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Nonlinear viscoelasticity of cheese

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Abstract

Cheese viscoelasticity is commonly measured using steady uniaxial compression, steady uniaxial extension, shear and compressive creep, and stress relaxation in shear and compression. Viscoelastic properties for many cheeses have also been studied using small amplitude oscillatory shear (SAOS). However, there is little on the measurement of *nonlinear* viscoelastic properties. The large deformation test usually conducted on cheese to study nonlinear viscoelasticity is uniaxial compression, but this test hardly departs from linear behavior. In this work, the *nonlinear* viscoelasticity of four cheese varieties was studied using *large amplitude* oscillatory shear (LAOS). A sliding plate rheometer incorporating a shear stress transducer was used. The data were evaluated using spectral analysis, and results are presented mainly in the form of shear stress versus shear rate loops.

Keywords: Cheese; nonlinear viscoelasticity; oscillatory shear

1. Introduction

The rheological properties of dairy products have been studied for over half a century. Cheese is the most diverse group of dairy products, and considered to be the most academically interesting and challenging. Unlike many dairy products which are biologically, biochemically, and chemically stable, cheeses are biologically and biochemically dynamic, and consequently, inherently *unstable* (Fox, 1993). The process of cheesemaking is fascinating, both in itself and to rheologists, considering that a nearly Newtonian raw material (milk) produces such a diversity of mostly *viscoelastic* products. Up to 2000 cheese varieties have been

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developed, of which 700 have been described, with no two alike (Holsinger et al., 1995; Olson, 1995). Therefore, the rheology of each cheese variety is unique.

Rheological measurements on cheese using mechanical instruments are performed (1) for quality control by cheese makers and (2) for scientists to study cheese texture (Tunick and Nolan, 1992). The textural properties of cheese can be as important as flavor, and comprise a significant part of the total sensory score awarded by cheese graders (Farkye and Fox, 1990). For example, texture is a major determinant of quality in cheddar (Ma et al., 1996), followed by flavor and appearance. Therefore, an objective instrumental method of measuring cheese rheological properties would be valuable, especially when used in conjunction with its chemical properties. For example, the effects of pH on cheese during manufacturing and maturation are well recognized, and the most demonstrable effect of pH is to impart brittleness when pH falls below 5 in hard cheeses (Olson et al., 1996). Therefore, research into the origins of cheese texture is an important dairy science. The ultimate goal of cheese rheologists is to correlate the results of various instrumental tests to subjective evaluations by sensory panels and consumers (Tunick and Nolan, 1992).

The cheese varieties studied here were (1) natural mozzarella, (2) natural pizza cheese, (3) natural cheddar, and (4) process mozzarella. The effects of temperature, age, and fat content were evaluated, and comparisons were made to the Lodge rubberlike liquid theory to establish the amount of nonlinearity.

Mozzarella is a prominent member of the pasta filata, or stretched curd, cheese varieties that originated in Italy. Pasta filata cheeses are distinguished by their characteristic fibrous structure and melting and stretching properties. This unique fibrous structure is obtained by mixing and molding the cheese curd in hot water at a pH of approximately 5.2 using open discharge single screw extrusion. Mozzarella is primarily used as an ingredient in prepared foods such as pizza and lasagna. Pizza cheese is *unstretched* mozzarella. During manufacture, instead of processing the curd in hot water by the usual mixing and molding, the curd is steamed to a semi-plastic state and then pressed into blocks to produce what is called pizza cheese (Kindstedt, 1993). While mozzarella has a well defined fiber orientation, pizza cheese is isotropic. In our testing, mozzarella was sheared in the fiber orientation direction. Cheddar is a popular cheese variety, with most of its production concentrated in the former British colonies (Olson, 1995). It is used in many food products, such as burgers and sandwiches. Process cheese products are alternatives to natural cheeses produced directly from milk. They are produced by blending shredded natural cheeses differing in type and degree of maturity with emulsifying agents (primarily phosphates and citrates), and by heating the blend under partial vacuum with constant agitation until homogeneous (Caric and Kalab, 1993). Heat treatment destroys dangerous microorganisms and destroys any phosphates in cheese made from unpasteurized milk. Hence, a diversity of process cheese products can be made to satisfy consumer and food ingredient demands.

2. Theory

Consider the *simple shear* flow generated between two parallel plates with a constant gap (Fig. 1). One plate is fixed, while the other moves in its own plane subject to a force F acting in the plane. This deformation causes a change in shape without change in volume.

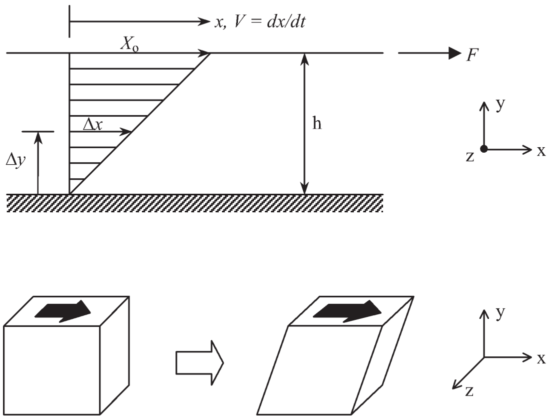

Fig. 1. Simple shear.

In oscillatory shear, the shear strain varies harmonically:

$$\gamma(t) = \gamma_o \sin 2\pi f_o t = \gamma_o \sin \omega t \tag{1}$$

and the shear rate is:

$$\dot{\gamma}(t) = \gamma_o \omega \cos \omega t = \dot{\gamma}_o \cos \omega t, \tag{2}$$

where γ_o is the shear strain amplitude, f_o is the Herzian frequency and ω is the angular frequency. By varying γ_o and ω independently, a wide range of test conditions can be attained, making oscillatory shear ideal for replicating various real life processes.

A useful diagram showing the regimes of behavior that can be exhibited at various combinations of strain amplitude and frequency is shown in Fig. 2. The shape of the shear stress versus shear rate (or shear strain) loops for the different regimes are also shown. Pipkin (1972) proposed a plot of strain amplitude (γ_o) versus frequency (ω) as a basis for such a diagram. Tanner (1985) later improved this to strain rate amplitude ($\dot{\gamma}_o$) versus ω and called it the Pipkin diagram.

In this work we use LAOS for our nonlinear characterization. LAOS is a shear flow, not an extensional flow. Hence, it cannot probe all aspects of the cheese's nonlinear behavior in extension.

