DYNAMIC RHEOLOGICAL PROPERTIES OF NATURAL AND IMITATION MOZZARELLA CHEESE

ABSTRACT

Suitability of Mozzarella cheese for various products involves the measurement of rheological properties of the cheese related to its meltability. The rheology in this work is determined dynamically with a Rheometrics RDA 700 mechanical spectrometer using 25 mm diameter parallel plates fabricated from aluminum. Bonding the cheese specimen directly to the plates with cyanoacrylate ester adhesive proved the most effective in countering the problem of specimen slip. Viscosity proved sensitive to addition of calcium caseinate, following an Arrhenius relationship with temperature. Both elastic and viscous components of the shear modulus increased with a 1% addition but a 2% addition decreased the elastic component below that observed for natural Mozzarella under the same conditions.

INTRODUCTION

The most important functional properties of Mozzarella cheese are its rheological properties, particularly those of meltability and stretchability. These properties are influenced by composition and by the plasticizing and kneading process to which the curd is subjected during manufacture. Studies of the textural characteristics of natural and imitation Mozzarellas have been reported (Chen *et al.* 1979; Imoto *et al.* 1979; Cervantes *et al.* 1983; Yang and Taranto 1982).

Low moisture, part skim Mozzarella cheese is routinely purchased by the U.S. Government for use in the National School Lunch Program. As part of our ongoing investigations of the effects of freezing and thawing on the functional characteristics of cheeses, we undertook an investigation of the rheological properties of Mozzarella as a means of establishing objective quality criteria for acceptance. In the course of our measurements of the dynamic shear moduli and viscosities of Mozzarella cheeses of different origins with a Rheometrics RDA 700 mechanical spectrometer, we observed inconsistencies in our measurements that we attributed to slippage of the specimen in the apparatus.

Specimen slippage has been previously reported. In their measurements of shear stress-shear strain of gels formed by wheat starch granules above 14% total starch concentration, Navickis and Bagley (1983) detected slip between the gel and the parallel plates of the Rheometrics Model KMS-71 mechanical spectrometer used in their studies. They resolved the problem by using a cyanoacrylate ester adhesive to attach the gel to the plates. Slippage has also been detected in the measurements of the flowability of molten cheeses by capillary rheology (Smith *et al.* 1980). However, this type of rheometer did appear to be satisfactory for the study of melted Mozzarella. Yoshimura and Prud'homme (1988) reported slip during dynamic oscillatory measurement of emulsions and foams. They suggested an analytical procedure to resolve the effect of slip and pointed out that evidence of slip or the absence thereof cannot be assumed from the shape of a stress-strain waveform. To establish whether slip has occurred, it is necessary to measure the waveforms with two different gap separations at the same strain and frequency. If identical stress waveforms are obtained from the two measurements, slip is not occurring. The results are due to the bulk properties of the material. Slip is occurring if the waveforms differ.

Our objective in this report is to describe our experiences with slippage of Mozzarella cheese specimens (visual observation suggests that a possible cause of slippage is diffusion of milk fat onto the specimen surface at room temperature) and our solution to prevent creation of artifacts in the measurements obtained with our mechanical spectrometer. We also report the dynamic shear moduli and viscosities of natural and imitation Mozzarella cheeses and describe the effects of compositional changes on these dynamic properties.

MATERIALS AND METHODS

Low moisture, part skim Mozzarella cheeses were made in the Eastern Regional Research Center's dairy pilot plant. Imitation cheeses were made by adding 1 or 2% (by weight of fluid milk) calcium caseinate powder (New Zealand Milk Products, Petaluma, CA) to fresh raw milk before pasteurization. Control and caseinate-containing milks were pasteurized at 62.8°C for 30 min, cooled and held 18 h at 3°C to hydrate the added protein before processing further, according to an adapted procedure of Kosikowski (1977). Samples were vacuum packaged and stored at 4.4°C until used. Commercially manufactured samples were obtained frozen from the Agricultural Marketing Service. They were tempered at 4.4°C for 1 to 3 weeks before use.

