RHEOLOGICAL MODELLING OF WORMLIKE MICELLES SYSTEMS USING FRACTIONAL VISCOELASTIC MODEL

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Abstract

Rheological constitutive equations with operators of fractional integration or differentiation play an increasing role at the phenomenological description of polymeric materials. The wormlike micelles system is formed by mixing Cetyltrimethylammonium bromide (CTAB) and sodium nitrate ($NaNO_3$). Two wormlike micelle systems belonging to the low and high salt regime are prepared. The effects of copolymer on the rheological behavior of the two worm like micelles system are investigated by rheological measurements. A fractional rheological description is obtained by replacing the first order time derivatives with fractional derivatives of order q and μ. The Friedrich-Braun model relating stress to strain is used to fit the experimental results on these wormlike micelle systems. The comparison between the experimental results and theoretical predictions showed good agreement.

Introduction

Rheological equations with fractional derivatives have become popular to describe the properties of polymers since the end of 1960s. Specifically, the various relaxation equations are of main interests. In general, these equations are derived from known models by substituting time ordinary derivatives of stress and strain by derivatives of fractional orders. Bagely and Torvik (1983) showed that fractional calculus models of viscoelastic material were consistent with the molecular theory and obtained the fractional differential equation of order ½ (Bagely and Torvik, 1983). Schiessel and Blumen (1993) showed that the fractional differential or integral equations arise naturally when expressing the rheological behavior of fractal model not as a mathematical artifact (Schiessel and Blumen, 1993).

Viscoelastic materials are of great interest in a variety of applications. Viscoelastic surfactant solutions have been studied over many years, both theoretically and experimentally (Binks *et al.,* 2003). These solutions contain long flexible or semiflexible micelles, described as worm- thread- or rodlike, that become entangled at high concentrations. Under certain conditions of concentration, salinity, temperature, presence of centurions, etc., the micelles present in aqueous solutions of surfactants tend to grow. In some systems, long wormlike micelles form at higher surfactant concentrations and/or upon addition of a salt (Hartman and Cressely, 1998). Also, in some systems, cosurfactants play an essential role for high viscoelasticity to appear (Cappelaere and Cressely, 1998).

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Previously, viscoelastic materials have been characterized primarily by Kelvin-Voigt model for constitutive relationship (Eldred *et al*., 1996). This type of materials posses a characteristic which can be descriptively referred to as a memory effect. The material response is not only determined by the current state of stress, but is also determined by all past states of stress, and in general sense, the material has a memory for all past state of stress. A similar situation exist if one considers the deformation as being specified, and thus, the current stress depends upon the entire past history of deformation (Christensen, 1982). One of the important problem areas associated with viscoelastic constitutive relations and analysis is the phenomenological curve fitting of actual creep and/or relaxation data by least square or other methods. Attempts were made to fit the properties of the fluid with conventional models of viscoelasticity. It was not possible to achieve satisfactory fit of the experimental data over the entire range of frequencies (Palade *et al*., 1999). In this work a fractional rheological description is obtained by replacing the first order time derivatives with fractional derivatives of order q and μ. The Friedrich-Braun model relating stress to strain is used to describe the experimental results on the wormlike micelle systems. The comparison between the experimental results and theoretical predictions are represented.

Experimental

The effects of copolymer on the rheological behavior of two wormlike micelles belonging to the low and high salt regime have been studied by our group (Siong *et al*., 2001). The wormlike micelles system is formed by mixing Cetyltrimethylammonium bromide (CTAB) and sodium nitrate ($NaNO_3$) in air tight glass tube. The two solutions correspond to the following compositions (A) CTAB (0.3 M), $NaNO_3$ (0.41 M) and (B) CTAB (0.3 M), $NaNO_3$ (1.79 M) were prepared. The rheological properties of the wormlike micelles as a function of copolymer concentration in water, for both compositions, are investigated. The (CTAB, 99%) and ($NaNO_3$, 98%) were purchased from Fluka and BDH chemical respectively. The copolymer is a commercially available symmetrical triblock copolymer with trade name synperonics F68 obtained from Fluka. Doubly distilled and deionised water having resistivity of 18.2 MΩ was used throughout the sample preparation. The final solutions were left standing for at least two days to achieve the equilibrium. The rheological properties of the copolymer doped wormlike micelles were measured using a Haake Rheo-Stress 150 rheometer with cone and plate geometry.

