike conventional light scattering techniques, which require transparent or nearly transparent samples, DWS requires highly turbid or opaque samples. When analyzing DWS data, the transmittance of light is considered to be a diffusion process, so it is necessary to use samples with strong multiple scattering, or with sufficient turbidity to provide a constant volume fraction and refractive index throughout the sample (Scheffold et al. 2004, Horne et al. 2005, Corredig & Alexander 2008). DWS has two operational modes: transmittance (forward scattering) and backscattering (**Figure 9**) (Corredig & Alexander 2008, Kimura 2009). The basic principle of DWS is as follows: A laser is shone through one side of the sample, resulting in an induced dipole moment in the particles. The light is scattered due to particle motion from resonance as a result of the dipole moment, causing fluctuations in light intensity. Photons from the laser that exit the sample strike a detector, which records the number and location of photons incident on its surface. Developing a correlation function for the pattern of photons on the detector allows the characteristics of the sample to be determined and examined (Corredig & Alexander 2008).

The main differences between transmittance and backscattering modes involve the placement of the detection system. In transmittance mode, the laser is shone into one side of the sample and the detector is placed on the opposite side. This mode requires a powerful laser, since the light intensity on the detection side of the sample must be sufficient for proper detection (Corredig & Alexander 2008). Backscattering mode, on the other hand, does not require as powerful a laser, since the laser and detection system are placed on the same side of the sample. However, data analysis in this mode is more difficult than in transmission mode due to the varying penetration depths of the detected photons (Corredig & Alexander 2008).

DWS may be used for opaque materials and is able to detect small changes in wavelength over short time periods (Cicuta & Donald 2007, Kimura 2009). It is also a nondestructive technique (Horne et al. 2005), requires very small sample volumes (Ubbink et al. 2008), and is sensitive to particle size changes (Hemar et al. 2004). In addition, DWS has been shown to correspond more

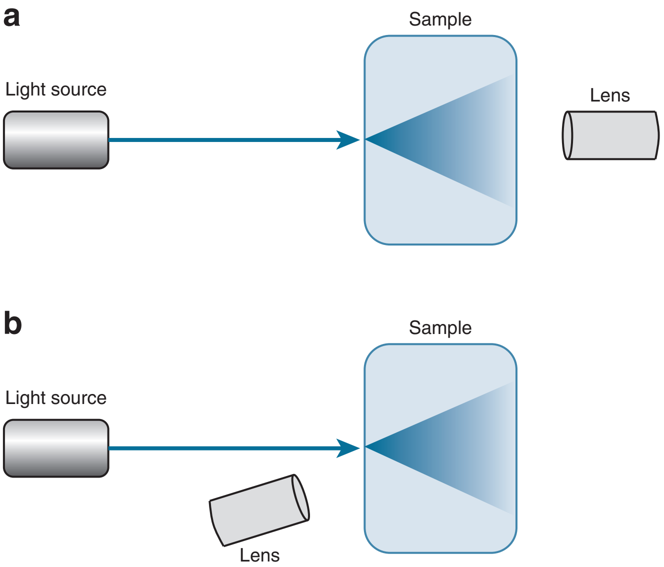

Figure 9

Diffusing wave sprectroscopy instrumentation setup in (*a*) forward scattering and (*b*) backscattering mode.

closely to traditional rheometry testing than other microscopy techniques (Ubbink et al. 2008). One major disadvantage of DWS is that samples need to be opaque or turbid, as the technique depends on multiple scattering events (Scheffold et al. 2004, Horne et al. 2005).

