The Lodge Rubberlike Liquid Behavior for Cheese in Large Amplitude Oscillatory Shear

Y.-C. Wang, S. Gunasekaran*, A. J. Giacomin[1]

Department of Biological Systems Engineering
460 Henry Mall
University of Wisconsin-Madison, Madison, WI 53706, USA

* Fax: x1.515.294.5444
E-mail: guna@facstaff.wisc.edu

[1] Department of Mechanical Engineering
University of Wisconsin-Madison, Madison, WI 53706, USA

Received: 29.12.2000, Final version: 10.11.2001

Abstract:
The viscoelasticity of reduced-fat Cheddar and Mozzarella cheeses was characterized in small (parallel disk rheometer, $\gamma_0 = 0.01$) and large (sliding plate rheometer, $0.2 < \gamma_0 < 7$) amplitude oscillatory shear at 40 and 60°C. We deduced the linear relaxation spectrum from the small strain measurements. At large strain amplitudes, we found sinusoidal stress responses whose amplitudes are well below those predicted from the linear relaxation spectrum, and yet remarkably linear with strain amplitude. We call this the *large strain linear regime*. We discovered that the Lodge rubberlike liquid can quantitatively explain the large strain linear regime if we scale down the relaxation moduli in the linear spectrum by a constant. This large strain linear regime persists to much higher strain amplitudes for Cheddar ($\gamma_0 \leq 4$) than for Mozzarella ($\gamma_0 \leq 1$). This is perhaps due to oriented structure of the protein matrix in the Mozzarella cheese.

Zusammenfassung:
Die Viskoelastizität von teilentrahmtem Cheddar und Mozzarellakäse wurde mittels SAOS (Parallelplatten-rheometer, $\gamma_0 = 0.01$) und LAOS (Sliding Plate Rheometer, $0.2 < \gamma_0 < 7$) Experimenten bei 40°C und 60°C gemessen. Das lineare Relaxationsspektrum wurde aus den SOAS Messungen hergeleitet. Bei LAOS Experimenten wurden sinusoidale Spannungsantworten beobachtet, deren Amplituden weit unter den aus dem linearen Relaxation-sspektrum vorhergesagten Werten liegen und dennoch bemerkenswert linear in der Amplidute sind ("Large strain linear regime"). Das Lodge Model für gummiartige Flüssigkeit kann das lineare Verhalten bei grossen Amplituden quantitativ erklären wenn die Relaxationsmoduli im linearen Regime mit einer Konstanten reskalieren werden. Der lineare Verhalten bei grossen Amplituden ist für Cheddar ($\gamma_0 \leq 4$) wesentlich grösser als für Mozzarella ($\gamma_0 \leq 1$). Dies kann vielleicht auf die orientierte Struktur der Proteinmatrix im Mozzarellakäse zurückgeführt werden.

Résumé:
La viscoélasticité de la Mozarella et du Cheddar à contenance réduite en matières grasses a été caractérisée à l'aide de cisaillements oscillatoires de petites (rhéomètre à disques parallèles, $\gamma_0 = 0.01$) et grandes (rhéomètre à plaques glissantes) amplitudes, à 40 et 60°C. Nous avons déduit le spectre de relaxation linéaire à partir des mesures à petite déformation. A grandes amplitudes de déformation, nous avons trouvé des réponses sinusoidales de la contrainte, avec des amplitudes qui sont bien en dessous de celles prédites par le spectre de relaxation linéaire. De plus, ces réponses sont encore remarquablement linéaires avec l'amplitude de la déformation. Nous appelons ceci le régime linéaire de grande déformation. Nous avons découvert que le liquide caoutchoutique de type Lodge permet quantitativement d'expliquer le régime linéaire de grande déformation, si nous divisons les modules de relaxation dans le spectre linéaire, par une constante. Ce régime linéaire de grande déformation persiste jusqu'à des amplitudes de déformation bien plus grandes pour le Cheddar ($\gamma_0 \leq 4$) que pour la Mozarella ($\gamma_0 \leq 1$). Ceci est peut-être du à une structure orientée de la matrice protéinique dans la Mozarella.

