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ORIGINAL CONTRIBUTION

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New models for the complex shear modulus of nondilute emulsions of two immiscible viscoelastic liquids

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Abstract New equations for the complex shear modulus of concentrated emulsions of nearly spherical droplets are developed using a differential scheme. The continuous phase and the dispersed droplets are treated as viscoelastic liquids in the derivation. Complex shear modulus data on polymer-thickened oil-in-water emulsions are obtained experimentally and are compared with the predictions of the equations proposed. The equations proposed describe the experimental data very well.

Keywords Emulsion · Rheology · Viscoelastic · Complex modulus

Introduction

Emulsions are a class of dispersed systems consisting of two immiscible liquids, one is the dispersed phase and the other is the continuous phase. The droplets of emulsions are generally larger than 0.5 μm in diameter. In many commercial emulsion formulations, high-molecular-weight polymers are often incorporated into the emulsion system, although the reasons for adding the polymers vary from one application to another. In a large number of applications, polymers are used as thickeners to modify the rheology of the continuous phase [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16]. The thickening effect causes the dispersed droplets to remain suspended in the continuous medium, and thus sedimentation/creaming of dispersed droplets is eliminated. In food emulsions, there is an additional purpose for adding polymeric thickeners to the continuous phase, other than simply to extend the shelf life of the product, that is, to impart the required mouth-feel properties, pleasing appearance, and texture to the food products and to improve moisture retention.

There is a substantial amount of literature on the rheology of dilute and concentrated emulsions, but for the most part it has been limited to emulsions of Newtonian liquids [17, 18, 19, 20, 21, 22, 23, 24, 25]. Little work has been reported on the linear viscoelastic behaviour of emulsions in which the dispersed and continuous phases are viscoelastic in nature.

The main objective of this study is to develop new equations for the complex shear modulus of concentrated emulsions of nearly spherical droplets. The dispersed and continuous phases are treated as viscoelastic materials in the derivation. The equations developed are compared with experimental data on emulsions of oil droplets in a polymeric liquid.

Brief background

For an infinitely dilute emulsion of spherical droplets at low capillary numbers, Palierne [26] has shown that the complex shear modulus, G^*, in the linear viscoelastic region is given by

$$G^* = G_c^*\left[1+\left(\frac{G_c^*+2.5G_d^*}{G_c^*+G_d^*}\right)\phi\right], \tag{1}$$

in which G_c^* is the complex shear modulus of the continuous phase, G_d^* is the complex shear modulus of the dispersed phase, and ϕ is the volume fraction of the dispersed phase. Note that G^* is defined as $G^* = G' + jG''$, where G' is the storage modulus, G'' is the loss modulus, and j is the imaginary number, equal to $\sqrt{-1}$.

For polymer-thickened emulsions of low-viscosity Newtonian droplets, $G_d^* \to 0$. Thus Eq. (1) reduces to

$$G^* = G_c^*(1+\phi). \tag{2}$$

The Palierne equation (Eq. 1) cannot be applied at finite concentrations of the dispersed phase as the hydrodynamic interaction between the droplets is ignored in its derivation; therefore, Palierne [26] also extended the dilute emulsion equation (Eq. 1) to concentrated emulsions using a self-consistent treatment similar to the Lorentz sphere method in electricity. The equation for nondilute emulsions derived by Palierne is given as

$$G^* = G_c^*\left(\frac{1+\frac{3}{2}\phi\left(\frac{5G_d^*+2G_c^*}{5G_d^*+5G_c^*}\right)}{1-\phi\left(\frac{5G_d^*+2G_c^*}{5G_d^*+5G_c^*}\right)}\right). \tag{3}$$

In the limit $G_d^* \to 0$, Eq. (3) reduces to

$$G^* = G_c^*\left(\frac{1+\frac{3}{5}\phi}{1-\frac{2}{5}\phi}\right). \tag{4}$$

The Palierne equation (Eq. 3) generally underpredicts the values of the storage and loss moduli at high concentrations of the dispersed phase. Furthermore, it fails to exhibit divergence in G^* at $\phi \to \phi_m$, where ϕ_m is the maximum packing volume fraction of the droplets. At $\phi = \phi_m$, G^* is expected to diverge especially for emulsions with $G_d^* \to \infty$.