DWS has been used to study gelation of various substances (Cullen et al. 2000; Nicolas et al. 2003a,b; van der Linden et al. 2003; Hemar et al. 2004; Alexander & Dalgleish 2007; Corredig &

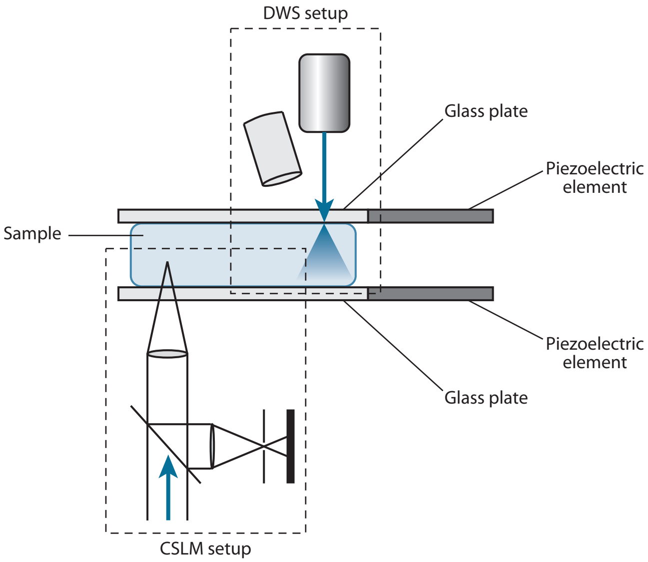

Figure 10

Combined diffusion wave spectroscopy–confocal scanning laser microscopy instrumentation setup.

Table 1 Comparison of rheological techniques

Method	Advantages	Disadvantages	Possible uses
Large amplitude oscillatory shear (LAOS)	Allows rheological properties outside of the linear viscoelastic region (LVR) to be determined	Not suitable for materials with shear-sensitive structure	Soft solids, viscous liquids, viscoelastic materials
	Gives physical meaning to storage and loss moduli calculated outside of the LVR	Computationally intensive	
	Accounts for higher oscillation harmonics		
Ultrasound	Nondestructive sample measurement	Velocity measurements are highly temperature dependent	Homogenous liquids and semisolid foods that are able to flow under measurement conditions
	Precise measurements	Slow measurement rate	
	May be used with opaque materials	Provides data at a single shear rate	
	Able to characterize volume viscosity	Measurement sensitivity depends on wave penetration depth (varies with food and frequency used)	
	Allows for measurement of rheological properties under process conditions	Inline measurements dependent on spatial resolution	
	Low cost imaging technique	Inline measurements require additional pressure drop measurements to calculate rheological properties	
Nulcear magnetic resonance (NMR)	Noninvasive technique	Measurement sensitivity limited by molecular diffusion	Gels and other foods with relatively few components
	May be used with opaque materials	Benchtop instruments have relatively low magnetic field strength and homogeneity	
	May be used with heterogeneous samples	Sample must contain a spin-active nucleus	
	Allows identification of multiple components with one measurement		
Magnetic resonance imaging (MRI)	Noninvasive technique	Benchtop instruments have relatively low magnetic field strength and homogeneity	Low-viscosity liquids, pumpable liquids, and semisolids
	May be used with opaque materials	Sample must contain a spin-active nucleus	
	May be used with heterogeneous samples	Possible image blurring at high velocities	
	Allows study of complex flow behavior	Large sample sizes required with time-of-flight methods	
	Enables velocity measurements without flow markers or optical access	Certain materials may not be used in a Couette cell	

(*Continued*)

Table 1 (*Continued*)