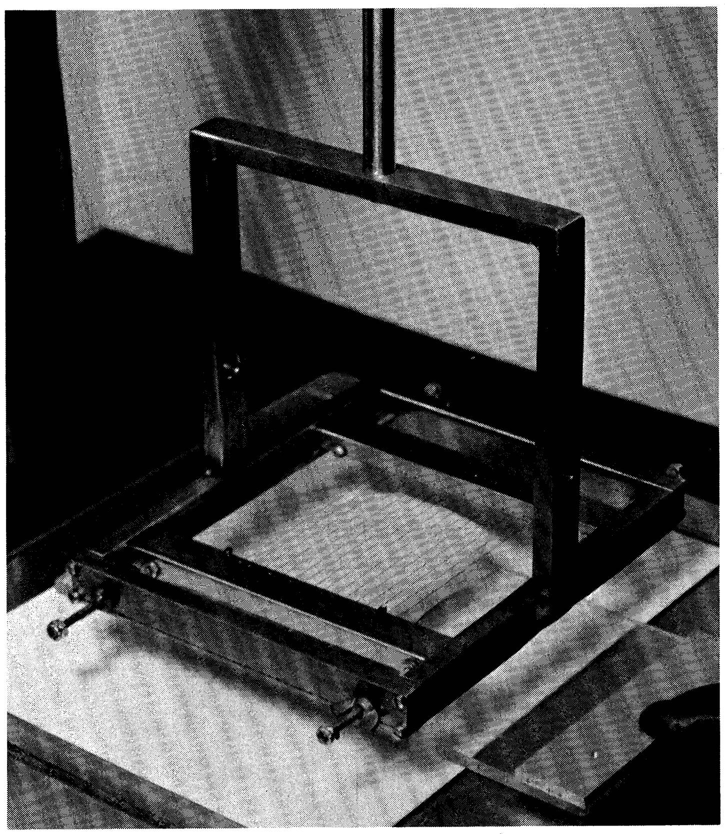

FIG. 1. METHOD OF PREPARING CHEESE SLICES

Measurements were made with an RDA 700 Dynamic Analyzer (Rheometrics, Inc., Piscataway, New Jersey) in a parallel plate configuration. For measurement, (Fig. 1) tempered cheese samples were sliced 4 mm and 8 mm thick at 20°C with piano wire mounted in a fixture attached to a hand operated drill press. Then a 4 mm × 25 mm or 8 mm × 25 mm disc was made with a stainless steel borer. Samples were bonded to the aluminum plates previously pitted by impressing them with coarse sandpaper as follows: The bottom plate was coated with one drop of cyanoacrylate resin distributed evenly over the plate with a wooden toothpick. The cheese specimen was placed on the plate and the bond was allowed to polymerize at room temperature for about 1 min. When bonding was complete, a drop of bonding agent was spread over the top surface of the cheese as before. The upper pitted plate was placed in contact with the cheese with an initial force of about 100 g supplied by the instrument for about 10 min to ensure a solid bond. Relaxation to zero force as noted on the instrument force indicator occurred about 5 min after contact.

Measurements of dynamic viscosities and shear viscoelastic moduli were determined at temperatures up to 70°C and frequencies from 0.10 to 100 radians/s in order to obtain an Arrhenius type relationship.

The data obtained from all the experiments included the elastic (shear storage modulus) G′ (dynes/cm^2) and viscous (shear loss modulus) G″ (dynes/cm^2) components of the shear complex modulus G* together with the complex viscosity η^* (poise). Here $G^* = [(G')^2 + (G'')^2]^{1/2}$ and $\eta^* = G^*/\omega$ where ω = frequency. These data were printed on a Texas Instrument Co. Silent 700 and results were plotted on a Hewlett Packard Plotter (Model 7470A). Experiments were carried out in an environmental chamber. When the environmental chamber was not used, for example at room temperature, the temperature fluctuated ±1°C.