Friedrich-Braun's Model

Even though fractional calculus dates back to last century, and some authors such as Gement and Scott Blair suggest using fractional derivatives to describe the behavior of viscoelastic materials, it is only in recent times that this mathematical technique has found an increasing application in the description of different physical phenomena including rheological behaviors. A fractional derivative is an operator that generalizes the differentiation order, allowing fractional values. The Riemann-Liouville (RL) fractional integral operator ${}_0D_t^{-q}$ (Oldham, 1974; Samko *et al*., 1993; Podlubny, 1999; Schiessel *et al*., 2000) order is given by

$$ {}_0D_t^{-q} f(t) = \int_0^t \frac{(t-\tau)^{q-1}}{\Gamma(q)} f(\tau)d\tau, 0 < q < 1. \quad (1) $$

where Γ is the gamma function. Next, the fractional derivative of order q is defined through

$$ D_t^q f(t) = \frac{d^n}{dt^n}(D_t^{q-n} f(t)) \ \ for\ 0 < n - q < 1 \quad (2) $$

The first fractional viscoelastic models (Bagely and Torvik, 1983) can be reduce to the form

$$ \tau(t) = G_0\gamma(t) + G_1\lambda^\alpha D^\alpha[\gamma(t)] \quad (3) $$

where, to the first term typical of an elastic solid a second term is added, containing fractional derivative of the deformation, which represents a viscoelastic behavior intermediate between that canonical of a Newtonian liquid ($\alpha = 1$) and that

of an elastic solid ($\alpha = 0$). Among all successive models that proposed by Friedrich and Braun appears to be one of the most promising, in particular for the description of mechanical spectra (Friedrich, 1992; Friedrich *et al*., 1995). Indeed, the application of thermodynamics consistency criteria do not result in a reduction of the number of the adjustable model parameter; accordingly, the expressions which are derived for $G'(\omega)$ and $G''(\omega)$ from this model are, beside very simple, also high flexible and apt to the description of quiet different behaviors. In its differential form, the model is given by

$$\tau + \lambda^q D^q[\tau] = G_\infty \{D^0[\gamma] + \lambda^q D^q[\gamma]\} + \Delta G \lambda^\mu D^\mu[\gamma] \quad (4)$$

where τ and γ are the stress and deformation tensors, respectively, λ is a characteristic time, G_e is the equilibrium modulus, ΔG quantifies the differences between G_e and the plateau modulus G_∞ ($\omega \to \infty$), and q and μ are the are the derivation orders. The relevant expression for $G'(\omega)$ and $G''(\omega)$ are

$$G'(\omega) = G_\infty + \Delta G \frac{(\lambda\omega)^\mu \left[\cos(\mu\frac{\pi}{2}) + (\lambda\omega)^c \cos((\mu - q)\frac{\pi}{2})\right]}{1 + 2(\lambda\omega)^q \cos(q\frac{\pi}{2}) + (\lambda\omega)^{2q}} \quad (5)$$

$$G''(\omega) = \Delta G \frac{(\lambda\omega)^\mu \left[\sin(\mu\frac{\pi}{2}) + (\lambda\omega)^q \sin((\mu - q)\frac{\pi}{2})\right]}{1 + 2(\lambda\omega)^q \cos(q\frac{\pi}{2}) + (\lambda\omega)^{2q}} \quad (6)$$

for $q = 0$, the model degenerate into equation (2).

Results and Discussion

Empirical data for wormlike micelle solutions with different copolymer concentration are used to illustrate how this model is able to describe the dynamic behavior in the fractional term.

A mechanical model for a viscoelastic fluid consists of an elastic spring with the Hookean constant G_0 and a dashpot with viscosity η_0 (Maxwell-model). If this combination is abruptly extended the resulting stress relaxes exponentially with a time constant which is given by $\lambda = \eta_0/G_0$. The zero-shear viscosity is thus a parameter that depends on both the structure of the system, because G_0 is determined by the entanglement points v, ($G_0 = vk$T), and the dynamic behavior of the system through λ both quantities are usually determined by oscillating rheological measurements. From the different equations for the viscosity fluid, the equations for the storage G' and the loss modulus G'' are given by:

$$G'(\omega) = G_0 \frac{\omega^2\lambda^2}{1 + \omega^2\lambda^2} \quad (7)$$

$$G''(\omega) = G_0 \frac{\omega\lambda}{1 + \omega^2\lambda^2} \quad (8)$$

Many rheological results of viscoelastic surfactant solutions can be represented over a large frequency range with a single structural relaxation time and a single shear modulus G_0. Fluids with such a simple rheological behavior are called Maxwell fluids. Figure 1 shows the variation of storage and loss modulus as a function of frequency for wormlike micelles with two different copolymer concentration. It also shows, the comparison between the experimental values and the curves predicted by equation (7) and (8) (solid lines) for the composition A with two copolymer concentrations. The fitting parameters are given in Table 1.

