Dynamic Rheological Properties of Mozzarella Cheese During Refrigerated Storage

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ABSTRACT

Storage (G') and loss (G") moduli of low-moisture, part-skim Mozzarella cheese were determined at 10 and 20°C during 1 mo of refrigerated aging. At both temperatures, G' was always greater than G". Averaged over aging, G' increased from 90 to 630 and G" from 44 to 52 kPa at 10°C, and at 20°C G' increased from 28 to 190 and G" from 14 to 53 kPa for the frequency range 0.005–20 Hz. Averaged over frequency, both G' and G" decreased about 20% at 10°C and 25% at 20°C during aging. Relaxation spectrum, computed from shear relaxation data, was used to calculate the G'. The calculated values of G' were in good agreement with those determined experimentally. These data help predict and compare melting behaviors of such cheeses.

Key Words: Mozzarella, cheese, aging, rheology, viscoelasticity

INTRODUCTION

DYNAMIC TESTING is a fundamental method for determining rheological properties of viscoelastic materials. It is normally performed by imposing a sinusoidally varying strain and measuring the resulting stress in the sample. The amplitude of strain is usually kept small to stay within a linear viscoelastic region (Ferry, 1980).

Interest in dynamic mechanical properties of cheeses has increased (Konstance and Holsinger, 1992). Diefes et al. (1993) performed dynamic tests to compare rheological properties of Mozzarella subjected to different storage protocols. Their results indicated that the cheese became harder and more elastic-solid after freezing, and softer and more elastic-liquid during refrigeration. Hsieh et al. (1993) made dynamic measurements to evaluate effects of temperature (10–60°C) on functional properties of Mozzarella containing various protein fillers. Yun et al. (1994) reported that cooking temperatures in the 38–44°C range had little effect on dynamic rheological properties of Mozzarella aged for 3 wk. Ustunol et al. (1994) also used dynamic rheological properties as an index of meltability for Cheddar cheese with varying fat content. They reported a significant correlation between dynamic complex modulus and meltability determined by traditional Arnott method.

In the linear viscoelastic region, it is possible to determine one viscoelastic function from another by computational methods (Ferry, 1980). The computational verification of rheological data generally has not been reported. Zoon et al. (1990) stated that if the same rheological property could be calculated from different types of experiments, it could provide a strong indication that true material properties had been measured. Accordingly, they calculated the shear relaxation modulus of skim milk gels from dynamic moduli data, and reported good agreement between calculated and measured values.

Our objectives were: (1) to determine changes in dynamic rheological properties of Mozzarella during 1 mo of refrigerated aging, and (2) to test the utility of a simple approximation formula (i.e., Alfrey's rule) in determining the dynamic storage modulus of cheese from shear relaxation data.

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MATERIALS & METHODS

Sample preparation and testing

Fresh, low-moisture, part-skim Mozzarella cheese blocks obtained from a commercial cheese plant were stored in a refrigerator (6–8°C) until sample preparation. Disk shape cheese samples (mean thickness 3.7 mm, diameter 30 mm) were prepared from blocks using a slicer and borer. A Bohlin VOR Melt Rheometer (Bohlin Reologi, Cranbury, NJ) with 30 mm parallel plates was used for rheological measurements. Sample temperature during testing was maintained with a recirculating water bath.

A sample was placed on the lower plate and the upper plate was brought into contact with it. The sample was held 4 min for temperature equilibration. The sample's perimeter was brushed with mineral oil, and a wet paper towel was placed around the lower plate to minimize drying.

Initial strain sweep experiments were conducted to determine the linear viscoelastic region for Mozzarella. A plot of complex modulus *vs* strain at two frequencies (Fig. 1) showed a linear behavior up to about 0.5% strain. This confirmed data of Nolan et al. (1989). Consequently, the strain levels used in the dynamic and relaxation measurements were less than 0.5%.

We made frequency sweep measurements (0.005–20 Hz) at 10 and 20°C and determined storage (elastic) modulus G' and loss (viscous) modulus G" of the cheese. We performed tests on days 7, 14, 21 and 28 after production date and repeated each test with 3 or 4 fresh specimens. In addition, we made stress relaxation measurements and recorded the stress decay for 150 s after deformation. We used the relaxation data to calculate the dynamic storage modulus of the cheese.

Analysis of variance was performed to evaluate the significance of the aging effect on storage and loss moduli of the cheese using Statgraphics software (STSC, Inc., Rockville, MD).