2.1. *Linear viscoelasticity*

In the linear viscoelastic region, Boltzmann superposition can be used to show that the shear stress response to SAOS is also sinusoidal:

$$\tau(t) = \tau_o \sin(\omega t + \delta), \tag{3}$$

where τ_o is the shear stress amplitude and $\delta(\omega)$ is called the *mechanical loss angle*. Thus, linear properties are typically reported in terms of the storage and loss moduli:

$$G'(\omega) = G_d \cos \delta, \tag{4}$$

$$G''(\omega) = G_d \sin \delta. \tag{5}$$

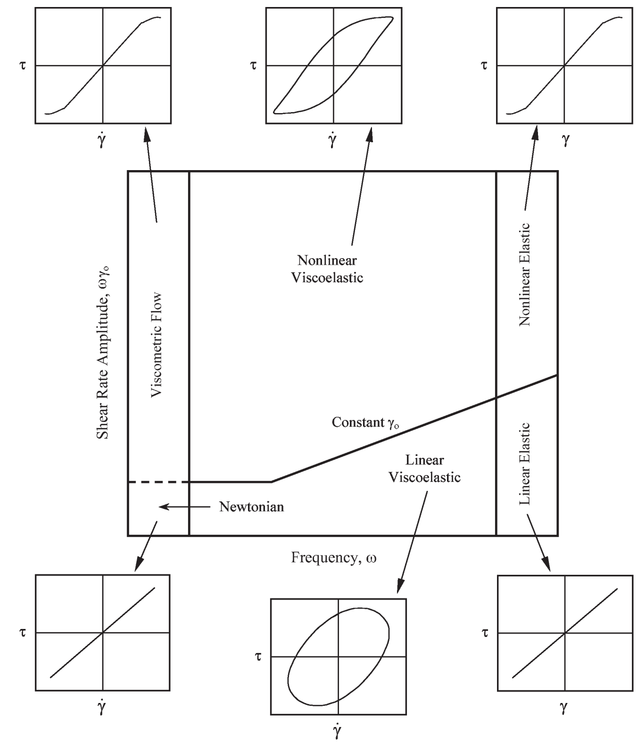

Fig. 2. Pipkin diagram showing shear stress versus shear rate (or versus shear strain) loops for the regimes in oscillatory shear.

G_d is the *dynamic modulus*, $G_\mathrm{d} \equiv \tau_\mathrm{o}/\gamma_\mathrm{o}$, and $G'(\omega)$ and $G''(\omega)$ are the in-phase and out-of-phase components of stress given by Eq. (3).

In oscillatory shear, the Lodge rubberlike liquid theory predicts a sinusoidal shear stress given by Eq. (3). It also predicts a *sinusoidal* first normal stress difference with a frequency of 2ω and a nonzero offset or average value equal to $\gamma_0^2 G'(\omega)$ (Lodge, 1964; Giacomin and Dealy, 1993). The second normal stress difference is predicted to be zero.

Mechanical analog models can simulate a material's response (Ferry, 1980). These models can be constructed by some suitable combination of springs (obeying Hooke's law) and viscous dashpots (obeying Newton's law). One of the most common mechanical analogs used in modeling linear behavior is the *generalized* Maxwell model:

$$\tau_{ij} = \int_{-\infty}^{t} \sum_k G_k \mathrm{e}^{(-(t-t')/\lambda_k)} \dot{\gamma}_{ij}(t')\,\mathrm{d}t', \qquad (6)$$

where G_k and λ_k are the initial modulus and relaxation time of each Maxwell element. The (G_i, λ_i) set is called the *discrete relaxation spectrum* of the material. Using Eq. (6), the functions defined in Eqs. (4) and (5) can now be represented in terms of G_i, λ_i (Dealy and Wissbrun, 1990):

$$G'(\omega) = \sum_{i=1}^{N} \frac{G_i(\omega\lambda_i)^2}{[1+(\omega\lambda_i)^2]}, \tag{7}$$

$$G''(\omega) = \sum_{i=1}^{N} \frac{G_i(\omega\lambda_i)}{[1+(\omega\lambda_i)^2]}. \tag{8}$$

The discrete relaxation spectrum, (G_i, λ_i) , can be obtained from SAOS test data using curve fitting techniques. In this research, the *parsimonious modeling* technique developed by Winter et al. (1993) was used (IRIS Development, Amherst, MA).

2.2. Nonlinear viscoelasticity

There is no unifying theory that describes nonlinear viscoelasticity, and for most polymeric liquids, the stress response in LAOS is *not* sinusoidal. After a few cycles, the shear stress becomes a standing wave that can be represented by a Fourier series of *odd* harmonics:

$$\tau(t) = \sum_{m=1,\mathrm{odd}}^{M} \tau_m \sin(m\omega t + \delta_m), \tag{9}$$

where $\tau_m(\omega, \gamma_o)$ and $\delta_m(\omega, \gamma_o)$ are the amplitudes and phase angles of the odd harmonics. They depend upon both the strain amplitude and frequency, and since only odd valued harmonics are observed, a plot of shear stress versus shear rate will always give a two-fold symmetric loop (Fig. 2). For cheese, the number of the highest significant harmonic does not normally exceed five. The existence of higher harmonics makes the property definitions $G'(\omega)$ and $G''(\omega)$ meaningless for a nonlinear viscoelastic response.

The cyclic integral of the shear stress with respect to the shear strain gives the energy dissipation per cycle per unit volume, W_L (Onogi and Matsumoto, 1981):

$$W_\mathrm{L} = \oint \tau \,\mathrm{d}\gamma = \pi \tau_1 \gamma_o \sin\delta_1. \tag{10}$$

Hence, all the energy dissipation is in the first harmonic. From the second law of thermodynamics, $W_\mathrm{L} \geqslant 0$; combining this with Eq. (10), the following inequality is obtained:

$$0 \leqslant \delta_1 \leqslant \pi. \tag{11}$$

Measured values of the phase angle for the first harmonic are always in the first quadrant, $0 \leqslant \delta_1 \leqslant \pi/2$, and by convention, phase angles for the higher harmonics lie between 0 and 2π radians.

LAOS test data are best evaluated with spectral analysis. A discrete Fourier transform (DFT) of the digitally sampled stress wave, $\tau(n\Delta t)$, determines the amplitudes and phase angles, which are then used to characterize the cheese at the given test condition. The DFT yields a set of complex numbers, the amplitudes and phase contents of which are:

$$\left|\tau_\mathrm{d}(k\Delta\omega)\right| = \sqrt{\mathrm{Re}^2[\tau_\mathrm{d}(k\Delta\omega)] + \mathrm{Im}^2[\tau_\mathrm{d}(k\Delta\omega)]}, \tag{12}$$

$$\delta_\mathrm{d}(k\Delta\omega) = \tan^{-1}\left[\frac{\mathrm{Im}[\tau_\mathrm{d}(k\Delta\omega)]}{\mathrm{Re}[\tau_\mathrm{d}(k\Delta\omega)]}\right], \tag{13}$$

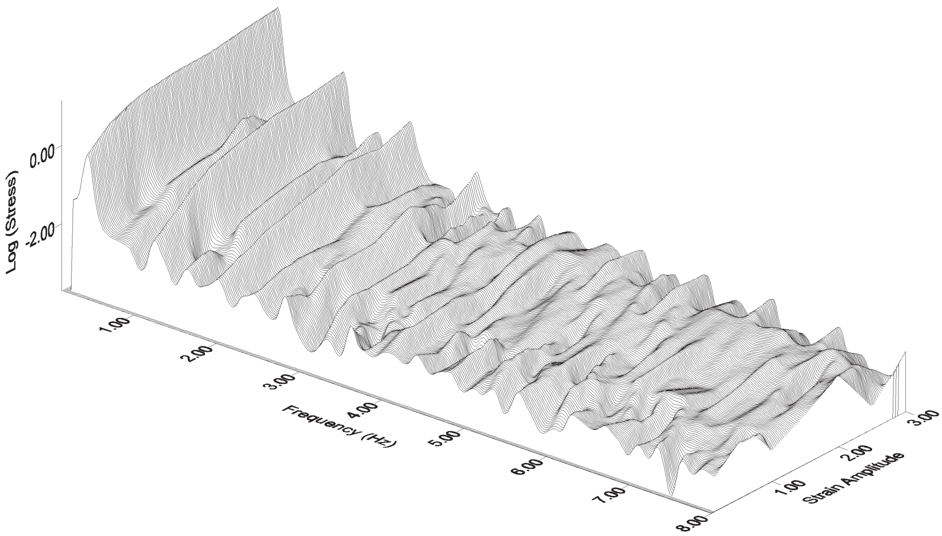

Fig. 3. 3D amplitude spectrum for 4 week old reduced-fat mozzarella at 40°C with $f_o = 0.4$ Hz. The higher, odd harmonics rise with strain amplitude.