Development of new complex shear modulus equations

New complex shear modulus equations are derived using a differential scheme originally proposed by Brinkman [27] and Roscoe [28] to derive the viscosity equations for concentrated suspensions. Let us consider an emulsion with a volume fraction of droplets ϕ. Into this emulsion, an infinitesimally small number of new droplets is added. The increment increase in the complex shear modulus, dG^*, resulting from the addition of the new droplets can be calculated from the Parlierne equation (Eq. 1) by treating the emulsion into which the new droplets are added as an equivalent effective medium of complex shear modulus G^*. Thus,

$$dG^* = 2.5\left(\frac{G_d^*+0.4G^*}{G_d^*+G^*}\right)G^* d\phi. \tag{5}$$

This equation is separable, since we can write it as

$$\left(\frac{G_d^*+G^*}{G_d^*+0.4G^*}\right)\frac{dG^*}{G^*} = 2.5 d\phi. \tag{6}$$

Upon integration with the limit $G^* \to G_c^*$ at $\phi \to 0$, Eq. (6) gives

$$\left(\frac{G^*}{G_c^*}\right)\left(\frac{2G^*+5G_d^*}{2G_c^*+5G_d^*}\right)^{3/2} = \exp(2.5\phi). \tag{7}$$

This equation, referred to as model 1 in the remainder of the article, reduces to the following equation for emulsions with $G_d^* \to 0$:

$$\frac{G^*}{G_c^*} = \exp(\phi). \tag{8}$$

Model 1 is expected to describe the complex shear modulus data of emulsions only at low to moderate concentrations of the dispersed phase ($\phi \le 0.20$). At high ϕ, model 1 is expected to underpredict G^*. This is because in the derivation of the differential equation (Eq. 5) leading to model 1, it is assumed that all the volume of the emulsion before new droplets are added is available as free volume to the new droplets. In reality, the free volume available to disperse the new droplets is significantly less, owing to the volume preempted by the droplets already present. When new droplets are added to the emulsion the increase in the actual volume fraction of the dispersed-phase is $d\phi/(1-\phi)$. Thus,

$$dG^* = 2.5\left(\frac{G_d^*+0.4G^*}{G_d^*+G^*}\right)G^*\frac{d\phi}{1-\phi}. \tag{9}$$

Upon integration with the limit $G^* \to G_c^*$ at $\phi = 0$, Eq. (9) gives

$$\left(\frac{G^*}{G_c^*}\right)\left(\frac{2G^*+5G_d^*}{2G_c^*+5G_d^*}\right)^{3/2} = (1-\phi)^{-2.5}. \tag{10}$$

This equation, referred to as model 2 in the remainder of the article, reduces to the following equation for emulsions with $G_d^* \to 0$:

$$\frac{G^*}{G_c^*} = (1-\phi)^{-1}. \tag{11}$$

One limitation of models 1 and 2 is that they assume that the volume fraction of the dispersed phase can reach unity as more and more droplets are added to the emulsion. This is physically unrealistic, especially for emulsions of rigid particles ($G_d^* \to \infty$). In reality, there is an upper limit for ϕ, referred to as ϕ_m (maximum packing volume fraction of droplets), where a divergence in G^* is expected. Model 1 does not exhibit a divergence in G^* at all, whereas model 2 exhibits a divergence in G^* only at $\phi = 1.0$.

