CONSTITUTIVE MODELS FOR FOOD SYSTEMS

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Contents

Summary

Constitutive modeling of food polymeric materials is useful in predicting the rheological behavior of food materials over a wide range of strain rates. The rheological behavior is directly related to food quality attributes such as texture, mouth feel, stability, etc. The rheological models chosen here to study food polymers are those commonly used to model general polymeric systems. These include several different types of rheological models, such as the integral and differential viscoelastic models, and those derived from dilute solution theories, concentrated dispersion theories, etc. The use of such models is discussed with real food systems. The experimental data for the food systems were obtained in the author's laboratory over the last two decades.

1. Introduction

Models able to describe the behavior of materials in all components of stress, strain, and strain rates are called "constitutive models". Constitutive models are often derived from fundamental molecular theories. Therefore, by relating rheological measurements to molecular structures and conformations of food polymers and food systems, one can use appropriate constitutive models to predict the rheological behavior over a wide range of strain rates.

Food systems are often polymeric materials consisting of long chain molecules, such as starch, proteins, lipids, polysaccharides, and other macromolecules. A typical approximation of a polymeric system is to consider the polymer molecules as a freely jointed chain consisting of springs and beads. Such approximations can help understand the deformations that occur during the processing of foods, which are generally a combination of shear and extensional flows. Examples include dough sheeting, extrusion (see *Extrusion*), mixing processes (see *Food Mixing*) and other unit operations common to the food industry.

The various constitutive models and their basis are discussed along with examples illustrating the use of constitutive models in predictive rheology.

2. Linear Viscoelasticity

Linear viscoelasticity is observed at small deformations where the polymeric material is negligibly disturbed from its equilibrium state (see *Viscoelasticity*). The shear relaxation modulus $G(t,\gamma_o)$ is one of the rheological properties used to characterize linear viscoelastic materials and is independent of the applied strain in the linear viscoelastic region:

$$G(t,\gamma_o) = \frac{\sigma(t)}{\gamma_o} \tag{1}$$

$\sigma(t)$ is the time dependent shear stress resulting from the applied deformation γ_o. In uniaxial extension, the tensile relaxation modulus is given by:

$$E(t,\varepsilon_O) = \frac{\sigma_{11}}{\varepsilon_O} \tag{2}$$

where $\sigma_{(11)}$ is the extensional stress and ε_o the extensional strain. In developing linear constitutive models, the "Boltzmann superposition principle" is used, which assumes one can simply superimpose stresses resulting from strains at different times and vice versa. This principle is shown mathematically as:

$$\sigma(t) = \sum_{i=1}^{N} G(t-t_i)\delta\gamma(t_i) \tag{3}$$

where $\delta\gamma(t_i)$ is the incremental strain applied at time t_i and $G(t-t_i)$ a function that links stress and strain behavior. The integral form of this equation when $\delta\gamma\rightarrow 0$ is:

$$\sigma(t) = \int_o^t G(t-t')d\gamma(t') \tag{4}$$

The measured relaxation modulus as a function of time can then be simulated using a

single element or a generalized multiple-element Maxwell model. The shear relaxation modulus for a single element is given by:

$$G(t) = G_o \exp(-t/\lambda) \tag{5}$$

And the linear constitutive model is given by:

$$\tau_{ij}(t) = \int_{-\infty}^{t} G_o \left\{\exp[-(t-t')/\lambda]\right\} \dot{\gamma}_{ij}(t')dt' \tag{6}$$

When the data needs more adjustable parameters, the generalized Maxwell model given below is used:

$$\tau_{ij}(t) = \int_{-\infty}^{t} \sum_{k=11}^{n} G_k \left\{\exp[-(t-t')/\lambda_k]\right\} \dot{\gamma}_{ij}(t')dt' \tag{7}$$

where G_k and λ_k are the appropriate moduli and relaxation times of the Maxwell element. Figure 1 shows the mechanical analog of the generalized Maxwell model.