The dynamic moduli were fitted in fractional term by using equation (5) and (6) for storage and loss modulus respectively. The results are given in Table 2. The basic fractional model parameters are q and μ, which are restricted to the range $0 < q, \mu \leq 1$ and $q < \mu$. Figure 2 and 3 shows the comparison between the experimental values and the curves predicted by equations (5) and (6) (solid lines). There are good agreements between the theoretical predictions and experimental data.

It is generally accepted that increasing in salt concentration will increase the curvature energy of hemispherical end cap relatives to the cylindrical part of the elongated micelle. This lead to an increase in micellar length and hence in the zero shear viscosity. The relaxation time decrease as one incorporate more copolymer into wormlike micelle systems. The copolymer will adsorb onto the wormlike micelles surface and decorating the surface with polymer brushes, as the copolymer concentration increases, steric interaction between the copolymer will cause a

thinning in the micelle monolayer and as further increase the concentration, the steric interaction is much stronger than the surfactant attraction forces between the surfactant molecules on the micellar monolayers thus breaking the micelles to for shorter wormlike micelles. The end cap energy will be stabilized by copolymer anchoring onto the end cap. The decreasing in the relaxation time can be explained by a decrease in the mean size of the wormlike micelles (Cappelaere and Cressely, 1998). Olsson suggested that the effects of ionic strength on micelle length and stiffness dominate the rheological behavior of a micellar system. They postulated that at the beginning, the effect of increasing the salt concentration was to lengthen the chains and thereby increase their flexibility as a result of the lower surface charge density (Hartman and Cressely, 1998). This increase in length and flexibility stops when the concentration binding exceeds 100% and the surface charge can change sign. Further addition of salt increases the surface charge density, which stiffens the micelle and promotes a change in morphology from wormlike.

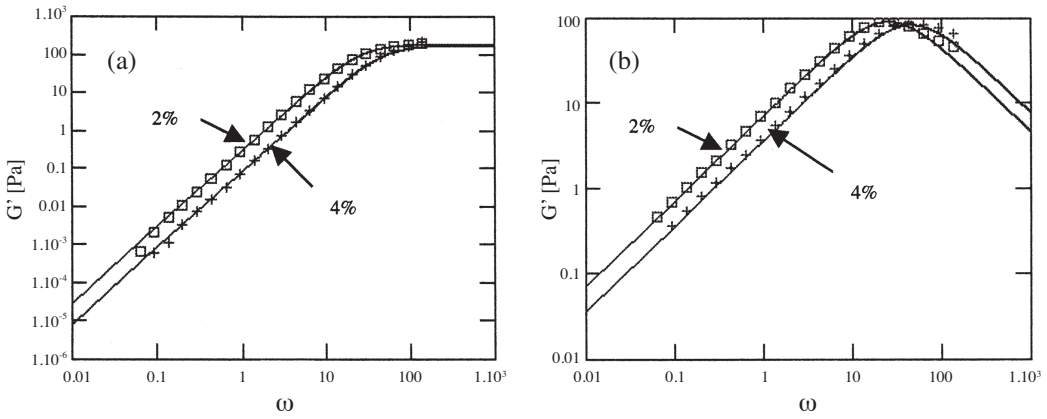

Figure 1. The storage modulus *G'* (a) and the loss modulus *G"* (b) as a function of frequency for composition A for two different copolymer concentrations using Maxwellian type fluids.

Table 1. The fitting parameters for Maxwell fluid.

Parameter	Composition A C = 2%	Composition A C = 4%	Composition B C = 2%	Composition B C = 4%
G_0 [Pa]	180	165	185.5	175.5
λ [s]	0.04	0.02	0.08	0.05

Table 2. The fitting parameters Friedrich-Braun's model.

Parameter	Composition A C = 2%		Composition A C = 4%		Composition B C = 2%		Composition B C = 4%	
	G'	*G"*	*G'*	*G"*	*G'*	*G"*	*G'*	*G"*
G_e [Pa]	76	76	78	78	51	51	54	54
ΔG [Pa]	260	260	265	265	255	255	255	255
λ [s]	0.03	0.01	0.03	0.01	0.05	0.03	0.05	0.03
q	0.85	0.89	0.89	0.87	0.88	0.89	0.87	0.88
μ	0.98	0.93	0.97	0.92	1	0.93	1	0.93

to spherical. Drye and Cates investigated theoretically the formation of cross links between wormlike micelles (Herb and Prud'homme, 1994). They concluded that the free energy cost for the formation of crosslinks is much higher than that for forming end caps. Also, the formation of smaller cylindrical micelles is easier than the formation of multi-connected network.