One possible way to account for the divergence in G^*at $\phi = \phi_m$ is to replace $d\phi$ in Eq. (5) by $d[\phi/(1-\phi/\phi_m)]$. Thus,

$$dG^* = 2.5\left(\frac{G_d^*+0.4G^*}{G_d^*+G^*}\right)G^* d[\phi/(1-\phi/\phi_m)]. \tag{12}$$

Mooney [29], in the derivation of his well-known equation for the viscosity of concentrated suspensions, made an equivalent assumption although the exact physics behind this modification is not clear at present. Upon integration, Eq. (12) gives

$$\left(\frac{G^*}{G_c^*}\right)\left(\frac{2G^*+5G_d^*}{2G_c^*+5G_d^*}\right)^{3/2} = \exp\left(\frac{2.5\phi}{1-\frac{\phi}{\phi_m}}\right). \tag{13}$$

This equation, referred to as model 3 in the remainder of the article, reduces to the following equation for emulsions with $G_d^* \rightarrow 0$:

$$\frac{G^*}{G_c^*} = \exp\left(\frac{\phi}{1-\frac{\phi}{\phi_m}}\right). \tag{14}$$

Another way to account for the divergence in G^* at $\phi = \phi_m$ for emulsions with $G_d^* \rightarrow \infty$ is to replace $d\phi$ in Eq. (5) by $d\phi/(1-\phi/\phi_m)$. Thus,

$$dG^* = 2.5\left(\frac{G_d^*+0.4G^*}{G_d^*+G^*}\right)G^* \frac{d\phi}{\left(1-\frac{\phi}{\phi_m}\right)}. \tag{15}$$

The justification for this modification is that the free volume of the continuous-phase fluid available when new droplets are added is $(1-\phi/\phi_m)$, instead of $1-\phi$; therefore, the increase in the volume fraction of the dispersed phase is $d\phi/(1-\phi/\phi_m)$. Krieger and Dougherty [30], in the derivation of their celebrated equation for the viscosity of concentrated suspensions, made an equivalent assumption.

Equation (15), upon integration, gives

$$\left(\frac{G^*}{G_c^*}\right)\left(\frac{2G^*+5G_d^*}{2G_c^*+5G_d^*}\right)^{3/2} = \left(1-\frac{\phi}{\phi_m}\right)^{-2.5\phi_m}. \tag{16}$$

This equation, referred to as model 4 in the remainder of the article, reduces to the following equation for emulsions with $G_d^* \rightarrow 0$:

$$\frac{G^*}{G_c^*} = \left(1-\frac{\phi}{\phi_m}\right)^{\phi_m}. \tag{17}$$

It is interesting to note that for emulsions with $G_d^* \rightarrow 0$, models 1–4 (Eqs. 8, 11, 14, 17) predict the phase-shift angle, δ, between oscillatory stress and strain to be independent of ϕ; from models 1–4, $\tan\delta$ is given by

$$\tan\delta = \frac{G''}{G'} = \frac{G_c''}{G_c'}. \tag{18}$$

Thus, $\tan\delta$ for emulsions with $G_d^* \rightarrow 0$ is the same as that of the continuous phase.

Finally, it should be emphasised that the models proposed are expected to be valid for emulsions of noncolloidal droplets having negligible nonhydrodynamic interactions (such as Coulombic, van der Waals, or depletion interactions).

Experimental

Materials

The emulsions of oil-in-water (O/W) type were prepared using a Newtonian petroleum oil (trade name EDM) supplied by Monarch Oil Company, Canada. This oil is widely used as a lubricant and as a solvent. The viscosity of the oil batch used in the present work was 5.8 mPas at 25 °C. The water used throughout the experiments was deionised. The surfactant used was Triton X-100, a commercially available nonionic surfactant currently manufactured by Union Carbide Co. The polymer used was Praestol 2540 TR, manufactured by Stockhausen, Greensboro, N.C., USA. Praestol 2540 TR is an anionic polymer based on the polymerisation of acrylamide. This polymer is used widely as a flocculating agent as well as a thickener in industries such as paper, textile, food, petrochemical, and mineral processing.