RESULTS AND DISCUSSION

Specimens were placed between the knurled aluminum parallel plates of the mechanical spectrometer and held in place by simple friction until slippage was identified. An example of slippage is shown with Mozzarella cheese in Fig. 2,

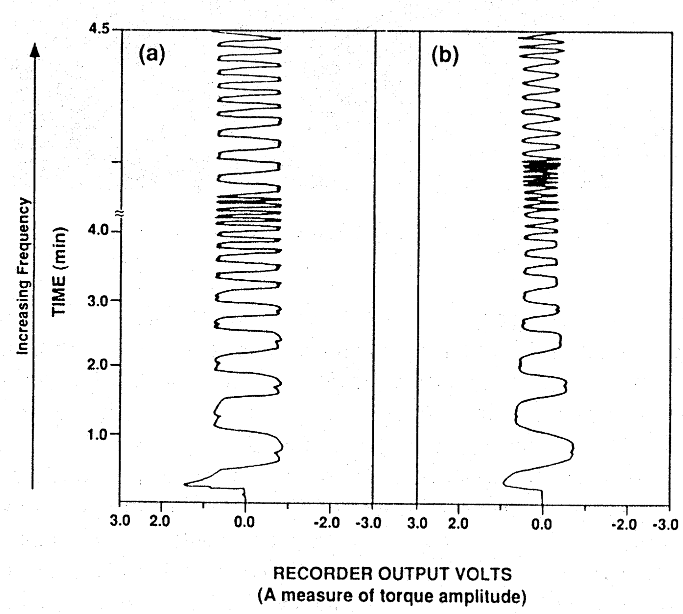

FIG. 2. TIME PROFILE OF FREQUENCY SWEEP AT 10% STRAIN
Mozzarella cheese not bonded to aluminum plates. A) 4 mm gap; B) 8 mm gap

TABLE 1.
TEMPERATURE LAG IN MOZZARELLA CHEESE USING ALUMINUM PLATES AND ALUMINUM PLATES WITH SANDPAPER

Instrument Set Temperature °C		25	30	35	40	45	50	55	60	65	70
Cheese Temperature using Aluminum Plates	30 sec	25.0	30.0	35.0	40.0	45.1	50.1	55.1	60.2	65.2	70.2
	60 sec	25.3	30.1	35.3	40.3	45.4	50.3	55.4	60.3	65.4	70.4
Cheese Temperature using Aluminum Plates With Sandpaper	30 sec	23.7	28.6	33.5	38.7	43.8	48.7	54.0	59.1	64.2	69.2
	60 sec	23.8	28.7	33.7	39.0	44.0	49.0	54.1	59.4	64.4	69.5

representing a frequency sweep at 10% maximum shear strain; two different gap sizes were used: 4 mm and 8 mm, respectively (Fig. 2a and b). The distortion in the harmonics of the waveforms obtained from the 4 mm gap is noteworthy. These are not repeated *in toto* in the waveforms of the 8 mm gap; this is indicative of slip. To counter this problem, several methods were tried: (1) Attachment of coarse sandpaper to the parallel plates; (2) a titanium plate combination in place of the knurled aluminum plates; (3) bonding the cheese sample directly to the aluminum plates with cyanoacrylate ester adhesive.

Use of the sandpaper was discarded after noting that during measurements at elevated temperatures (to 70°C), temperature lag occurred in the sample, because of resistance imparted by the sandpaper. Table 1 shows an example of the temperature lag, with a specimen from the same sample of cheese.

When measurements were made after 30 s, the temperatures of the cheese deviated from a set instrument temperature about −0.8°C to −1.4°C, and after 1 min with sandpaper-coated aluminum plates, the temperatures deviated about −0.5°C to −1.3°C. In contrast, with aluminum plates, after 30 s, the cheese temperatures deviated 0 to 0.2°C; when measurements were made after 1 min, the temperatures deviated 0.1°C to 0.4°C.