Calculating storage modulus from relaxation data

The shear relaxation modulus G(t) and dynamic storage modulus G'(ω) are given as follows (Ferry, 1980):

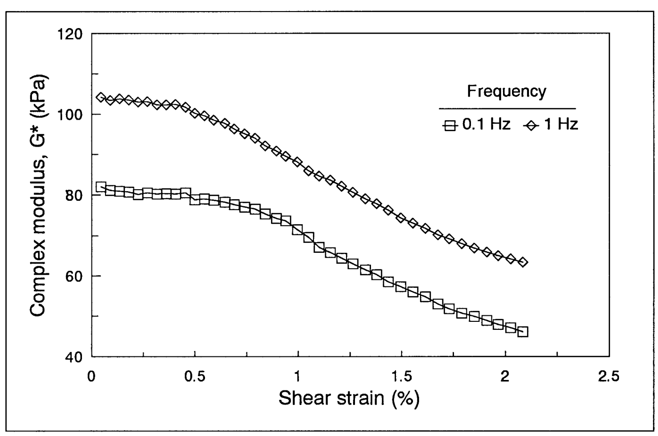

Fig. 1—Variation of complex shear modulus G* of 7 day old Mozzarella cheese with strain at two frequencies (test temperature: 10°C).

$$G(t) = G_e + \int_{-\infty}^{\infty} H(\tau)\exp(-t/\tau)d\ln\tau \quad [1]$$

$$G'(\omega) = G_e + \int_{-\infty}^{\infty} H(\tau)\frac{\omega^2\tau^2}{1+\omega^2\tau^2}d\ln\tau \quad [2]$$

The relaxation spectrum $H(\tau)$ was obtained from the shear relaxation modulus *vs.* time data using Alfrey's rule (Ferry, 1980). From the $G(t) - \log t$ curve, the $H(\tau)$ was determined as a constant H^* (Fig. 2). Then, Eq. 2 gives:

$$G'(\omega) = G_e + \frac{H^*}{2}\ln\left(\frac{1+\omega^2\tau_u^2}{1+\omega^2\tau_l^2}\right) \quad [3]$$

where, τ_l and τ_u are the lower and upper limits of integration in Eqn. 2 (i.e., truncated relaxation times) as described by Tobolsky (1960), and G_e is the equilibrium shear modulus or the value of stress which does not relax after a specified long time. As an approximation we assumed the value of G_e equal to the G(t) at the last data point (i.e., G(150 s)). It is clear that the value of G_e depends on the duration of relaxation tests. The selected value of G_e accounts for contributions to modulus of relaxation processes in the cheese with relaxation times greater than 150 s.

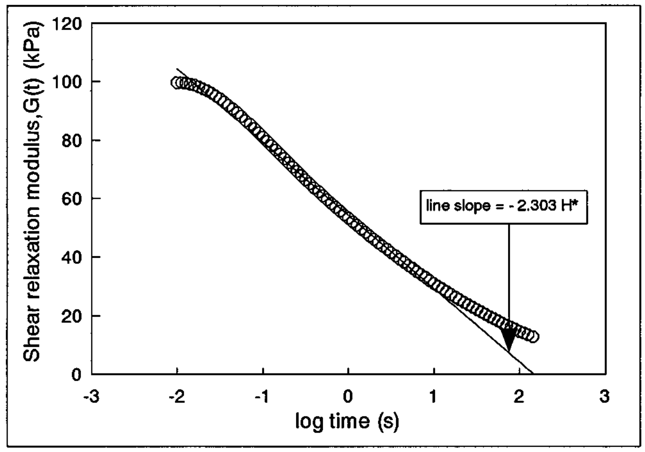

Fig. 2—Stress relaxation of 14 day old Mozzarella cheese in shear at 20°C. [Regression line is used to obtain relaxation spectrum.]

RESULTS & DISCUSSION

THE STORAGE (G') and loss (G") modulus of aging Mozzarella cheese were determined as a function of frequency at 10°C (Fig. 3) and 20°C (Fig. 4). Frequency dependence of G' and G" was nearly linear (on log-log scale) in the range of 0.1-100 rad/s, as reported by Nolan et al. (1989). At a given frequency, the value of G' was significantly greater than G", indicating a dominant elastic character of the cheese. This type of response for Mozzarella has been reported by others, even for melted cheese tested at frequencies higher than 10 rad/s (Diefes et al., 1993; Hsieh et al., 1993; Nolan et al., 1989).