Procedure

A solution of 0.82% by weight Praestol 2540 TR was prepared by slowly sifting a known amount of polymer granules into a known volume of gently agitated deionised water at room temperature (about 21 °C). A variable-speed homogenizer (Gifford-Wood, model 1-L) was used to provide the necessary agitation and mixing of the fluid. The agitation was continued until the polymer had dissolved completely and the solution was lump-free. The required amount of surfactant (Triton X-100) was then added to the polymer solution; the surfactant dissolved readily with gentle agitation. The resulting solution had a surfactant concentration of 0.5% by weight. The solution was stored at room temperature for about 16 h prior to use.

The emulsions of O/W type were prepared in batches of approximately 300 g. The known amounts of aqueous polymer solution (containing 0.5% by weight surfactant) and oil were sheared together in a homogeniser for about 5 min at a fixed speed. The emulsions produced were very stable with respect to coalescence.

The droplet sizes of the emulsions were measured by taking photomicrographs of the emulsion samples. The samples were diluted with the surfactant solution (0.5% by weight Triton X-100) before taking the photomicrographs. The photomicrographs were taken with a Zeiss optical microscope equipped with a camera. The droplet size distributions of emulsions at different values of the dispersed-phase volume fraction, ϕ, are shown in Fig. 1. The droplet size increases somewhat with an increase in ϕ, although the increase is moderate. The number-volume mean diameters for various emulsions are as follows: $\phi = 0.20$, $d = 7.6$ µm; $\phi = 0.51$, $d = 9.3$ µm; $\phi = 0.65$, $d = 11.7$ µm.

The rheological experiments were carried out at 25 °C using a Bohlin controlled-stress rheometer (Bohlin CS-50). A cone-and-plate measuring system was used. The cone diameter was 40 mm and the plate diameter was 60 mm. The cone angle was 4° and the

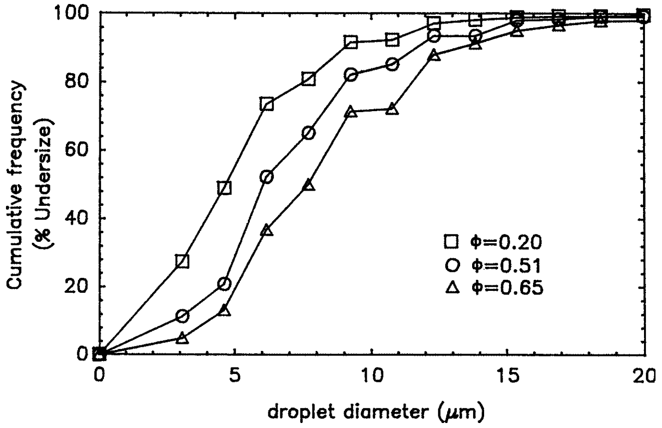


Fig. 1. Droplet size distributions of emulsions

gap at the cone tip was 150 μm. In order to establish the linear viscoelastic region, the rheological parameters were first measured as a function of stress amplitude at a fixed frequency of 0.05 Hz. Once the linear viscoelastic region had been established, measurements were then made at a low stress amplitude of 0.2 Pa (which was well within the linear viscoelastic region) as a function of frequency.

Comparison of experimental data with model predictions

The frequency-sweep results for the continuous phase of the emulsions, i.e., the polymer/surfactant solution, within the linear viscoelastic region are shown in Fig. 2. The magnitude of G^* as well as tanδ are plotted as a function of frequency. With the increase in the oscillation frequency of the stress, G^* increases, whereas tanδ decreases. This behaviour is typical of polymer solutions.

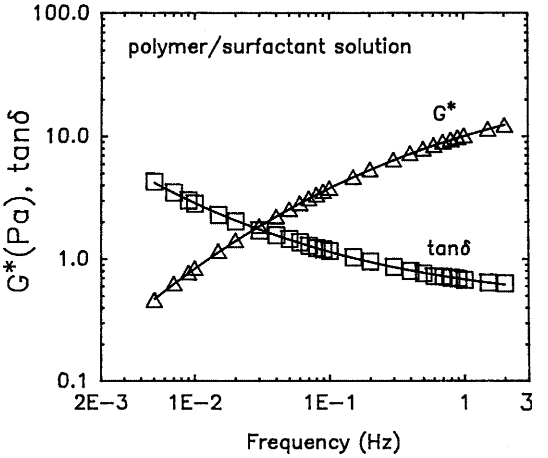


Fig. 2. Complex shear modulus, G^*, and tanδ data of polymer/surfactant solution, i.e., the continuous-phase fluid of emulsions