Conclusions

The fractional constitutive relationship model is more useful than the conventional model for describing the properties of viscoelastic fluids. Fractional derivatives provide an excellent instrument for the description of memory and hereditary properties of various materials and processes. This is the main advantage of fractional derivatives in comparison with classical integer-order models, in which such effects are in fact neglected. The advantage of fractional derivatives become apparent in the description of rheological properties of materials as well as in the modelling mechanical and electrical properties of materials, and in many other fields. All fractional derivative models posses memory kernels of the form t^{-q}, where $0 < q < 1$, see equation (1). Under some restrictions, $0 < q$, $\mu \leq 1$ and $q < \mu$, a good fit was achieved. The Friedrich-Braun model is

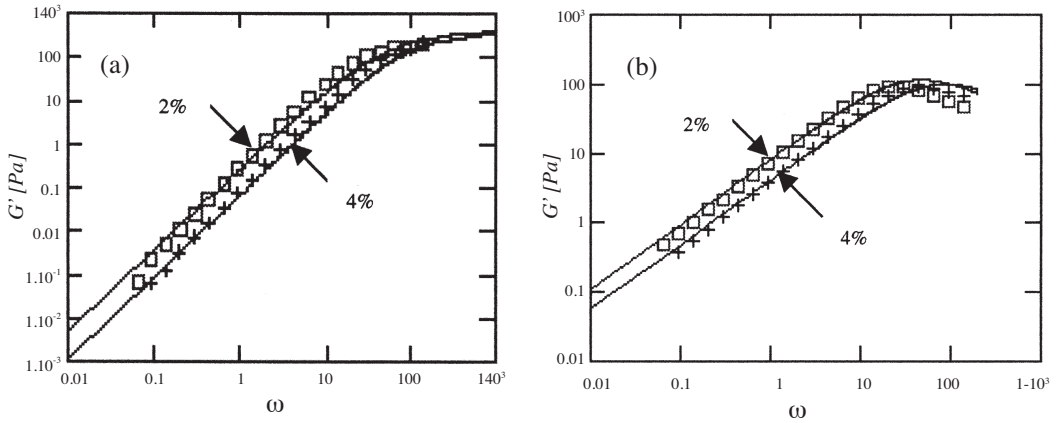

Figure 2. The storage modulus *G'* (a) and the loss modulus *G"* (b) as a function of frequency for composition A for two different copolymer concentrations.

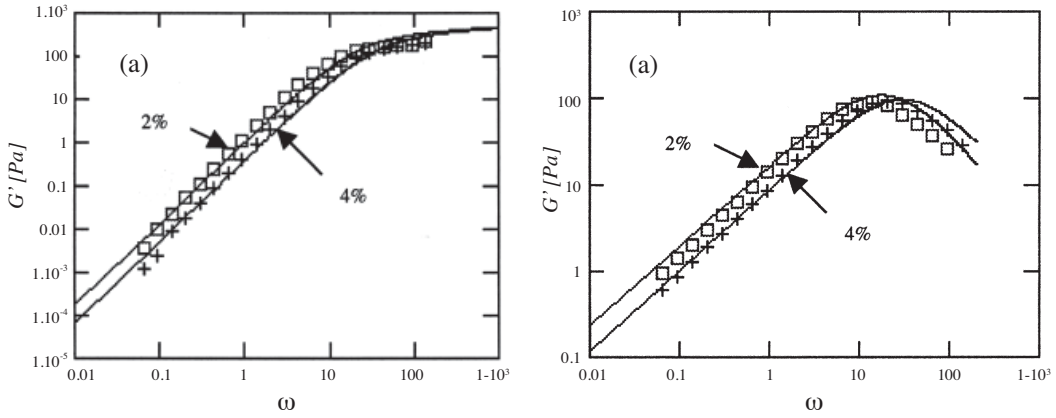

Figure 3. The storage modulus *G'* (a) and the loss modulus *G"* (b) as a function of frequency for composition B for two different copolymer concentrations.

appropriate to describe the behaviors for wormlike micelles systems in the presence of triblock copolymer. The evaluation of rheological parameter is correlated to the growing size of micelles. Physically, the longer the micelles, the easier their alignment in the shear flow (Herb and Prud'homme, 1994). The rheological results presented in this work are in agreement with the simple hypothesis that excess salt content brakes the micelle network junctions and so reduces the micelle length. The reduce in micelle length results in decreasing the relaxation time.

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