where Im and Re mean the imaginary and real parts. The left side of Eq. (12) can be plotted against frequency to give an *amplitude spectrum* of the stress response in oscillatory shear. A more useful way to evaluate and compare nonlinear viscoelastic behavior is to plot the amplitude spectrum for increasing strain amplitudes in three dimension (τ, f, γ_o) , as shown in Fig. 3. The higher, odd harmonics exceed the signal noise with increasing strain amplitude. Low strain amplitudes create a flat bed, while higher values create peaks and valleys, the peaks being the odd harmonics. Plots like this can therefore be used to approximate the conditions at which the stress response will no longer be sinusoidal, and the degree of nonlinearity with respect to the strain amplitude. Other useful plots are the effect of γ_o on $\tau_m(\omega, \gamma_o)$ and $\delta_m(\omega, \gamma_o)$.

The DFT provides a complete mathematical description of the nonlinear viscoelastic response to LAOS. However, these results are more complex than the linear viscoelastic case, where $G'(\omega)$ and $G''(\omega)$ can be used. They now consist of amplitudes and phase angles for as many harmonics as can be identified in the response. Therefore, an extremely useful technique to characterize material response in LAOS is with shear stress versus shear rate loops (Dealy and Wissbrun, 1990; Tee and Dealy, 1975). For the linear viscoelastic case these loops are ellipses, but with higher harmonics, the loops distort (Fig. 2). Although higher harmonics might not exceed 5% of the fundamental, they profoundly affect the loop shape (Giacomin and Dealy, 1993). These loops provide both qualitative and quantitative information about cheese rheology. Such loops may be useful for comparing cheese behavior in industry.

3. Method

The *sliding plate rheometer* (SPR) developed by Giacomin et al. (1989) was used for the LAOS tests (Fig. 4). Unlike classical shear rheometers, such as rotational rheometers,

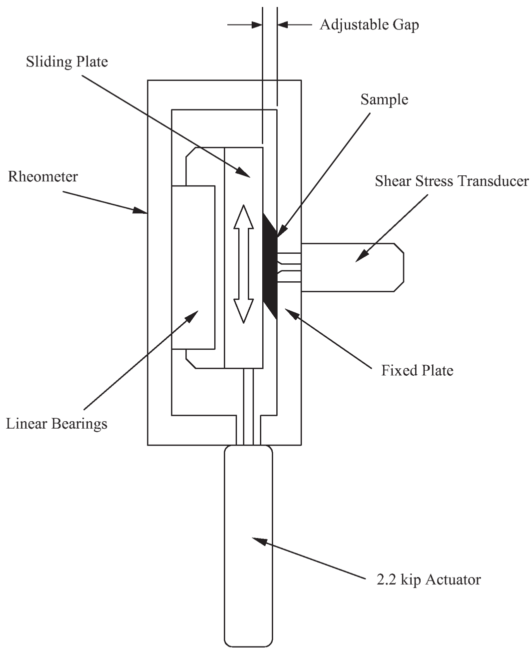

Fig. 4. Interlaken sliding plate rheometer incorporating Dealy *shear stress transducer* (SST). The SST is flush-mounted on the fixed plate and measures the shear stress locally, thereby eliminating error due to flow heterogeneity.

the SPR generates a homogeneous, simple shear flow field, except near the sample edges. We measure the shear stress locally in the region of uniform deformation, away from the free boundaries, using a Dealy (1984) *shear stress transducer* that is flush-mounted on the fixed plate. This eliminates error due to flow heterogeneity near the sample edges, a problem primarily associated with rotational rheometers.

3.1. Sample preparation and testing

Fresh full-fat and reduced-fat pizza cheese, reduced-fat mozzarella, and reduced-fat cheddar blocks were obtained from the University of Wisconsin dairy plant and refrigerated at 4°C until sample preparation. The blocks were vacuum packed to prevent moisture loss and contamination. Table 1 shows the average cheese compositions. A food slicer sliced the cheese into samples with the desired thickness (approximately 1.2 mm); mozzarella was sliced in the fiber orientation direction. A laboratory knife was used to trim the edges, and the samples were cut to approximately $50 \times 80 \times 1.2$ mm dimensions. Each sample was then carefully wrapped in plastic and placed in an airtight zipper bag to maintain freshness. Kraft™ *fat-free* process mozzarella singles were obtained from a grocery store and refrigerated at 4°C until sample preparation. Before testing, the square slices were cut into rectangles measuring approximately $50 \times 80 \times 1.5$ mm.

Tests on process mozzarella were conducted at two temperatures: 30 and 35°C, and at a test frequency of 0.25 Hz. The tests on natural cheese were conducted over 12 weeks at

Table 1
Composition of the *natural* cheeses

Cheese age, weeks	Cheese type	Fat, %	Moisture, %	MNFP[1], %	FDM[2], %	Salt, %	S/M[3], %	pH
1	RF Pizza[4]	12.4	53.2	60.7	26.7	1.95	3.67	5.48
1	FF Pizza	21.1	51.4	6501	43.4	2.01	3.91	5.39
1	RF Ched	13.0	46.4	53.3	24.3	1.66	3.58	5.15
1	RF Mozza	10.2	52.2	58.1	21.3	1.32	2.53	5.39
4	RF Pizza	12.8	53.1	60.9	27.3	1.89	3.56	5.44
4	FF Pizza	21.6	51.2	65.3	44.3	1.94	3.79	5.33
4	RF Ched	11.8	46.8	53.1	22.2	1.74	3.72	5.10
4	RF Mozza	7.5	52.4	56.6	15.8	1.27	2.42	5.31
6	RF Pizza	11.5	52.9	59.8	24.4	1.56	2.95	5.41
6	FF Pizza	18.0	51.6	62.9	37.2	1.78	3.45	5.29
6	RF Ched	9.5	46.5	51.4	17.8	1.51	3.25	5.00
6	RF Mozza	9.9	52.3	58.0	20.8	1.44	2.75	5.25
12	RF Pizza	11.3	53.0	59.8	24.0	2.07	3.90	5.34
12	FF Pizza	20.3	49.9	62.6	40.5	1.39	2.79	5.21
12	RF Ched	10.3	47.2	52.6	19.5	1.63	3.45	5.00
12	RF Mozza	8.25	52.4	55.3	17.3	1.32	2.52	5.07

[1] Moisture-in-the-nonfat-portion;
[2] Fat in the dry matter;
[3] Salt/moisture;
[4] FF = full fat, RF = reduced fat, Pizza = pizza cheese, Ched = cheddar, and Mozza = mozzarella.

the following intervals from the manufacture date: 1, 4, 6, and 12 weeks. Two temperatures were studied: 40°C at which the cheeses were solid, and 60°C at which the cheeses had melted. Mozzarella was sheared in the fiber orientation direction. The test frequency for both temperatures was 0.4 Hz, aimed to approximate the real-life chewing frequency. A fresh sample was used for each new strain magnitude, and the tests were repeated using the same sample to check for repeatability.