Both G' and G" decreased with aging. This effect was more noticeable at 20°C and in the first 2 wks of storage (Fig. 4). At 10°C, the G' values at days 7 and 14 differed ($p < 0.05$) from each other and also from those at days 21 and 28. The same was true for G" values. At 20°C, the G' at day 7 was different ($p < 0.05$) from those at the other testing days. Basically, a similar trend was found for G" values (Table 1). Hydrolysis of caseins in Mozzarella cheese during refrigerated storage has been reported (Ak et al., 1993; Ak and Gunasekaran, 1995; Farkye et al., 1991). As in the case of milk gels (Zoon, 1988), it is likely that degradation products from casein hydrolysis contributed less to the moduli of the cheese as compared to intact caseins. Loss of protein network by proteolysis implies a decrease in G' during aging, which we observed. By the same reason, however, we expected an increase in viscous contribution (i.e., in G"), which we did not observe. This was probably related to the fact that proteolysis generates ionic groups (Creamer and Olson, 1982) that bind water and that would consequently reduce viscous dissipation. Hence, G" decreases over storage time. Binding of water, however, can contribute to the elastic behavior of the cheese. Apparently, this contribution was not adequate to compensate for the decrease due to proteolysis.

At both temperatures, G' of the cheese increased with frequency. However, G" showed a different behavior, depending upon the test temperature. At 10°, the G" first increased with frequency in the intermediate range, and then decreased at higher frequencies (Fig. 3). Such a response has not been reported, since other researchers made dynamic measurements over 20°C. This decreasing part had disappeared at 20°C, and hence the G" continuously increased with frequency (Fig. 4), in agreement with published data (Diefes et al., 1993; Nolan et al., 1989; Yun et al., 1994). We expected a low G" at low temperature-high frequency combinations as the molecular adjustments causing viscous dissipation would be slow, and there would be less time for them to occur.

Dynamic data from our results on Mozzarella and those published on Mozzarella (Diefes et al., 1993), Cheddar and process

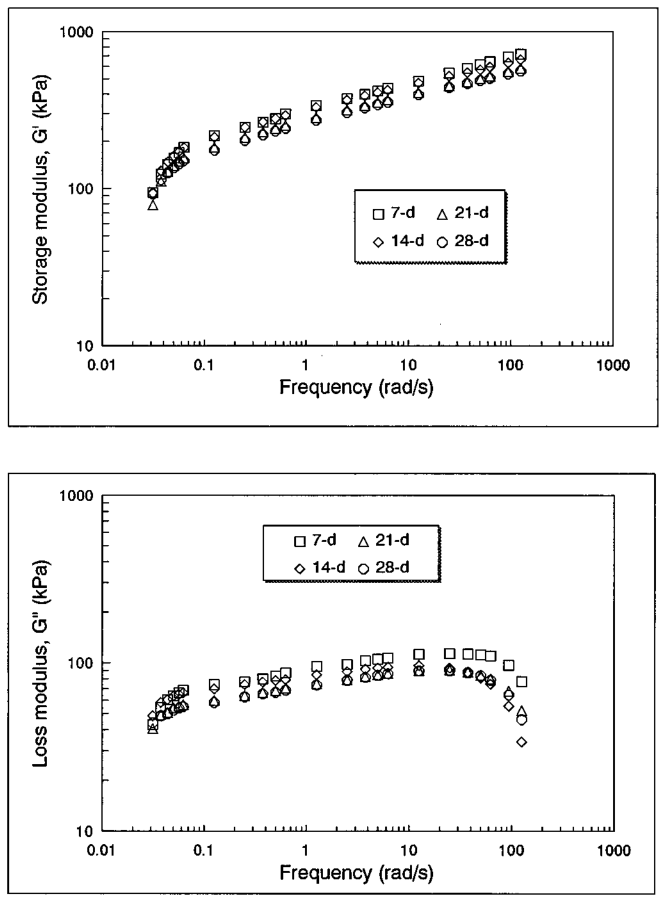

Fig. 3—Variation of dynamic moduli (G', G") of Mozzarella cheese with frequency at different aging (test temperature: 10°C).