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
http://www.appliedrheology.org

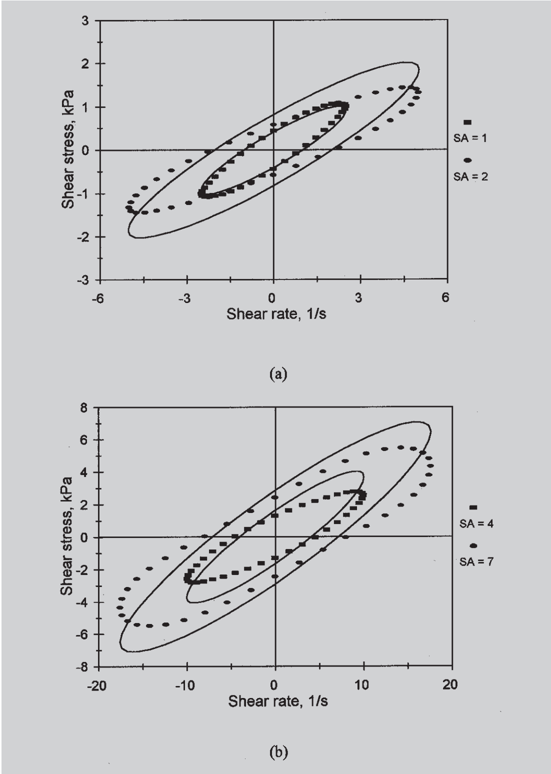

Figure 10 (left): The predicted shear stress (•) versus shear strain rate loop (lines) for Mozzarella cheese at 60°C using the relaxation spectrum determined from LAOS test compared with the experimental σ versus $\dot{\gamma}$ loop (•) (0.4 Hz, $1 \leq \gamma_O \leq 7$).

down by the ratio of the stress amplitudes using the following equation:

$$G_i = \frac{\sigma_1}{\sigma_o} \qquad (12)$$

where, σ_O is the stress amplitude evaluated at 0.4 Hz and at γ_O = 0.01 and calculated from the discrete relaxation spectra (see Tab. 2). σ_1 is the measured shear stress amplitude at 0.4 Hz and at γ_O = 0.2. We call this the relaxation spectrum for the large strain linear regime.

The predictions using the relaxation spectrum for the large strain linear regime are in Figs. 5 and 6. The measured σ versus $\dot{\gamma}$ loops are elliptical at γ_O = 0.2 for both cheeses at 40 and 60°C. The predicted and experimental σ versus $\dot{\gamma}$ loops match at 60°C for both cheeses. At 40°C, the predicted slightly exceed the experimental σ versus $\dot{\gamma}$ loops for Cheddar cheese, but do not fit the Mozzarella data well. Figs. 7 and 8 show the predicted and experimental σ versus $\dot{\gamma}$ loops for Cheddar cheese at 60°C: 0.4 Hz and $\gamma_O < 1$ and $\gamma_O > 1$, respectively. Figs. 9 and 10 show similar results for the Mozzarella cheese. The predicted and experimental data match up to γ_O = 4 for Cheddar, and up to γ_O = 1, for Mozzarella. Comparing these, we can state that the Cheddar cheese exhibits large strain *linear viscoelastic behavior* over a wider strain range than Mozzarella $\gamma_O \leq 4$ for Cheddar compared to $\gamma_O \leq 1$ for Mozzarella. Why? Cheddar cheese may be more uniform and more structurally homogeneous than Mozzarella. The mixing-molding step in the Mozzarella manufacture orients the protein fiber structure [24]. The effect of this oriented structure has also been observed in other rheological measurements [18].

The large strain linear behavior is equally difficult to explain. It would appear that at rest, the cheese has one equilibrium structure, and that in large amplitude oscillatory shear, it converts to another non-equilibrium structure. Whereas the equilibrium structure is independent of small amplitude deformations, its non-equilibrium counterpart appears to be equally independent large amplitude deformations.

5 CONCLUSION

Cheddar and Mozzarella cheeses at 40 and 60°C were characterized in large amplitude oscillatory shear. At large strain amplitudes, we found sinusoidal stress responses whose amplitudes are well below those predicted from the linear relaxation spectrum, and yet remarkably linear with strain amplitude. We call this the large strain linear regime. We discovered that the Lodge rubberlike liquid can quantitatively explain the large strain linear regime if we scale down the relaxation moduli in the spectrum by a constant. This large strain linear regime persists to much higher strain amplitudes for Cheddar ($\gamma_O \leq 4$) than for Mozzarella ($\gamma_O \leq 1$).

