Modeling for nonlinear rheological behavior of mixed polysaccharide gels

メタデータ	言語: eng 出版者: 公開日: 2020-11-24 キーワード (Ja): キーワード (En): 作成者: Flores Stephen Lanoy メールアドレス: 所属:
URL	https://oacis.repo.nii.ac.jp/records/2048

MODELING FOR NONLINEAR RHEOLOGICAL BEHAVIOR OF MIXED POLYSACHARIDE GELS
Doctoral Dissertation
Flores Stephen Lanoy
Tokyo University of Marine Science and Technology
September 2020

SUMMARY

Carrageenan is a family of polymeric sulfated polygalactans extracted from various species of red seaweed. They form thermo-reversible hydrogels which are defined in rheological terms as swollen polymeric systems which fracture or rupture in the application of steady shear deformation. Their rheological properties are major factors for determining the functionality in any applications. Carrageenan has been widely used commercially in the food industry. It is used in food preparation for its gelling, thickening and emulsifying properties. In this study, two commercially important types of carrageenan due to their gelling properties, kappa and iota, are studied. The physico-chemical properties of kappa iota and their mixtures have been well studied. The gelation mechanism and resulting size of the phase separation in the cured gel is important for applications as these factors determine the flavor-release attributes. Furthermore, several studies about the rheological properties of mixed kappa-iota carrageenan gels have been published but have solely focused on the linear viscoelastic regime for providing the structure and behavior of the gels. An exploration to the nonlinear rheological properties of the gels may provide a more complete fingerprint of the structural behavior of the polymer network. Industrial processes involve large and fast deformation which makes large strains and frequencies (nonlinear region), before the material fractures or ruptures, the more relevant tests to analyze the properties of the polysaccharide gels. Nonlinear oscillatory measurements utilize Lissajous curves formed from the rheometer's raw strain and stress data. In the nonlinear region, the plot of the stress as a function of strain gives a non-elliptical Lissajous curve. They also bear the linear and nonlinear properties of the probed material. Owing to the wide applications of kappa-iota carrageenan mixed gels, central to this thesis is the nonlinear rheological study, specifically applying differential nonlinear rheological measurements (differential strain and pre-stress) and formulating a simple model to analyze nonlinear rheological properties of viscoelastic materials.

Nonlinear viscoelastic analysis aids to understand the rheological behavior of soft matter and complex fluids such as polymeric liquids, emulsions, biopolymer gels and synthetic polymers. These materials exhibit a wide variety of nonlinear viscoelastic response during their processing and applications. In this experiment, large amplitude oscillatory shear, differential strain and pre-stress measurements were performed on sample solutions of mixed kappa carrageenan and iota carrageenan solutions. As measurements enter the nonlinear regime, properties of soft materials and complex fluids yield a wide array of responses due to flow instabilities or network structure. LAOS experiments reveal that mixed carrageenan solutions exhibit intermediate properties of the kappa and iota components. At large enough strains, all gels exhibit strain softening in the elastic moduli due to irreversible deformations introduced in the gel networks. However, there is an expressed increase in the viscous moduli of both iota and the mixed gel until both transitions from a predominantly elastic to a viscous material. The softening of the elastic moduli and expressed increase in the viscous moduli is a hallmark behavior of soft glassy materials. Furthermore, analysis of the Lissajous curves from the raw oscillatory stress and strain data reveal that the mixtures of carrageenan an intracycle hardening. The onset of the softening is dependent on the component gels.

Dynamic rheology usually refers to tests where an input oscillatory strain results in an output oscillatory stress, or vice versa. In the linear region, where the stress is proportional to the strain (for solids) or strain rate (for liquids), material properties represented by the storage (G') and loss (G'') shear moduli are sufficient to describe the macroscopic state of the system. Measurements done within the linear region are referred to as small amplitude oscillatory shear (SAOS) experiments. SAOS has become the best-known method for probing linear viscoelastic properties. It is unable, however, to distinguish between complex fluids that may show similar linear properties, but very different nonlinear properties. The difference in nonlinear behavior may be due to their microstructure (gels, concentrated emulsions or suspensions) or molecular topology (linear or long chain

branching polymers). The amount of information collected from the test can thus be improved by deliberately increasing the strain or stress to the large amplitude oscillatory shear (LAOS) region, i.e., measuring under nonlinear conditions.