The time profile of the strain sweep experiment with aluminum plates bonded with sandpaper, shown in Fig. 3, was a sinusoidally varying strain which showed that the torque amplitude (volts output) did not increase monotonically. Eight minutes after starting, abnormalities in the curves obtained with the 4 mm gap

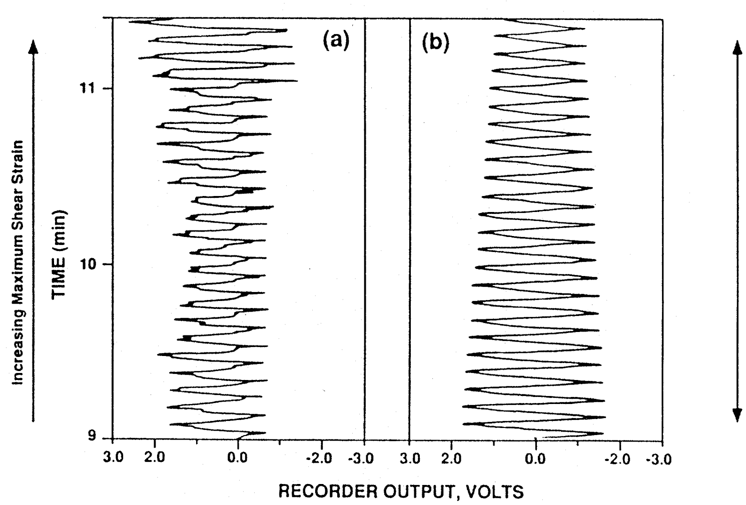

FIG. 3. MOZZARELLA CHEESE TIME PROFILE OF STRAIN SWEEP AT A FREQUENCY 1.0 RAD/S

Aluminum plates bonded to sandpaper; Mozzarella cheese A) 4 mm gap; B) 8 mm gap

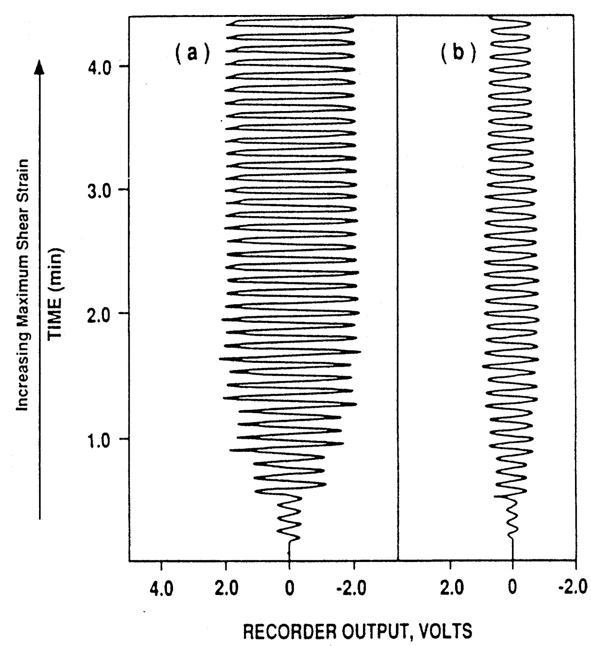

FIG. 4. TIME PROFILE OF STRAIN SWEEP AT A FREQUENCY OF 1.0 RAD/S
Mozzarella cheese not bonded to titanium plates. A) 4 mm gap; B) 8 mm gap

were observed near the peaks (Fig. 3a). These artifacts in the amplitude did not appear in the curves obtained with the 8 mm gap, once more indicative of slip (Fig. 3b).

A quantity of Mozzarella cheese (4 mm and 8 mm thick, respectively), was placed between two titanium plates 25 mm in diameter. Experiments were conducted in the strain sweep mode from 0 to 20% at 0.5% per step. Results from strain sweep, shown in Fig. 4, indicate that after about 3 min, distortions occurred in the amplitude of the curves obtained with the 4 mm gap (Fig. 4a) that did not occur in the curves obtained with the 8 mm gap (Fig. 4b); this suggests slip.