Method	Advantages	Disadvantages	Possible uses
	Allows for measurement of rheological properties under process conditions		
Confocal scanning laser spectroscopy (CSLM)	Several different compounds may be viewed at once by use of different stains	Beam penetration depth ranges from a few micrometers to a few millimeters	Foods with sensitive structures, foams, gels, semisolid, and solid foods
	Allows for three-dimensional imaging	Optical spatial resolution limited to the submicron level	
	No image blurring in static conditions	Penetration depth is a property of the sample examined	
	Relatively little sample preparation as compared to other microscopy techniques	Acquisition rate of points is inversely proportional to desired spatial resolution	
		Images may become distorted under dynamic conditions	
		Rheological measurements are not directly convertible to traditional measurements	
Atomic force microscopy (AFM)	Able to differentiate between length, diameter, and conformation of molecules in the sample	Hydrodynamic drag on the cantilever due to friction between the tip and the sample may affect measurements	Semisolid and solid foods
	Image generated contains quantitative information on sample surface	Certain subdomain structures are not resolvable	
	Nanoscale image resolution	Artifacts may be present in fragile samples	
	Small sample size requirements	Rheological measurements are not directly convertible to traditional measurements	
	Little sample damage in preparation		
	Allows observation of molecular interactions		
	Allows examination of interfacial behavior		
Diffusing wave spectroscopy (DWS)	May be used for opaque materials	Samples must be turbid or opaque	Semiopaque or opaque liquids, semisolids, and solids
	Able to detect small changes in wavelength over short time periods	Rheological measurements are not directly convertible to traditional measurements	
	Nondestructive technique		
	Small sample size requirements		
	Sensitive to particle size changes		
	Corresponds more closely to traditional rheometry testing than other microscopy techniques		

Alexander 2008), emulsion behavior (Blijdenstein et al. 2003; Nicolas et al. 2003a,b; Horne et al. 2005; Gancz et al. 2006; Alexander & Dalgleish 2007; Ruis et al. 2007; Corredig & Alexander 2008), and behavior of concentrated suspensions (Pinder et al. 2006). Other studies involving DWS and rheology include optical rheology at near-zero shear (Corredig & Alexander 2008) and the use of tracer particles to increase turbidity for solutions that do not have sufficient light-scattering properties (Alexander & Dalgleish 2007). Foods studied by DWS include milk and dairy proteins (Cullen et al. 2000; Nicolas et al. 2003a,b; Hemar et al. 2004; Alexander & Dalgleish 2007; Ruis et al. 2007) and various hydrocolloids (van der Linden et al. 2003, Gancz et al. 2006, Pinder et al. 2006, Corredig & Alexander 2008). The majority of the available studies focus on skim milk and milk-based systems, as they have properties ideal for study with DWS (Alexander & Dalgleish 2007). As with CSLM and AFM, DWS results have been generally in agreement with and provided insights into traditional rheological data. Several studies have remarked upon the versatility of DWS and its potential use in industry (Nicolas et al. 2003a,b; Hemar et al. 2004; Corredig & Alexander 2008).

Several studies have used DWS in combination with CSLM (**Figure 10**) to study structural changes in gels and emulsions under various conditions (Blijdenstein et al. 2003; Nicolas et al. 2003a,b; Corredig & Alexander 2008). This combined technique was able to determine network formation and strengthening, sample relaxation behavior, behavior during oscillatory shear (emulsion droplet mobility and network elasticity), surface properties, interfacial tension, and phase change behavior (Blijdenstein et al. 2003; Nicolas et al. 2003a,b; Corredig & Alexander 2008). Nicolas et al. (2003a,b) noted that this approach to studying rheological properties, and microrheology in general, was highly versatile, able to be used for both food and nonfood substances, and able to overcome the limitations of traditional rheological techniques. Microrheological techniques appear to have great potential for use in the food industry, provided that the data gathered from microrheological testing may be related to traditional rheometry results. However, more work remains to be done in the correlation of microrheology to traditional rheometry.

All of the techniques discussed in this paper have certain advantages and disadvantages, as well as applications to which they are suited. Advantages, disadvantages, and suggested applications are summarized in **Table 1**.

CONCLUSIONS

Novel rheological techniques have been developed to gain a deeper understanding of various properties of foods. Other techniques not usually associated with rheology, such as microscopy, magnetic resonance, and ultrasonics, have been coupled with traditional rheological measurements to provide valuable insight into material behavior. These coupled rheological techniques, particularly the microscopy techniques, have been used primarily on model food systems. It has been suggested that the use of these techniques be expanded to foods and food products, as the techniques may be used for an in-depth investigation of food behavior under various conditions. Additionally, many of the techniques discussed in this paper are novel to food science but not necessarily novel to rheology in general. The polymer industry in particular has developed a number of rheological techniques able to measure properties of materials that are viscoelastic, exhibit slip, undergo phase transitions during testing, or exhibit other phenomena that confound the measuring of rheological properties. The majority of these techniques may be adapted for measuring rheological properties of foods.