LAOS experiments are carried out by imposing either a high enough strain (LAOS Strain) or stress (LAOS Stress) to cause nonlinear deformation. In the linear region, fixed-strain and fixed-stress oscillatory experiments yield the same material properties. However, it has been shown these two types of experiments yield different material properties in the LAOS regime. The difference was attributed to the inertial effects present in stress-controlled rheometers. Plots of the stress as a function of strain, also known as Lissajous curves, are elliptical in the linear regime, with deviations from ellipticity bearing evidence of nonlinear behavior.

Different analyses have been applied to interpret experimental LAOS results. Approaches such as Fourier Transform Rheology (FTR) Stress Decomposition (SD), the utility of Chebyshev polynomials of the first kind (Ewoldt et al., 2008), and Sequence of Physical Processes (SPP) have been used in this context. To be descriptive, treatments need to generalize deviations from the linear (sinusoidal) regime and to extract nonlinear material properties. Although these approaches successfully quantify nonlinearity, they do not make use of constitutive models (e.g., Maxwell model and Kelvin-Voigt model). Studies have emphasized that material properties (such as G' and G") are more readily interpreted when they are derived from constitutive equations. Mechanical models incorporating these equations can be used as a guide in the physical interpretation of nonlinear properties.

Models require an inherent simplicity, mathematical robustness, and ease of the physical interpretation. Giacomin et al. (2011) showed that the tensorial model of the corotational Maxwell element could be the simplest way to predict the nonlinear shear stress in LAOS flow, where the corotational derivative of the stress tensor generates the nonlinearity. The average experimentalist, however, may lack experience in the use of tensors and fluid dynamics models, thus finding this model inaccessible. Consequently, simpler scalar one-dimensional versions of the Maxwell model have been developed. In simple cases, the nonlinearities can occur in the spring (hardening or softening) or the dashpot (thickening or thinning). A combination of these nonlinear phenomena can be used to classify the material. Other studies have modified either the function for the elastic modulus of the spring or the viscous modulus of the dashpot. Models have been developed for yield-stress fluids wormlike micelles, and other materials, by modifying either modulus. These models, however, are specific to the material probed and may not always provide a viable tool for general classification. For most viscoelastic materials, the nonlinear behavior is unknown before the experiment.

A simple analysis of large amplitude oscillatory shear (LAOS) using a modified Maxwell model is presented. The set up describes a range of nonlinear behaviors by representing the general response of the spring and dashpot as a power series expansion. The behavior of the model is simulated with oscillatory input. The simple Maxwell model is extended to the nonlinear regime by introducing a series expansion to represent the nonlinearities in the spring and dashpot components. We set forth to propose a framework that could identify the general nonlinear viscoelastic behavior in LAOS based only on a few parameters in the simplest mechanical model. The Maxwell model is modified to obtain general constitutive equations that have parameters that can quantify combinations of linear and nonlinear viscoelastic phenomenon. One advantage of this approach is that the model is kept simple focusing only on the spring and dashpot. The power series and its inverse function can also be used to express other fading or accelerating responses with certain limitations. A model that utilizes four parameters that can be used to describe the linear and nonlinear properties of viscoelastic responses is derived. Average lines derived from the spring and dashpot responses are introduced. These average lines visually quantify the nonlinearities in the Lissajous curves and can be directly attributed to a physical definition. The model and its parameters have the potential to analyze the nonlinear properties of different complex fluids.

For different viscoelastic materials, linear rheology can be conveniently used to compare the different bulk structural changes happening during a test measurement. However, in the nonlinear region, nonlinear rheological techniques are still not standardized to be able to compare common measurement parameters. In this study, the constitutive equations of the previously developed Maxwell model-based analysis for large amplitude oscillatory shear (LAOS) rheology were normalized to derive a standard measurement curve. This method yields two new parameters, one linear and one nonlinear, to describe the properties of the Lissajous curves. This normalization can be used to compare different nonlinear behaviors. It is shown that the normalization technique can be used to directly compare different nonlinear phenomena by collapsing the component stress, strain and strain rate of the spring and dashpot into a single curve.

As a summary, the linear and nonlinear rheological behavior of the kappa-iota carrageenan mixed gel has been measured. The experimental results in this experiment show the first exploration of the nonlinear oscillatory rheological measurement of the kappa-iota carrageenan mixed gel. It is to be noted however that these observations are based on macroscopic rheological data. A complete characterization of its properties paves the way to designing materials that can be tweaked depending on a specific use. It is also demonstrated that the analysis based on the modified Maxwell model can be used to study the nonlinear rheological properties of viscoelastic materials.