A parallel disk rheometer (Bohlin-CVO Melt Rheometer, Bohlin Instruments Inc., Cranbury, NJ) was used to measure linear viscoelastic properties of six week old reduced-fat mozzarella and cheddar (40 and 60°C) and fat-free process mozzarella (30 and 35°C). The linear viscoelastic range was first determined by measuring dynamic properties using SAOS strain sweep tests. SAOS frequency sweep measurements were then made, and the storage and loss

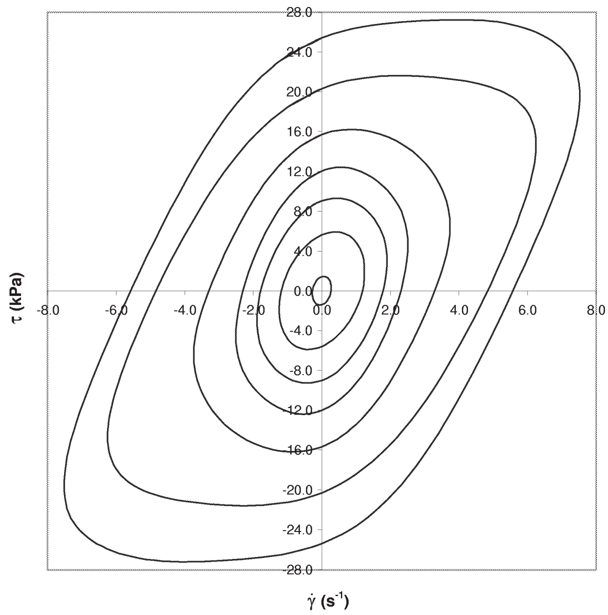

Fig. 5. Shear stress versus shear rate loops for 4 week old reduced-fat mozzarella at 40°C with $f_0 = 0.4$ Hz. Strain amplitudes are 0.1, 0.5, 0.75, 1, 1.5, 2.5, and 3.

moduli, $G'(\omega)$ and $G''(\omega)$, reported. These experimental moduli were then used to calculate the discrete relaxation spectrum for the respective cheeses.

4. Results

The stress response during start-up of LAOS was studied for the different cheeses. The stress waves for the natural cheeses reached steady state within four cycles at 60°C. The peak stresses first increased, then leveled off. Similar behavior was observed at 40°C. However, unlike at 60°C, the peak stresses at 40°C decreased as they steadied, and then continued to decline over time, signifying cheese structure damage. Fat-free process mozzarella also reached steady state within four cycles at both test temperatures.

4.1. Effect of strain amplitude and temperature

Figure 5 shows shear stress versus shear rate loops for reduced-fat mozzarella at 40°C. At 1 week, the loops are elliptical for $\gamma_0 \leqslant 0.75$, after which they distort as higher harmonics matter (Fig. 3). As mozzarella aged, the elliptical range extended to $\gamma_0 \leqslant 1$. However, strains of 3 could not be exceeded due to slip. This was attributed to the entrapped fat globules in the casein network, which began to agglomerate at high shear rates. When this happened at the plate-cheese interface, it caused slip. We do not know how to prevent such slippage. Repeatability using same samples was poor for mozzarella at 40°C. Figure 6 shows shear stress versus shear rate loops for reduced-fat mozzarella at 60°C. The loops are elliptical at all strain amplitudes, meaning only the fundamental components of the stress response matter.

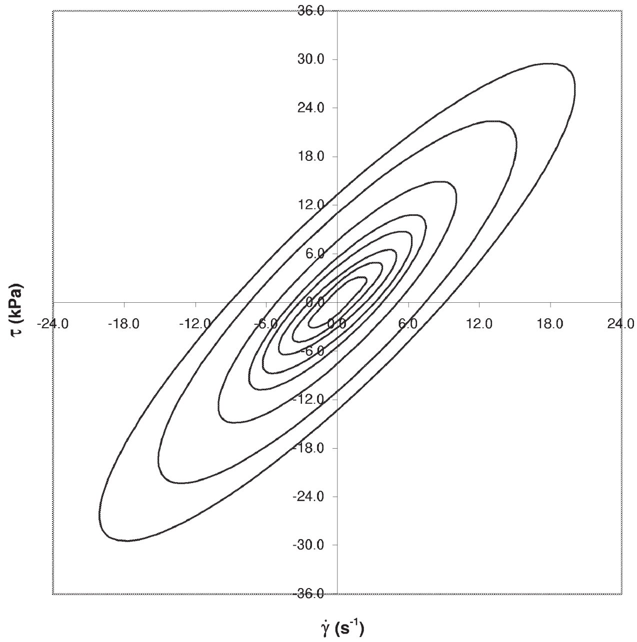

Fig. 6. Shear stress versus shear rate loops for 1 week old reduced-fat mozzarella at 60°C with $f_o = 0.4$ Hz. Strain amplitudes are 1, 1.5, 2, 2.5, 3, 4, 6, and 8. All the loops are ellipses.

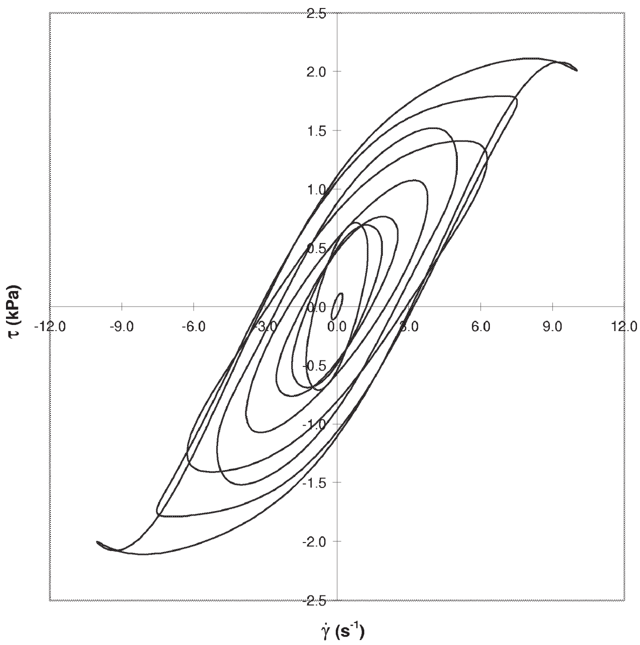

Fig. 7. Shear stress versus shear rate loops for 6 week old full-fat pizza cheese at 40°C with $f_o = 0.4$ Hz. Strain amplitudes are 0.1, 0.5, 0.75, 1, 1.5, 2, 2.5, 3, and 4. Twisting at $\gamma_o = 4$ is caused by slip.