Over the past decade, the focus of rheological techniques has shifted from the macro scale to the micro scale, especially with the introduction of coupled rheological techniques. Microrheology is able to overcome several limitations of traditional shear rheology; however, microrheological measurements are not directly related to macrorheological measurements. Further study of microrheological measurements compared to macrorheological measurements is necessary to develop fundamental equations to relate the two sets of measurements. Developing these equations, however, will allow rheological behavior in materials and areas previously considered too difficult for accurate measurement to be explored, providing a deeper understanding of the rheological behavior of foods.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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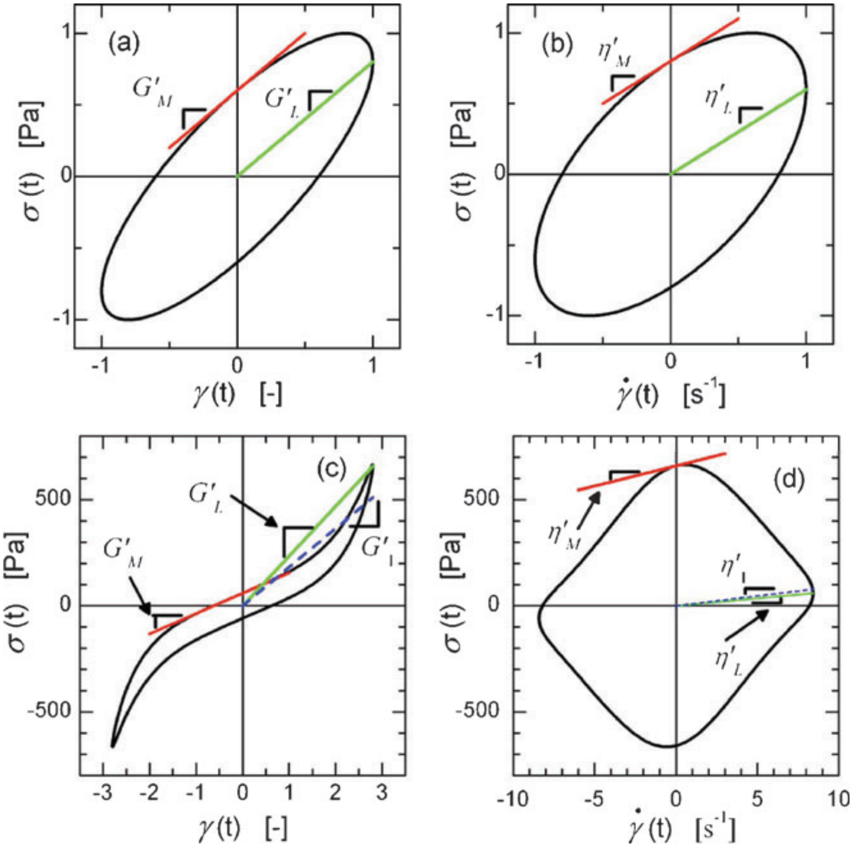

Figure 1

Lissajous plot showing minimum strain modulus (G'_M), large strain modulus (G'_L), instantaneous viscosity at minimum shear rate (η'_M), and instantaneous viscosity at maximum shear rate (η'_L). In *a* and *b*, elastic modulus and dynamic viscosity are shown, respectively, for a system under linear viscoelastic conditions, whereas *c* and *d* responses show elastic modulus and dynamic viscosity, respectively, for a system under nonlinear viscoelastic conditions. In *c* and *d*, the subscript "1" denotes the elastic modulus and dynamic viscosity, respectively, that is calculated based on the assumption that only the first harmonic contributes to these parameters.

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Errata

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