The best results were obtained by bonding the sample directly to the aluminum plates after pitting them with sandpaper. A strain sweep was conducted at a frequency of 1 rad/s. The storage modulus (G′) and the shear loss modulus (G″) were obtained under normal bonded conditions during the strain sweep from 0 to 20% strain. Also, the time profile of the strain sweep, shown in Fig. 5a and 5b, showed that the amplitude of the torque increased in proportion to input strain; the curves show no artifacts of the type noted in Fig. 2 and 3.

The experimental cheeses appeared to have a wide melting range. Initial softening was noticed at 35 to 40°C and continued over the range of temperatures

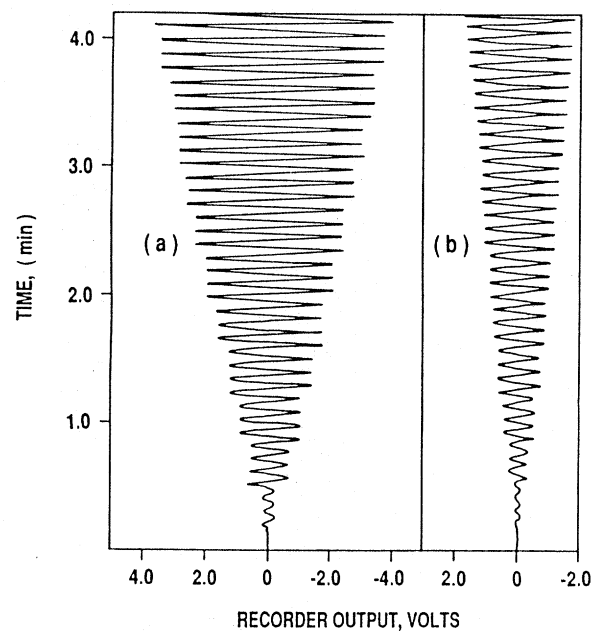

FIG. 5. TIME PROFILE ON STRAIN SWEEP AT FREQUENCY 1.0 RAD/S
Mozzarella cheese bonded to aluminum plates. A) 4 mm gap; B) 8 mm gap

(to 70°C) employed in the investigation. Addition of calcium caseinate reduced the initial softening point to about 30°C, a reduction of 5 to 6°C. The Schreiber melting index also declined with increasing calcium caseinate (data not shown). The cheese made with added caseinate occasionally had a marbled appearance, suggesting that the caseinate was not sufficiently dispersed in the milk, in spite of an 18 h hydration period.

The viscosity followed an Arrhenius relationship with temperature, i.e., $\eta = 0.032\ e^{4100/T}$ poise, where T is the absolute temperature and η the viscosity. The corresponding correlation with cheese containing 2% added calcium caseinate was found to be $\eta = 0.005\ e^{4750/T}$ poise. The addition of 1% calcium caseinate during processing increased the viscosity of the mixture by a factor of about 30%; 2% added calcium caseinate resulted in about a 50% increase in viscosity at room temperature.

The viscoelastic shear modulus is frequency dependent; the addition of 1% calcium caseinate increased the elastic and viscous components of the shear modulus over the corresponding values of natural Mozzarella cheese (Table 2). At the 2% calcium caseinate level, the elastic component of the modulus G′ showed a decrease below the baseline values of the natural cheese but the viscous

TABLE 2.
SHEAR MODULI OF NATURAL AND IMITATION MOZZARELLA CHEESES AT 20°C

Sample	G' (dynes/cm^2)	G" (dynes/cm^2)
Natural Mozzarella	$2.27 \times 10^5\ \omega^{0.17}$	$1.03 \times 10^5\ \omega^{0.19}$
with 1% calcium caseinate	$5.92 \times 10^5\ \omega^{0.20}$	$1.98 \times 10^5\ \omega^{0.14}$
with 2% calcium caseinate	$1.59 \times 10^5\ \omega^{0.21}$	$1.98 \times 10^5\ \omega^{0.16}$

Here the frequency ω is in radians per second; G' and G" are the elastic and viscous components of the shear modulus respectively. The data were obtained at 0.5% strain with a 4 mm gap.

component G″ increased. We are at a loss to explain this effect. Compositional analysis showed that moisture content tended to increase with increasing levels of calcium caseinate but samples still met Standards for moisture (Code of Federal Regulations 1987). Figure 6 shows the variations of G′, G″, and η* with frequency (at a maximum shear strain of 0.5%) for natural Mozzarella, corresponding to the first line of data shown in Table 2. Up to a 0.5% maximum shear strain, the G* values were almost constant, indicative of linear behavior in the frequency range 0.1 to 100 rad/s.