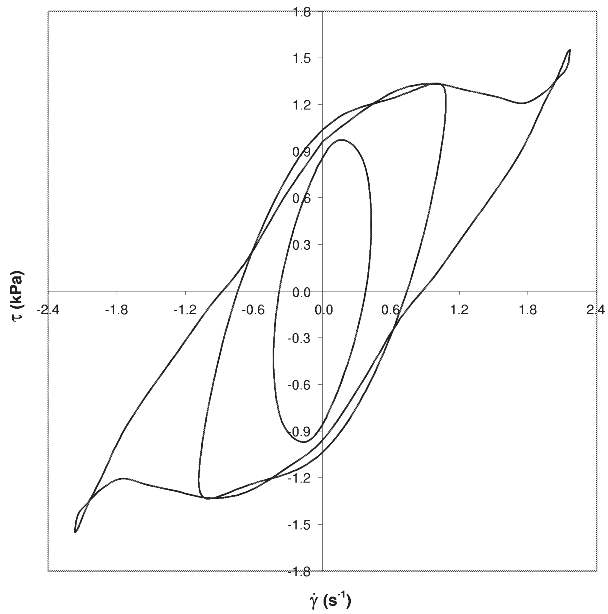

Fig. 8. Shear stress versus shear rate loops for fat-free process mozzarella at 30°C with $f_o = 0.25$ Hz. Strain amplitudes are 0.3, 0.8, and 1.4. Twisting at $\gamma_o = 1.4$ is caused by slip.

Melted mozzarella has a strong structure that adheres well to the plate surfaces and does not slip. Thus, strains up to 10 were reached. Mozzarella also exhibited good repeatability at 60°C, with slightly higher stresses. Melted mozzarella therefore has good shearing properties at 60°C, meaning it does not fracture easily at high shear rates. However, as mozzarella aged to 12 weeks, repeatability worsened as its structure weakened. Similar behavior was observed for cheddar and pizza cheese at both test temperatures. However, pizza cheese exhibited poor repeatability with significant structure damage at both test temperatures and fat contents. An interesting feature with full-fat pizza cheese was twisting of the loops upon slip (Fig. 7). A plot of stress vs. time showed a complex waveform with double peaks (Tariq, 1998). This "double peak" behavior in LAOS was also observed by Hatzikiriakos and Dealy (1991) during slip studies on high density polyethylene.

Figure 8 shows shear stress versus shear rate loops for fat-free process mozzarella at 30°C. The cheese is extremely soft and ruptures at strains exceeding 1. Rupture is caused by fracture of the cheese structure at high shear rates, and this is seen by loop twisting at a strain amplitude of 1.4. At 35°C, higher strains were reached without rupture, and the loops were concentric in contrast to the behavior at 30°C. At both temperatures, higher harmonics mattered at strains above 0.5, making the loops two-fold symmetric. Repeatability on same samples was poor at both test temperatures due to the weak structure.

4.2. Effect of age on natural cheeses

Mozzarella, cheddar, and pizza cheese softened with age due to proteolysis. Figure 9 shows the effect of age on shear stress versus shear rate loops for reduced-fat mozzarella at 40°C.

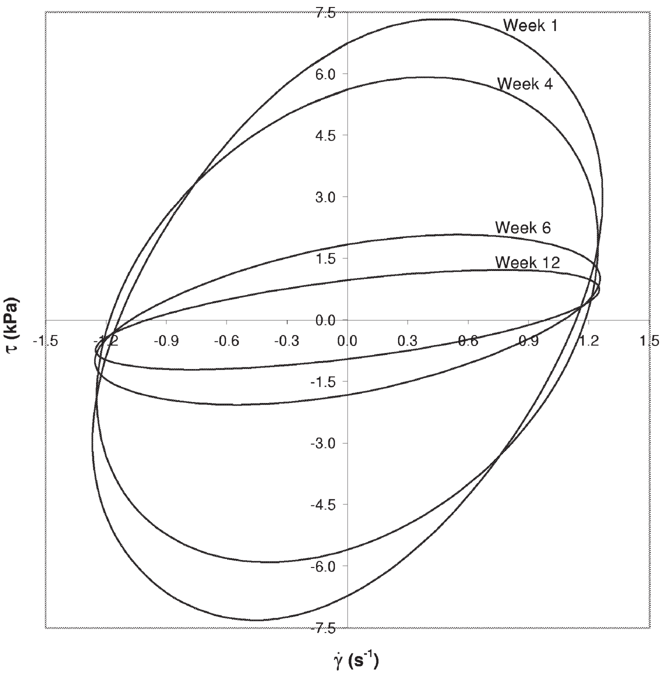

Fig. 9. Effect of age on shear stress versus shear rate loops ($\gamma_0 = 0.5$) for reduced-fat mozzarella at 40°C with $f_0 = 0.4$ Hz. Mozzarella softens with age.

The stresses decrease with age, and the loop areas reduce. Similar results were obtained for reduced-fat cheddar and reduced-fat and full-fat pizza cheese. In general, the cheese structure weakens with age due to proteolytic changes, thus improving flow characteristics and cheese meltability.

4.3. Comparing the natural cheeses

Mozzarella, cheddar, and pizza cheese behaved similarly at both test temperatures. At 40°C, the loops were elliptical up to strain amplitudes of about 0.75, after which they became two-fold symmetric. 3D amplitude spectra at 40°C showed the higher, odd harmonics rising with increasing strain amplitude (Fig. 3). Strain amplitudes above 2.5 caused agglomeration of the fat globules, which led to sample slip, and this was more pronounced in full-fat pizza cheese. Repeating the tests at 40°C caused structure damage for all three cheeses. At 60°C, the loops were elliptical at all strain amplitudes and strains up to 10 were reached, and unlike at 40°C, the loops were intersecting. 3D amplitude spectra at 60°C showed only the fundamental harmonic at the test frequency being significant. Mozzarella and cheddar had good repeatability at 60°C, but pizza cheese did not. In general, all three cheeses exhibited good shearing properties at 60°C with a stronger structure compared to 40°C.

Figure 10 compares shear stress versus shear rate loops for 4 week old reduced-fat mozzarella, cheddar, and pizza cheese at 40 and 60°C. Mozzarella and cheddar have similar shapes and stresses, while pizza cheese is much softer with significantly lower stresses. Similar

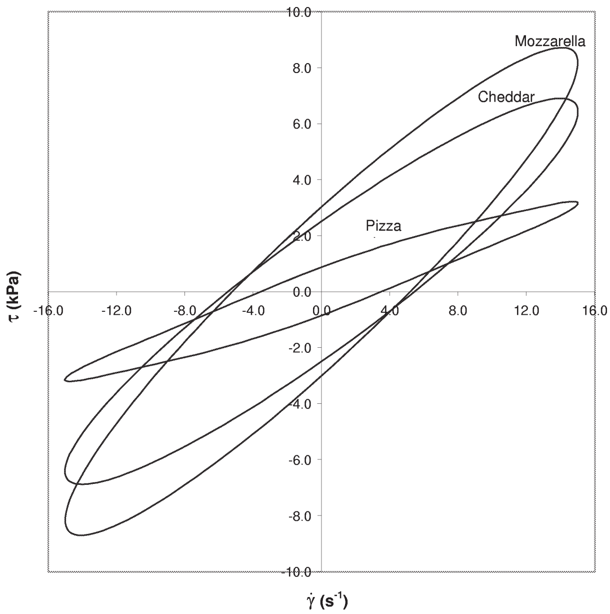

Fig. 10. Comparing shear stress versus shear rate loops ($\gamma_o = 0.75$) for the reduced-fat, natural cheeses at 4 weeks and 60°C, with $f_o = 0.4$ Hz. Mozzarella and cheddar are similar; pizza cheese is much softer.

results were obtained at the other ages. Pizza cheese therefore has better melt properties. Since pizza cheese is *unstretched* mozzarella, the difference between the two cheeses is attributed to the fiber orientation in mozzarella.