American cheeses (Nolan et al., 1989) were plotted (Fig. 5) as loss tangents (i.e., $\tan\delta = G''/G'$ *vs* frequency at various temperatures. For a given frequency, the loss tangent of each variety increased with temperature. Below 45°C, the loss tangent of each variety was less than unity and remained fairly constant as frequency increased. At 60°C, however, the loss tangent of Mozzarella decreased by a factor of 6.5 in the frequency range studied. Among the 3 cheeses, Cheddar exhibited the highest loss tangent at 60°C and 10 rad/s, probably due to more proteolysis in longer aging and to compositional differences. Ustunol et al. (1994) reported that for 4 mo old Cheddar cheese tested at 1 rad/s, the loss tangent was less than 1.0 prior to melting and

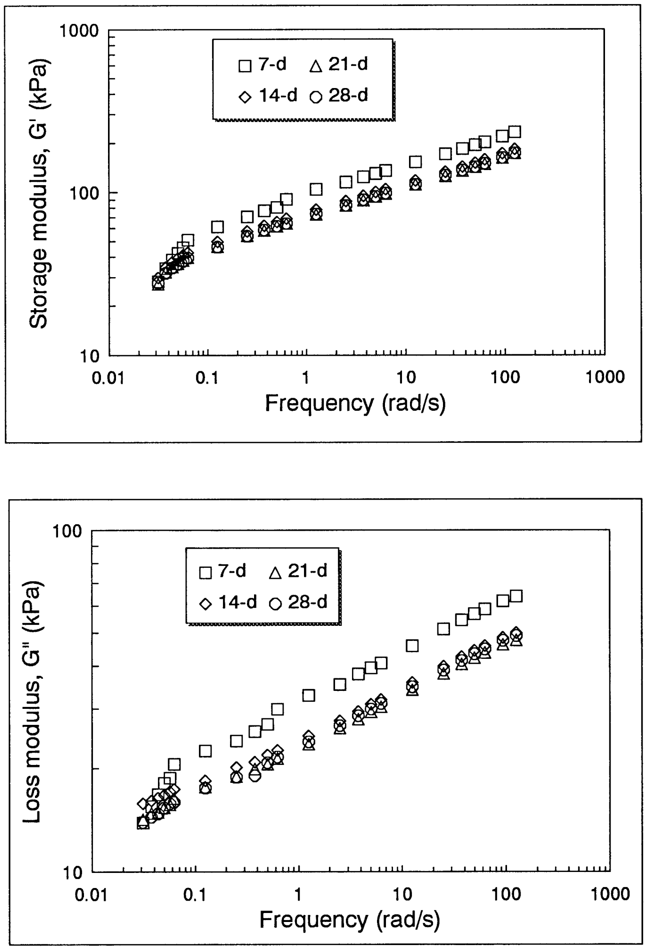

Fig. 4—Variation of dynamic moduli (G', G") of Mozzarella cheese with frequency at different aging (test temperature: 20°C).

Table 1—Statistical comparison of storage (G') and loss (G") modulus at different aging for Mozzarella during one month of refrigerated storage[a]

Age (days)	G' at 10°C	G" at 10°C	G' at 20°C	G" at 20°C
7	a	a	a	a
14	b	b	b	b
21	c	c	b	c
28	c	c	b	bc

[a] Different letters in a column indicate differences at $p \leq 0.05$. The comparison was made on the data in a given column only for the age effect.