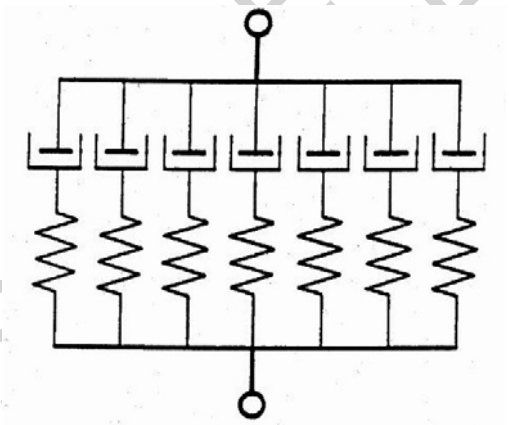

Figure 1. A mechanical analog of the generalized Maxwell model.

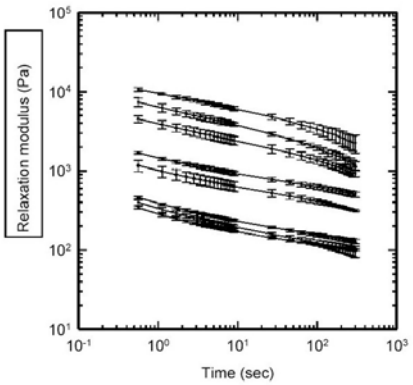

Figure 2. Linear and nonlinear shear relaxation moduli for 18.8% protein flour dough.

The behavior of the relaxation modulus over sufficiently long periods will be dominated by the relaxation time with the largest value and is called the "longest relaxation time" or "terminal relaxation time." Simulation of the relaxation modulus using the generalized Maxwell model for wheat flour dough is shown in Figure 2.

Small amplitude oscillatory measurements are also commonly used to characterize linear viscoelastic properties. The following equations are used for the storage and loss modulus when a generalized Maxwell model is used to simulate linear viscoelastic behavior.

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

$$G''(\omega) = \sum_{i=1}^{N} \frac{G_i\omega\lambda_i}{[1+(\omega\lambda_i)^2]} \tag{9}$$

3. Dilute Solution Theories

For linear high molecular weight food polymers in dilute solutions such as tomato pectins and alginates, the Rouse and Zimm theories provide a basis for quantitative predictions of linear viscoelastic properties.

The Rouse model is based on the assumption that large polymer molecules can be simulated using straight segments that act as simple linear elastic springs. The springs are connected by beads, which give rise to viscous resistance. The combination of elastic and viscous effects causes viscoelastic behavior. The equations to predict the reduced storage and loss moduli and relaxation time of flexible random coil molecules of the Rouse and Zimm type are given below:

$$[G']_R = \sum_{p=1}^{n} \frac{\omega^2\tau_p^2}{(1+\omega^2\tau_p^2)} \tag{10}$$

$$[G'']_R = \sum_{p=1}^{n} \frac{\omega\tau_p}{(1+\omega^2\tau_p^2)} \tag{11}$$

where $[G']_R$ is the reduced storage modulus given by:

$$[G']_R = \frac{G'M}{CRT} \text{ in the limit c->0.} \tag{12}$$

where G' is the storage modulus of the dilute solution, M the molecular weight, C the concentration, R the ideal gas constant, and T the absolute temperature. The reduced modulus $[G'']_R$ is then given by:

$$[G"]_R = \frac{(G"-\omega\eta_s)M}{CRT} \tag{13}$$

where η_s is the solvent viscosity, ω the frequency of oscillation, and G" the loss modulus. The relaxation time necessary to calculate the reduced storage and loss moduli is given as follows:

$$\tau_p = \frac{K_p[\eta]\eta_s}{CRT}M \tag{14}$$

where [η] is the intrinsic viscosity of the solution. The theories of Rouse and Zimm were used to study the conformation of apple, tomato, and citrus pectins in solution, including sodium alginate and propylene glycol alginate.

Estimation of intrinsic moduli [G'] and [G"] necessitates measurement of the storage modulus G' and the loss modulus G" at several concentrations in the dilute solution region and then extrapolation to zero concentration.

Small amplitude oscillatory measurements were conducted in 0.25 M NaCl to achieve maximum dissociation between chains in 95 percent glycerol and 5 percent de-ionized water mixtures as the solvent.

The reduced moduli were then calculated from intrinsic moduli by taking molecular weights and temperature into account. The longest relaxation time was calculated using the Rouse approximation:

$$\tau = \frac{6[\eta]\eta_s \mathrm{M}}{\pi^2 \mathrm{R\ T}} \tag{15}$$

where [η] is the intrinsic viscosity, η_S the solvent viscosity, M the molecular weight, and T the absolute temperature. Experimental reduced moduli are compared with predictions of the Rouse and Zimm models (Figures 3a, 3b and Figures 4a, 4b).