4.4. Effect of fat content in pizza cheese

Figure 11 shows the effect of fat content on shear stress versus shear rate loops for pizza cheese at 40 and 60°C. Full-fat pizza cheese is much softer, with approximately half the stresses of reduced-fat pizza cheese. Therefore, it will flow more easily.

4.5. Fourier analysis

Figure 12 shows the effect of strain amplitude on the first three odd harmonics of shear stress for reduced-fat mozzarella at 4 weeks and 40°C. Mozzarella is linear up to a strain amplitude of 1 (i.e., τ_1 is proportional to γ_o and shear stress versus shear rate loops are elliptical), after which the higher harmonics, τ_3 and τ_5, emerge. Cheddar and pizza cheese were linear for $\gamma_o \leqslant 0.75$. These results agree with the previous findings. However, unlike mozzarella and cheddar, pizza cheese appeared to exhibit a yield stress since τ_1 versus γ_o did not extend to the origin. Interpretation of oscillatory data for yield materials is not straightforward though. Figure 13 shows the effect of strain amplitude on the phase angles of the principal harmonics of shear stress for reduced-fat mozzarella. δ_1 increases with increasing strain amplitude, while δ_3 and δ_5 behave irregularly. Similar behavior was observed for reduced-fat cheddar and pizza cheese. Upon comparing δ_1, δ_3, and δ_5 for the three cheeses at 40°C, it was found that δ_1 rose

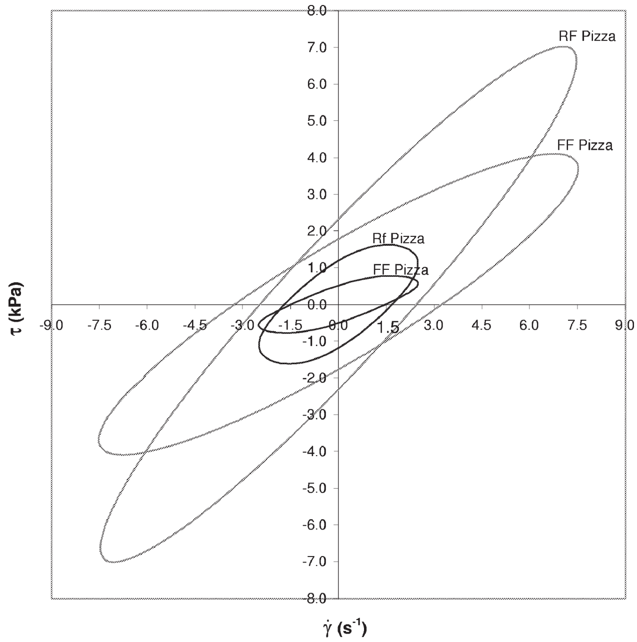

Fig. 11. Effect of fat content on pizza cheese. Outer two loops are at 60°C and $\gamma_o = 3$, inner loops are at 40°C and $\gamma_o = 1$; with $f_o = 0.4$ Hz. Fat nearly halves the stresses.

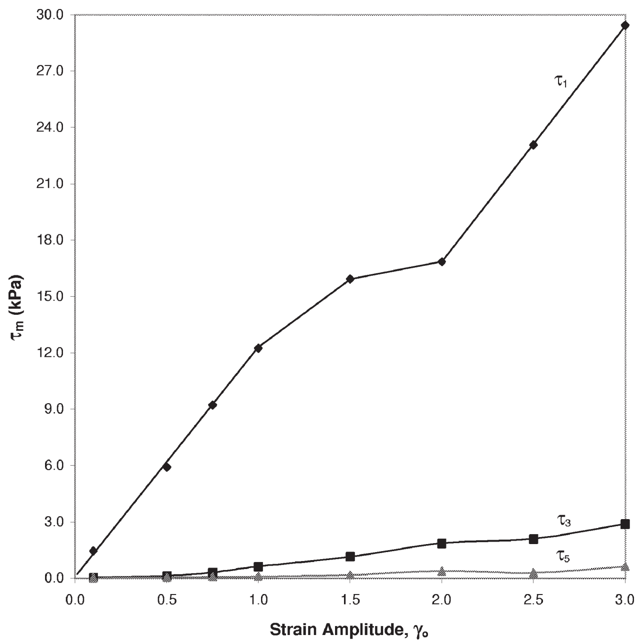

Fig. 12. Effect of γ_o on fundamental, third and fifth harmonics of shear stress for reduced-fat mozzarella at 4 weeks and 40°C, with $f_o = 0.4$ Hz. The higher, odd harmonics rise with γ_o.

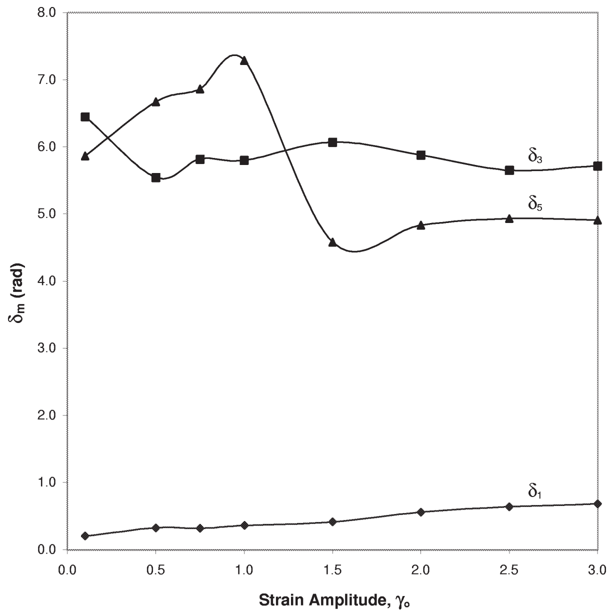

Fig. 13. Effect of γ_o on the phase angles of the principal harmonics of shear stress for reduced-fat mozzarella at 4 weeks and 40°C, with $f_o = 0.4$ Hz. δ_1 rises with γ_o, while δ_3 and δ_5 are not monotonic with γ_o.

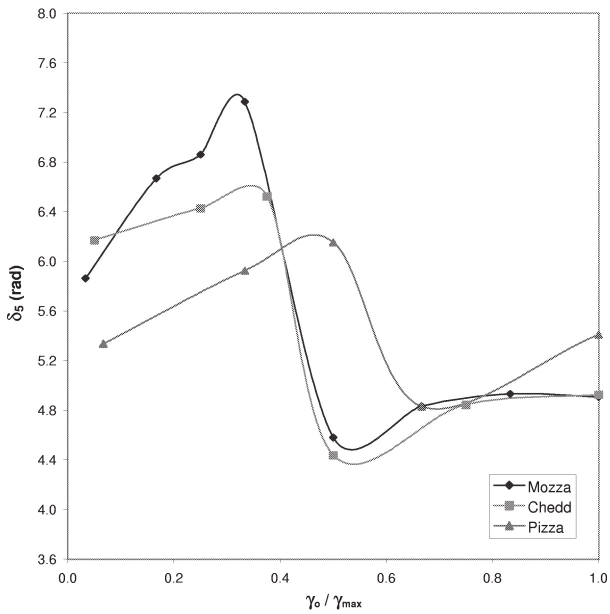

Fig. 14. Comparing phase angles of the fifth harmonic (δ_5) for the reduced-fat, natural cheeses at 4 weeks and 40°C, with $f_o = 0.4$ Hz. δ_5 for all cheeses follow a similar trend, with mozzarella and cheddar almost overlapping at $\gamma_o/\gamma_{max} \geqslant 0.4$.