REFERENCES

[1] van Vliet T: Mechanical properties of concentrated food gels. in: *Food macromolecules and colloids*. The Royal Society of Chemistry, Oxford, England (1995).

[2] Clinard RL: Rubber-metal parts testing simulates service condition. Ind. Res. Dev. 3 (1982) 130-133.

[3] Gunasekaran S, Ak MM: Dynamic oscillatory shear testing of foods B selected applications. Trends in Food Science and Technology 11 (2000) 115-127.

[4] Giacomin AJ, Dealy JM: Large amplitude oscillatory shear, in *Techniques in Rheological Measurement*. Collyer AA, Clegg (ed.). Elsevier Applied Science Publishers Ltd., London. (1993) 99.

[5] Giacomin AJ, Samurkas T, Dealy JM: A novel sliding plate rheometer for molten plastics. Polym. Eng. Sci. 29 (1989) 499-504.

[6] Tariq S, Giacomin AJ, Gunasekaran S: Nonlinear viscoelasticity of cheese. Biorheology 35 (1998) 171-191.

[7] Giacomin AJ, Oakley JG: Upper convected Maxwell models for molten plastics in large amplitude oscillatory shear. J. Rheology 36 (1992) 1529.

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
http://www.appliedrheology.org

[8] Pearson DS, Rochefort WE: Behavior of concentrated polystyrene solutions in large amplitude oscillatory. J. Polym.Sci.: Pol. Phys. Ed. 20 (1982) 83.

[9] Mewis J, Denn MM: Constitutive equations based on the transient network concept. J. Non-Newtonian Fluid Mech. 12 (1983) 69.

[10] Giacomin AJ. Jeyaseelan RS: A constitutive theory for polyolefins in large amplitude oscillatory shear. Polym. Eng. Sci. 35 (1995) 768-777.

[11] Liu TY, Soong DS, Williams MC: Transient and steady rheology of polydisperse entangled melts: prediction of a kinetic network model and data comparisons. J. Polym. Sci. 22 (1984) 1561.

[12] Jeyaseelan RS, Giacomin AJ: Structural network theory for a filler polymer melt in large amplitude oscillatory shear. Polym. Gels and Network 3(1995) 117-133.

[13] DeKee D, Fong CF: Modelling of complex suspensions. In *Theoretical and Applied Rheology*. Edited by Moldenaers and Keunings, Elsevier Science Publishers Ltd.,Oxford, Amsterdam (1992).

[14] Vanderwarn MA: *Analysis of cheese and cheese products for moisture*. MS thesis, University of Wisconsin-Madison, Madison, WI. (1989).

[15] Bradley RL Jr., Arnold E Jr., Barbano DM: *Standard Methods for the Examination of Dairy Products*. 16th ed. (Ed. R. T. Marshall), Am. Publ. Health Assoc., Washington, DC. (1992) 433-531.

[16] Johnson ME, Olson NF: A comparison of available methods for determining salt levels in cheese. J. Dairy Sci. 68 (1985) 1020-1024.

[17] Van Slyke L L, Price WV: *Cheese*. Ridgeview Publ. Co., Atascadero, CA (1979) 4760-4786.

[18] Ak MM, Gunasekaran S: Anisotropy in tensile properties of Mozzarella cheese. J. Food Sci. 62 (1997) 1031-1033.

[19] Casiraghi EM, Bagley EB, Christianson DD: Behavior of Mozzarella, Cheddar and processed cheese spread in lubricated and bonded uniaxial compression. J. Text. Studies, 16 (1985) 281-301.

[20] Bird RB, Armstrong RC, Hassager O: *Dynamics of polymeric liquids*. Volume 1: Fluid mechanics, second edition. John Wiley & Sons, Inc., New York. (1987).

[21] Dealy JM, Wissbrun KF: *Melt rheology and its role in plastics processing*. Van Nostrand Reinhold, New York (1990).

[22] Winter HH, Baumgaertel M, Soskey PR: A parsimonious model for viscoelastic liquids and solids. In: Techniques in Rheological Measurement. Collyer AA (ed.). Chapman & Hall, New York (1993).

[23] Tee TT, Dealy JM: Nonlinear viscoelasticity of polymer melts. Trans. of the Soc. Of Rheology 19 (1975) 595-615.

[24] Oberg CJ, McManus WR, McMahon DJ: Microstructure of Mozzarella cheese during manufacture. Food Structure 12 (1993) 251-258.

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
http://www.appliedrheology.org