Experimental data of emulsions are compared with the complex shear modulus equations developed earlier in the article in Figs.3, 4, 5, 6, and 7. The experimental data, consisting of G^* and tanδ as functions of the oscillation frequency of the stress, are plotted and compared with the model predictions at various volume fractions of the dispersed phase.

Fig. 3. Comparison of $G^*$and tanδ data of emulsions with the predictions of the Palierne model (Eq. 3)

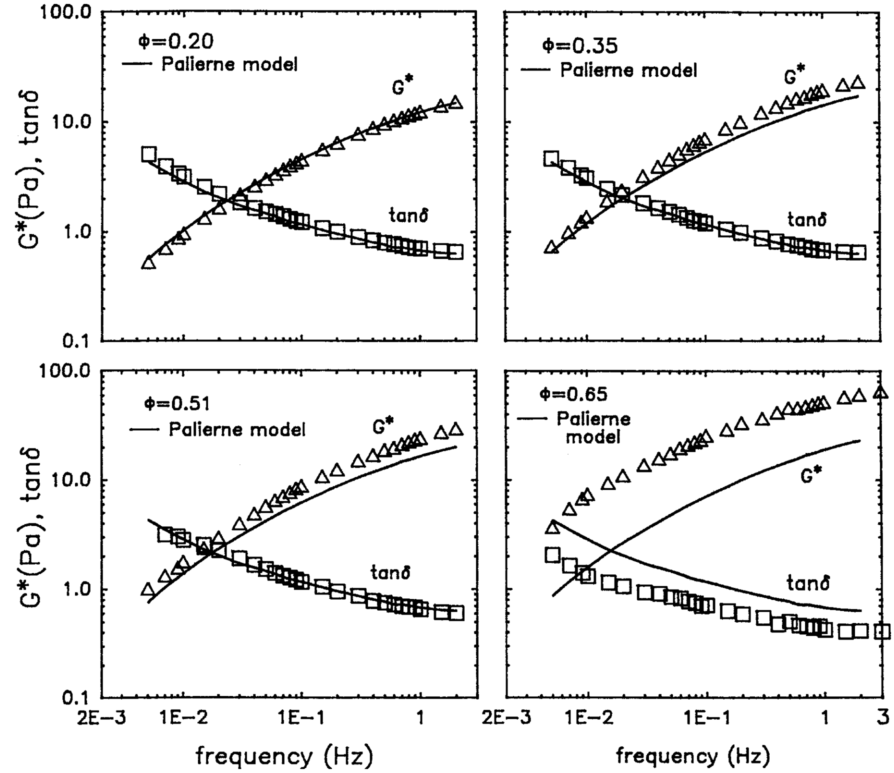


Fig. 4. Comparison of $G^*$and tanδ data of emulsions with the predictions of model 1 (Eq. 7)