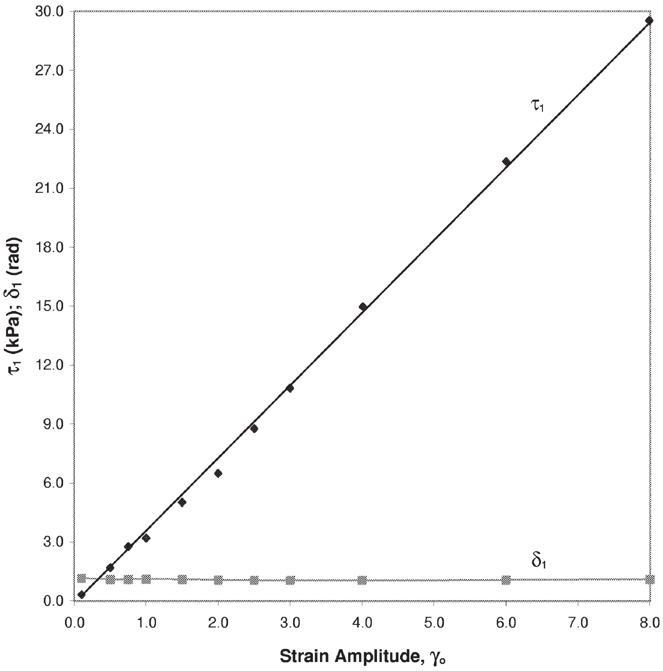

Fig. 15. Effect of γ_o on fundamental harmonics τ_1 and δ_1 for reduced-fat mozzarella at 1 week and 60°C, with $f_o = 0.4$ Hz. δ_1 stays nearly constant with γ_o.

from an average value of 0.3 radians to about 0.65 radians; δ_3 and δ_5 for the three cheeses had similar shapes, with δ_5 for mozzarella and cheddar almost overlapping at $\gamma_o/\gamma_{max} \geqslant 0.4$ (Fig. 14). In summary, all three cheeses behaved similarly at 40°C, with mozzarella and cheddar being the closest.

For the natural cheeses at 60°C, only the fundamental harmonic of the shear stress mattered. Figure 15 shows the effect of strain amplitude on τ_1 and δ_1 for reduced-fat mozzarella at 1 week. τ_1 is linear for $\gamma_o \leqslant 8$ at 1 week, and stayed linear for $\gamma_o \leqslant 7$ at weeks 4 and 6. The linear range of τ_1 for cheddar and pizza cheese did not extend to such high strain amplitudes, and pizza cheese again exhibited a yield stress. Probably the most interesting feature at 60°C was that δ_1 for all three cheeses was independent of strain amplitude. Also, τ_1 at 60°C exceeded τ_1 at 40°C for all three cheeses. Figure 16 compares the effect of age on the average fundamental phase angles $\langle\delta_1\rangle$ for the three cheeses at 60°C. $\langle\delta_1\rangle$ increases with age for all three cheeses, with pizza cheese having the highest value. $\langle\delta_1\rangle$ for mozzarella and cheddar nearly overlap at weeks 1 and 4, but not at week 6. $\langle\delta_1\rangle$ for mozzarella and pizza cheese run parallel to each other. $\tan\delta_1$ has been found to serve as an indicator of cheese meltability (Ruegg et al., 1991; Olson et al., 1996). Therefore, since pizza cheese has a higher $\tan\delta_1$, it will have better melting characteristics than mozzarella. This agrees with previous findings.

For fat-free process mozzarella at 30°C, the linear range of τ_1 was narrow, extending only to a strain amplitude of 0.4, after which the higher harmonics became significant. The phase angles followed trends similar to reduced-fat natural mozzarella at 40°C. δ_1 increased with

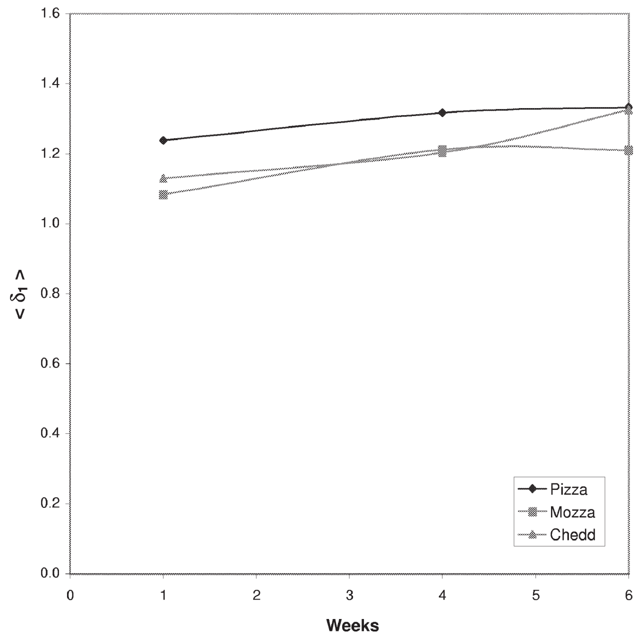

Fig. 16. Effect of age on *average* fundamental phase angles ($\langle\delta_1\rangle$) for the reduced-fat, natural cheeses at 6 weeks and 60°C, with $f_o = 0.4$ Hz. $\langle\delta_1\rangle$ increases with age for all three cheeses.

increasing strain amplitude, while the higher harmonics, δ_3 and δ_5, were irregular with shapes similar to natural mozzarella.

4.6. Comparisons to the Lodge rubberlike liquid

The discrete relaxation spectrum for select cheeses was calculated from SAOS test data using parsimonious modeling. To expose the departures from linearity, we decided to normalize the shear stress with the Lodge rubberlike liquid prediction:

$$\frac{\tau(t)}{\tau_o} = \frac{\tau(t)}{\gamma_o\sqrt{(G')^2 + (G'')^2}} \tag{14}$$

A peak value of $\tau(t)/\tau_o$ falling below one indicated nonlinear behavior.

For 6 week old reduced-fat mozzarella and cheddar at 40 and 60°C, four to six (G_i, λ_i) pairs sufficed to fit experimental data reasonably. Figure 17 compares the Lodge rubberlike liquid to LAOS results for reduced-fat cheddar at 40°C. There is reasonable agreement. Cheddar was almost linear at 40°C, though it slightly over predicted the stresses; but at 60°C it was highly nonlinear, predicting only 4–5% of the linear stresses (Fig. 18). Unlike cheddar, mozzarella was nonlinear at 40°C, predicting 24–40% of the linear stresses. At 60°C, mozzarella became highly nonlinear, predicting only 8–12% of the linear stresses. Therefore, although the shear stress versus shear rate loops for both cheeses are elliptical at 60°C, they are still highly nonlinear. We are unaware of any constitutive equation that predicts nonlinearity without loop distortion.