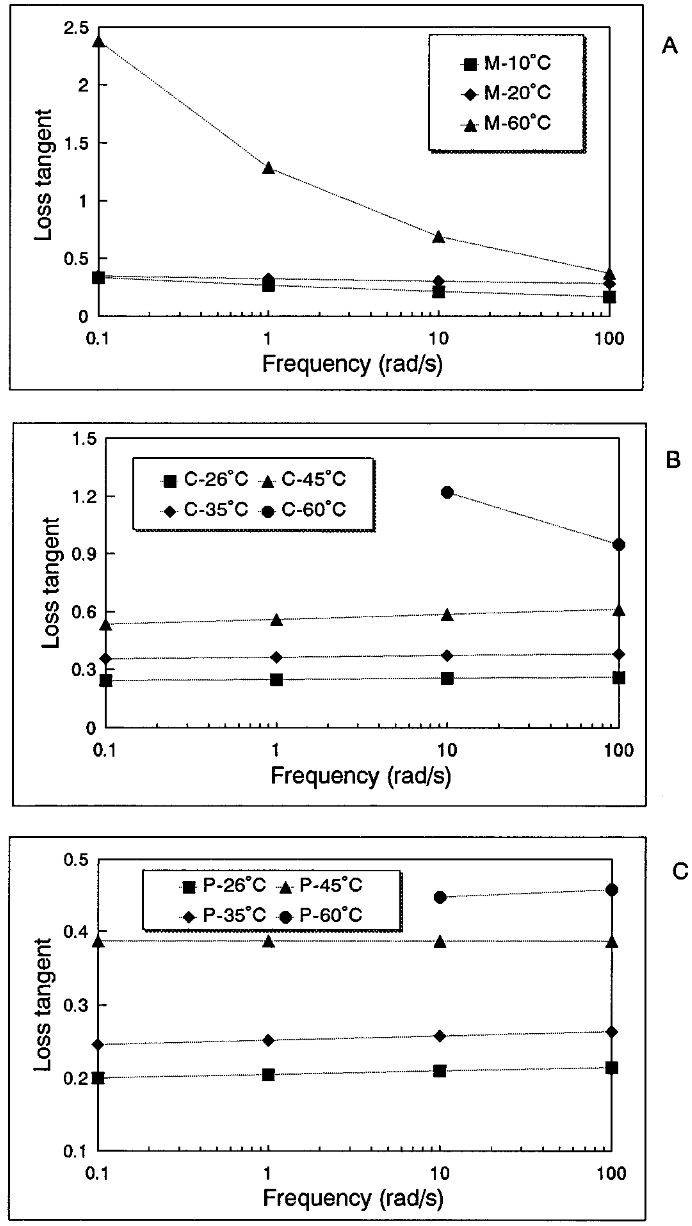

Fig. 5—Dependence of loss tangent of Mozzarella (A), Cheddar (B) and pasteurized process American (C) cheeses on frequency at different temperatures. Data at 60°C in (A) are taken from Diefes et al. (1993) and those in (B) and (C) from Nolan et al. (1989).

greater than 1.0 after melting. The loss tangent of Mozzarella was also greater than 1.0 at 60°C and 1 rad/s (Fig. 5-A). Note that the process American cheese had the lowest loss tangent at all frequencies and temperatures.

A comparison was made (Fig. 6) of measured storage moduli with those calculated from stress relaxation data using the computation method. The agreement between calculated and measured values was good. Calculated values were generally higher than measured data (Fig. 6). This may be due to our selection of the G_e. If the stress relaxation tests were continued for a longer time, the equilibrium shear modulus (i.e., the actual value of G_e) would be lower than the selected value of the G_e. Consequently, the calculated storage moduli would be lower than those shown. However, other factors (e.g., time scale of the tests and inherent variation in samples) can also affect agreement (Zoon, 1988; Zoon et al., 1990). For our data, the calculated storage modulus differed, in the worst case, by 30% from the measured one. Hence, the Alfrey's approximation rule was simple and fairly adequate to verify experimental results on Mozzarella cheese.—*Continued on page 584*

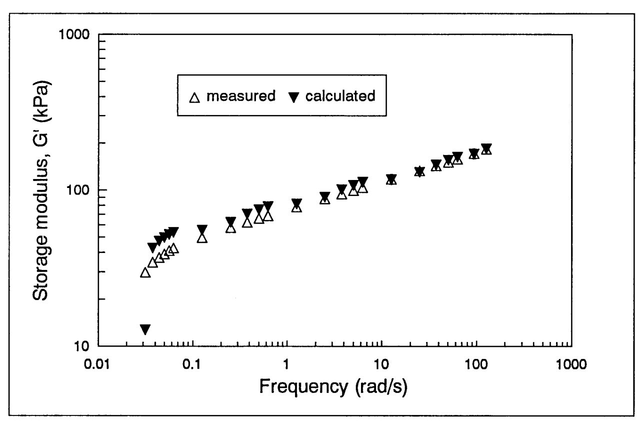

Fig. 6—Measured and calculated (from shear stress relaxation data) dynamic storage modulus of 14-day old Mozzarella cheese (test temperature: 20°C).

CONCLUSIONS

THE STRAIN LIMIT for linear viscoelastic behavior of Mozzarella cheese was confirmed to be below 0.5%. The elastic nature of the cheese was dominant at 10 and 20°C (i.e., $G' > G''$). The moduli of the cheese changed considerably with frequency and test temperature and, to a lesser degree, with aging. Frequency dependence of the loss modulus of Mozzarella was more pronounced at 20°C than 10°C. Agreement was found between the calculated and measured values of storage modulus. The Alfrey's rule was practical for computing storage modulus from relaxation data and can be applied for immediate verification of experimental results.

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