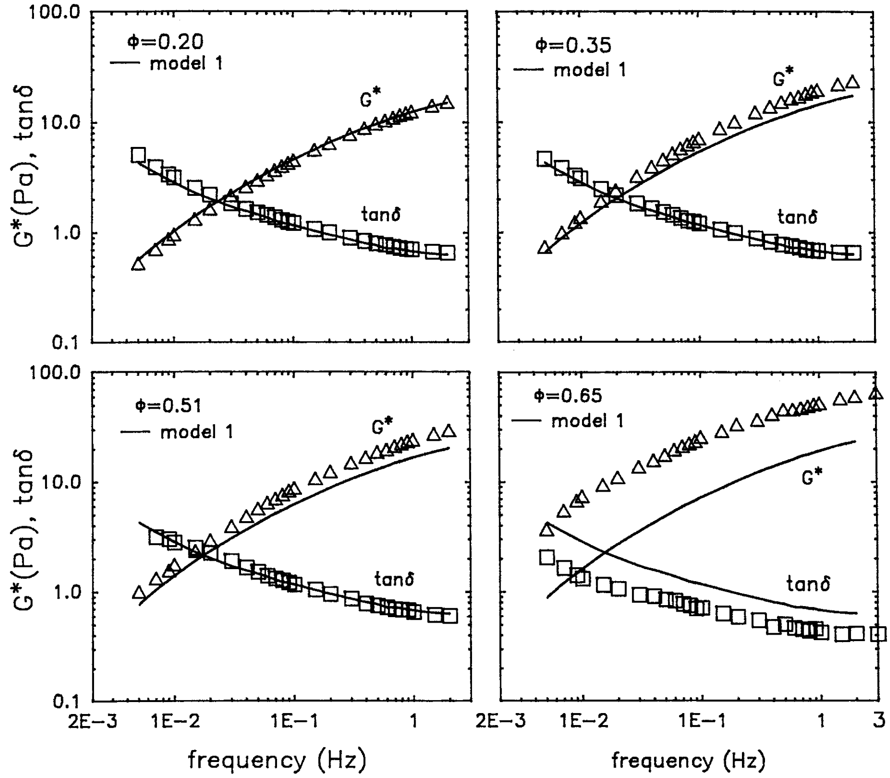


Fig. 5. Comparison of $G^*$and tanδ data of emulsions with the predictions of model 2 (Eq. 10)

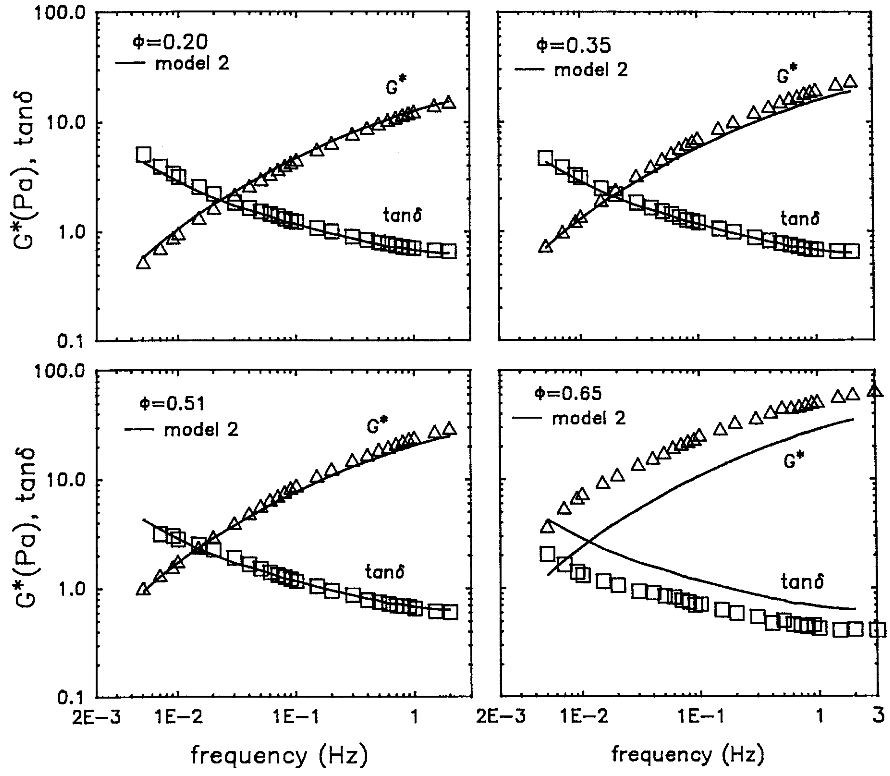


Fig. 6. Comparison of G^* and tanδ data of emulsions with the predictions of model 3 (Eq. 13)