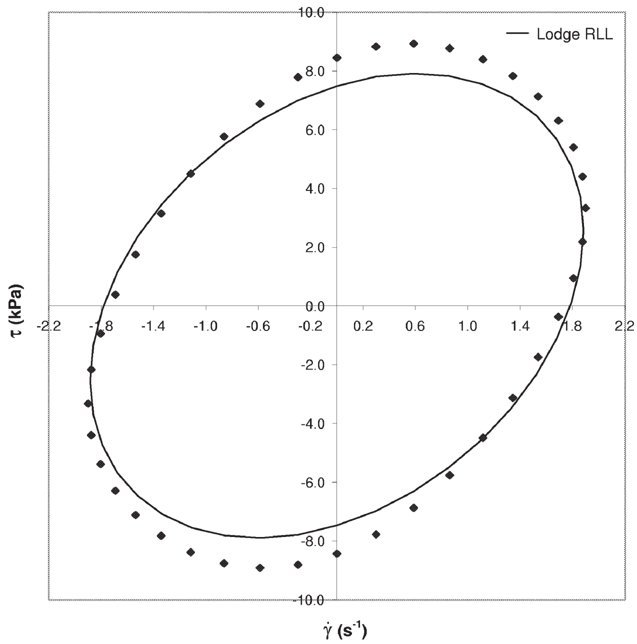

Fig. 17. Comparing the Lodge rubberlike liquid to LAOS results for reduced-fat cheddar at 40°C with $f_o = 0.4$ Hz. Strain amplitude is 0.75. Cheddar slightly overpredicts the linear stresses.

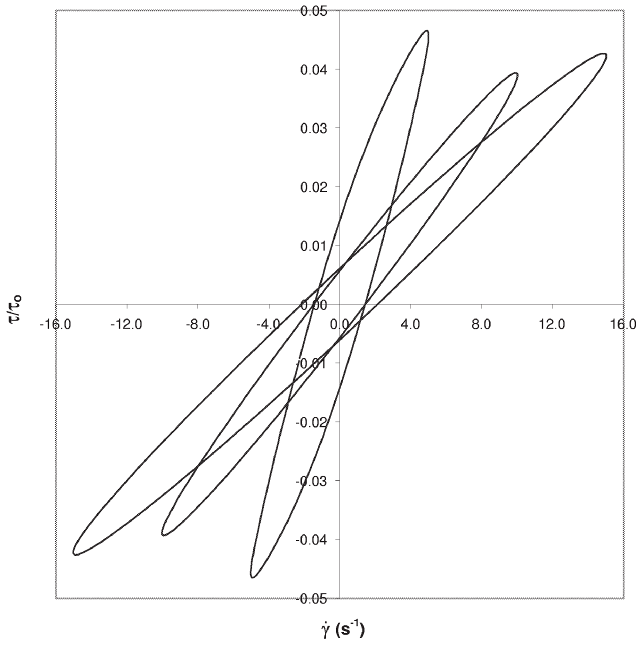

Fig. 18. Departures from linearity for reduced-fat cheddar at 6 weeks and 60°C with $f_o = 0.4$ Hz. Shear stress has been normalized with Lodge's rubberlike liquid theory. Strain amplitudes are 2, 4, and 6. Cheddar is highly nonlinear.

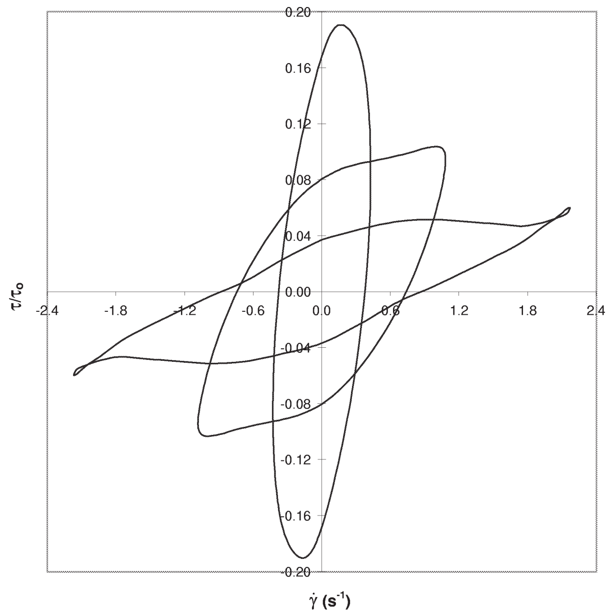

Fig. 19. Departures from linearity for fat-free process mozzarella at 30°C with $f_0 = 0.25$ Hz. Shear stress has been normalized with Lodge's rubberlike liquid theory. Strain amplitudes are 0.3, 0.8, and 1.4. Process mozzarella is highly nonlinear.

For fat-free process mozzarella at 30 and 35°C, five to nine (G_i, λ_i) pairs sufficed to fit experimental data reasonably. Fat-free process mozzarella was highly nonlinear (Fig. 19) at both test temperatures, and this behavior resembled reduced-fat natural mozzarella.

5. Conclusion

LAOS adequately measured the nonlinear viscoelasticity of cheese, and spectral analysis proved useful in characterizing and comparing the different cheese types. Natural mozzarella, pizza cheese, and cheddar demonstrated similar behavior in both the melted and solid states. They exhibited a strong structure with good shearing properties at 60°C, but not at 40°C. The loops were elliptical at all strain amplitudes at 60°C, but highly nonlinear when compared to the Lodge rubberlike liquid. Pizza cheese was softer than mozzarella, with better melt properties. The difference between the two cheeses was attributed to fiber orientation in mozzarella. All three natural cheeses softened with age due to proteolysis, thus weakening the structure and improving flow properties. Process fat-free mozzarella was much softer compared to the natural cheeses, and highly nonlinear. Fat reduction in pizza cheese roughly doubled the stress amplitudes. This underscores the contemporary industrial challenge of formulating reduced-fat pizza cheese while matching its texture to full-fat pizza cheese.

LAOS was therefore extremely useful in evaluating and comparing cheese rheologies. However, work is needed in overcoming slip at 40°C, so that large strain behavior can be studied. More work is also needed in understanding how nonlinear viscoelasticity affects cheese texture. Other constitutive theories should also be evaluated to gain a better understanding of the nature of cheese in relation to its chemical and physical structure. There are no known constitutive equations that predict intersecting loops (such as those in Figs. 7 and 8), and none that predict nonlinearity without loop distortion (i.e., strain amplitude dependent loops that remain elliptical).

Mozzarella mixing during manufacture employs open discharge single screw extrusion, and classical screw design requires only the steady shear viscosity curve (Baird and Collias, 1995). In the plastics industry, the Cox–Merz rule is frequently used to obtain the steady shear viscosity:

$$\eta(\dot{\gamma}) = |\eta^*(\omega)|; \quad \omega = \dot{\gamma}, \tag{15}$$

where $|\eta^*(\omega)|$ is the complex viscosity. In future work, the relationship between $\eta(\dot{\gamma})$ and $|\eta^*(\omega)|$ for molten mozzarella should therefore be explored experimentally.

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