Taranto and Yang (1981) reported a disturbance in the milk fat globule distribution in imitation Mozzarella cheeses made with soybean protein. Tunick *et al.* (1989) found that the distribution of fat globules in Mozzarella with added calcium caseinate is not uniform, resulting in lipid-free zones in the cheese matrix. This nonuniform distribution has been shown to reduce the thermal stability of the imitation cheese and could have a similar effect on the viscoelastic modulus.

CONCLUSIONS

Repeatable results with no evidence of slippage may be obtained with Mozzarella cheese samples bonded to the aluminum parallel plates of the mechanical spectrometer with cyanoacrylate resin adhesive. This procedure has also worked well with Cheddar cheese.

The viscosity of low moisture, part skim Mozzarella is sensitive to calcium caseinate added during processing, following an Arrhenius relationship with temperature.

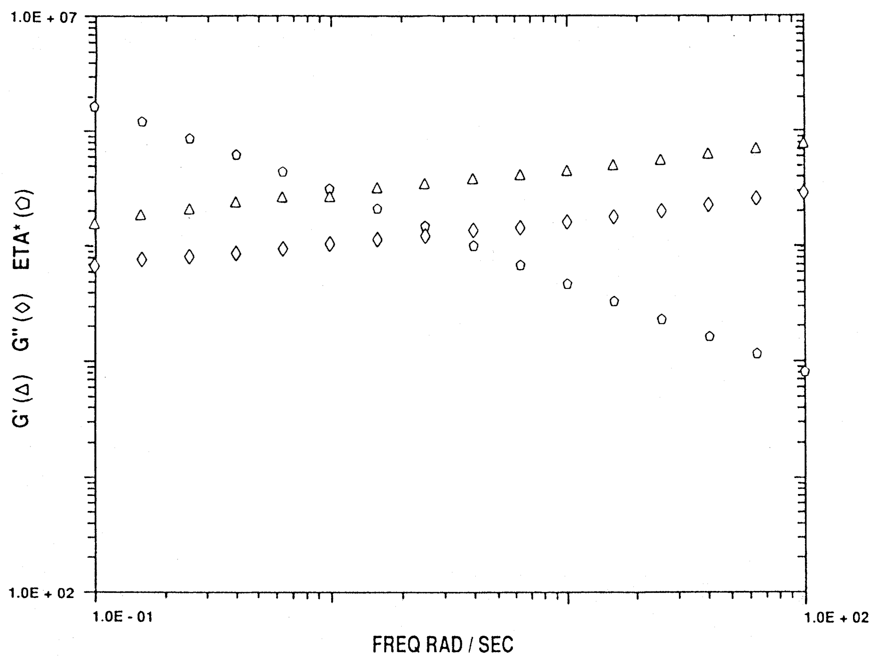

FIG. 6. STORAGE MODULUS (G′), LOSS MODULUS (G″) AND COMPLEX VISCOSITY (η^*) WITH RESPECT TO FREQUENCY AT 0.5% STRAIN
Mozzarella cheese bonded to aluminum plates, 4 mm gap

The addition of 1% calcium caseinate resulted in an increase in both elastic and viscous components of the shear modulus at room temperature whereas a 2% addition resulted in a decrease of the shear storage modulus G′ below that observed for natural Mozzarella under the same conditions.

Changes in cheese properties observed help provide an objective basis for distinguishing between imitation and natural low moisture, part skim Mozzarella cheeses.

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