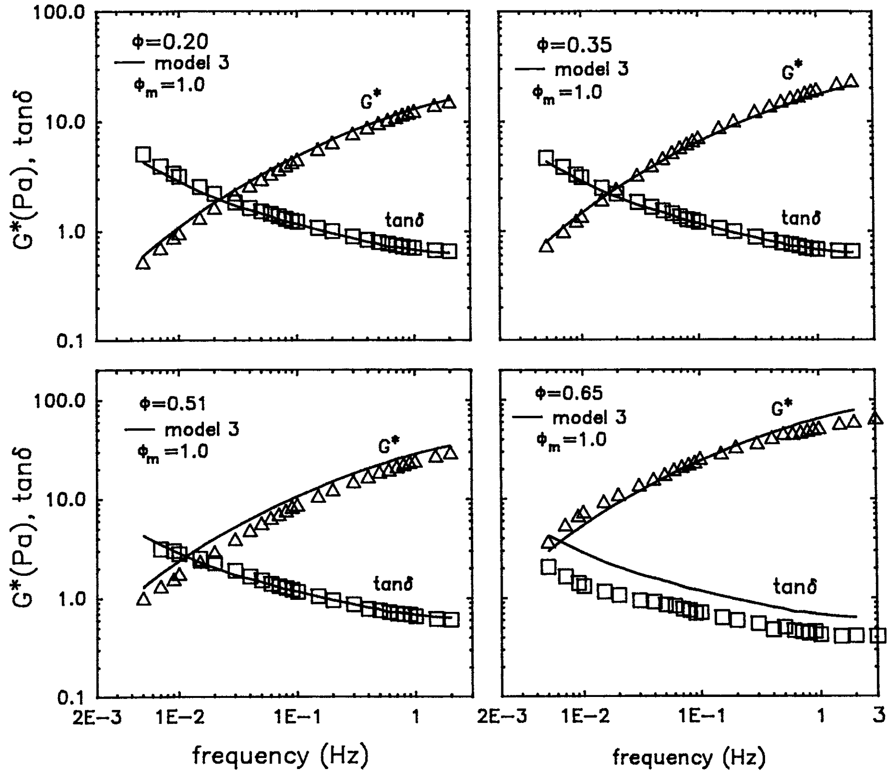
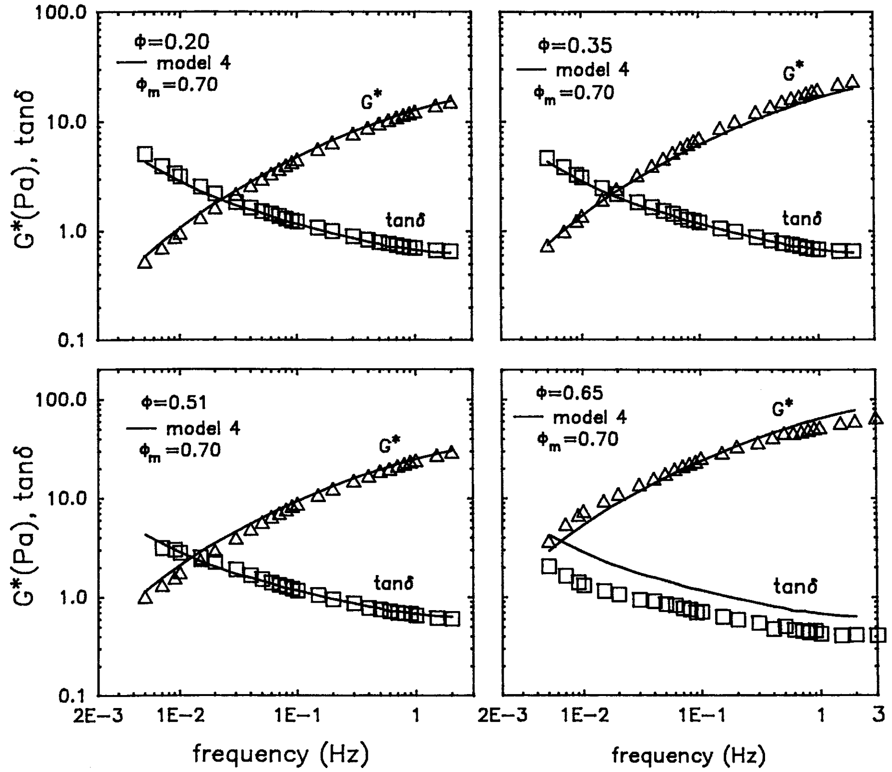