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Biographical Sketches

Dr. Jozef L Kokini currently is Professor II, Distinguished Professor of Food Engineering, in the Food Science Department, Chair of the Food Science Department and Director of the Center of Advanced Food Technology. He received his Ph.D. in Chemical Engineering from Carnegie-Mellon University in 1977. Over the last 21 years he focused his research on understanding the effect of molecular structure of food polymers on rheological properties. He led the groundwork to utilize constitutive and network theories to simulate rheological properties of food materials like wheat glutenin and wheat flour doughs, as well as carbohydrate polymers such as guar, gum, and pectins. His work also led to the understanding that wheat glutenin and gliadin were amorphous polymers undergoing glass transitions, and to the development of state diagrams to define the glassy, rubbery, and reactive regions in state diagrams, which help predict transformations in these proteins during processing and storage. The use of rheology has enabled the inclusion of entangled polymer flow and reactive regions as well as glass to rubber transition into state diagrams. Current studies continue to involve understanding the structural origins of rheological properties and the numerical simulation of complex viscosity flows pertaining to dough sheeting and extrusion, as well as gaining better and quantitative understanding of expansion phenomena.

Dr. Kokini was honored with the Harold Macy Food Science and Technology Award from the Institute of Food Technologists, as a Fellow of the Institute of Food Technologists in 2000, received the George W. Scott Blair Award from the American Association of Cereal Chemists in 1996, and in 1986 was recognized by IFT with the Samuel Cate Prescott Award. He was appointed Honorary Professor of Beijing Agricultural Engineering University in 1988. The research in his laboratory generated 115 publications, including a book he co-edited on "Food Extrusion Science and Technology." He was a Guest Editor of the *Journal of Rheology*, invited to prepare a special issue of the *Journal of Rheology* on Food Polymer Rheology and Processing. He has made 186 presentations nationally and internationally. He has supervised 20 Ph.D. students and 16 Master students and has provided opportunities for more than 20 undergraduate students and 26 visiting scientists to conduct research in his laboratory. He has been an invited speaker to 31 international and 41 national meetings and symposia, and has served on national panels for the National Science Foundation, National Academy of Sciences, USDA, and NASA. He has been a member of the Industrial Achievement Award Jury and Expert Panel of IFT, a member of the Program Committee of the American Association of Cereal Chemists and of the Development of NASA's Center Proposal and CELSS DWG Program, and of USDA and NASA NSF's research proposal review panels. Currently he is on the editorial board of 4 journals, secretary of New York IFT and an associate editor of *Cereal Chemistry*. He has been instrumental in bringing more than $11.7 million in grants and contracts to Rutgers University from the National Science Foundation, U.S. Army, Natick, NASA and numerous industrial member companies. He is a member of American Association for the Advancement of Science, American Association of Cereal Chemists, Society of Rheology, IFT, AIChE and Sigma Xi.

Dr. Muthukumar Dhanasekharan currently is a Computational Fluid Dynamics (CFD) Applications Engineer at Fluent Inc., Lebanon, New Hampshire. At Fluent Inc., Dr. Dhanasekharan works with eminent Chemical and Process Industry scientists to solve challenging engineering problems using CFD. He received his Ph.D. in 2001 from Dr. Jozef L. Kokini's laboratory at Rutgers University. He received

his Bachelors in Chemical Engineering in 1995 from the prestigious Indian Institute of Technology (IIT), Chennai, India. Dr. Dhanasekharan's Ph.D. work was in the areas of predictive rheological modeling of wheat doughs using various constitutive models, and their application in numerical simulation of flow and heat transfer in food extrusion. He has made more than 10 conference presentations at the annual meetings of Institute of Food Technologists (IFT), American Institute of Chemical Engineers (AIChE), Society of Rheology (SoR), and the Society of Plastics Engineers (SPE). He also has 5 refereed publications in recognized journals such as Journal of Texture Studies, Journal of Food Process Engineering, etc. He is an active member of the Institute of Food Technologists, the American Institute of Chemical Engineers, and the Society of Rheology.