Fig. 7. Comparison of G^* and tanδ data of emulsions with the predictions of model 4 (Eq. 16)



The Palierne model for nondilute emulsions (Eq. 3) gives good predictions of G^* at a dispersed-phase volume fraction, ϕ, of 0.20. At higher values of ϕ, the Palierne model tends to underpredict G^* and the deviation increases with the increase in ϕ.

Model 1 (Eq. 7) gives predictions very similar to that of the Palierne model for nondilute emulsions (Eq. 3). At a low ϕ value of 0.20, model 1 exhibits excellent agreement with the experimental data. The model underpredicts the complex modulus at higher values of ϕ.

Model 2 (Eq. 10) is a significant improvement over model 1 and the Palierne model. This model shows good agreement with the experimental data over a wider range of ϕ, i.e., $\phi \le 0.51$. At a higher ϕ value of 0.65, model 2 also (like model 1 and the Palierne model) underpredicts the values of G^*.

Models 3 (Eq. 13) and 4 (Eq. 16) contain ϕ_m as an adjustable parameter. Different values of ϕ_m were tried to fit the data. Model 3 gives good predictions of G^* over the full range of ϕ investigated in this work, i.e., $0 \le \phi \le 0.65$, provided that a ϕ_m value of 1.0 is used in the model. Model 4 (Eq. 16) also gives excellent predictions of G^* over the full range of ϕ investigated, when a ϕ_m value of 0.70 is used in the model. While model 3 gives an unrealistically high ϕ_m value of 1.0, model 4 gives a realistic ϕ_m value of 0.70. Note that ϕ_m is 0.74 for an hexagonal close-packed arrangement of uniform spheres, and for random close packing of uniform spheres ϕ_m is approximately 0.64.

Interestingly, all the models (Figs. 3, 4, 5, 6, 7) give good prediction of tanδ when $\phi \le 0.51$. As expected from the models, tanδ for emulsions is nearly the same as that of the continuous phase. However, at a high ϕ value of 0.65, all the models overpredict tanδ. The disagreement between the models and the experimental data is probably related to deformation of droplets at $\phi = 0.65$.

Conclusions

Four new equations were developed for G^* of concentrated emulsions of nearly spherical droplets (low capillary numbers). The dispersed and continuous phases were treated as viscoelastic liquids in the derivation. G^* data on polymer-thickened O/W emulsions were obtained experimentally and were compared with the predictions of the equations proposed. Model 1 (Eq. 7) gives good predictions at low values of ϕ ($\phi \le 0.20$); at higher values of ϕ, model 1 underpredicts G^*. Model 2 (Eq. 10) gives good predictions of G^* over a wider range of ϕ, i.e., $0 \le \phi \le 0.51$; at a higher ϕ value of 0.65, model 2 also underpredicts G^*. Models 3 (Eq. 13) and 4 (Eq. 16) describe the experimental data very well over the full range of ϕ investigated, i.e., $0 \le \phi \le 0.65$; however, the values of ϕ_m obtained from the two models are different. Model 3 gives an unrealistically high ϕ_m value of 1.0, whereas model 4 gives a realistic ϕ_m value of 0.70. All the models predict that for emulsions with $G_d^* \rightarrow 0$, the phase shift angle, δ, between oscillatory stress and strain is the same as that of the continuous phase alone at any given frequency of oscillation. The experimental data show good agreement with this prediction.

In this work, the predictions of new shear modulus models were compared with one set of experimental data on emulsions. Further comparisons between experimental data and model predictions are needed to determine the general validity of the models proposed.

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