Viscoelastic Properties of Suspensions with Weakly Interacting Particles

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ABSTRACT: Rheological characterization of a model suspension containing hydroxyl-terminated polybutadiene and glass beads with filler concentration up to 30% by volume was performed by using a Haake parallel disk rheometer. The rheological tests conducted were the measurement of the storage modulus, G', loss modulus, G'', and complex viscosity, η^*, as functions of the frequency and the steady shear viscosity as a function of the shear rate. The linear viscoelastic region was determined to extend up to 50% strain by measuring G', G'', and η^* as functions of strain amplitude. By using multiple gap separations between the disks, it was found that the suspension did not exhibit slip at the walls of the rheometer. G' and G'' were used to determine the relaxation times distribution, $G_i(\lambda_i, \varnothing)$ as functions of the relaxation time, λ_i, and the filler content, $\varnothing$. The relaxation moduli, $G_i(\lambda_i, \varnothing)$, decreased with the relaxation time, but increased with the filler content. The Cox–Merz rule was also observed to be valid for these suspensions. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 507–514, 1998

Key words: suspensions; suspension rheology; viscoelastic properties; Cox–Merz rule; relaxation times

INTRODUCTION

Rheological properties of suspensions are of interest in polymer, food, detergent, ceramic, and solid rocket fuel industries. These properties depend on the solid content, particle shape, size and size distribution, viscosity of the matrix, and also measurement conditions such as temperature and shear rate. Several reviews exist on the rheological properties of suspensions.[1–4] Characterization of the rheological behavior of concentrated suspensions may also be complicated by slip at the walls of the rheometer.[5,6]

Viscoelastic properties of suspensions with high filler content were investigated by Bigg,[7,8] Schreuder and colleagues,[9] Poslinski and colleagues,[10]

Strivens,[11] Doraiswamy and colleagues,[12] and Kalyon and colleagues.[13] In other studies of viscoelastic properties of suspensions by Lakdawala and Salovey,[14] Matsumoto and colleagues,[15] Rong and Chaffey,[16] and Lobe and White,[17] the particle sizes were considerably smaller than the one in this study. In suspensions with high filler content or small particle size, the particle interactions are strong and either there exists a yield stress such as in the studies of Lobe and White,[17] Bigg,[7,8] Lakdawala and Salovey,[14] Doraiswamy and colleagues,[12] and Poslinski and colleagues,[10] or the viscoelastic properties are strain-dependent and nonlinear.[7–10,13,15,18]

The applicability of the Cox–Merz rule[19] was investigated in some of these systems. Kitano and colleagues,[18] Doraiswamy and colleagues,[12] Matsumoto and colleagues,[15] and Bigg[7,8] have found that, in these suspensions, the Cox–Merz rule was not applicable. Doraiswamy and coworkers[12]

Table I   Volumetric Size Distribution of Particles Used in This Study

Size (μm)	% Cumulative Volume of Particles
18.21	0
22.04	0.01
26.68	3.15
32.29	12.13
39.08	29.23
47.30	57.06
57.25	84.06
69.30	96.78
83.67	99.63
101.52	100

proposed a modified Cox–Merz rule for highly concentrated suspensions.

In this study, the linear viscoelastic properties of a moderately concentrated (up to 30% by volume) weakly interacting system containing glass beads were investigated. The emphasis of the investigation was linear versus nonlinear viscoelastic behavior, strain amplitude dependency of viscoelastic properties, slip at the wall, and applicability of the Cox–Merz rule. Also, the relaxation spectra of the suspensions were calculated by using experimental oscillatory shear data using the linear regression method.[20] For the first time, the steady shear viscosity of such suspensions were predicted by using the relaxation spectra.

EXPERIMENTAL

Materials and Sample Preparation

The polymer matrix used in this study is hydroxyl-terminated polybutadiene, which is manufactured by Atlantic Richfield. This polymer is a Newtonian fluid with a density of 0.85 g $\cdot$ mL^{-1} and a number average molecular weight of 2500 g $\cdot$ gmol^{-1}. Its viscosity was determined experimentally as 7.7 Pa $\cdot$ s at 23°C.

Spherical glass beads by Sivalco were used as fillers. The fillers have a volume average particle diameter of 45.94 μm and a density of 2.53 g $\cdot$ mL^{-1}. Size distribution of the glass beads is given in Table I. Suspensions were prepared with 10, 20, and 30% filler contents by volume.

Samples were prepared by mixing the polymer matrix with the glass beads for a period of 30 min in a beaker. The samples were then placed in a 60-mL injector and connected to a vacuum pump (AEI Ltd.) for 10 min to remove the air bubbles

trapped in the sample. The tip of the injector was 4 mm in diameter. To prevent settling of particles, the injector was continuously rotated until the start of the experiment, and the samples were placed on the parallel disk with the injector for rheological characterization.

Rheological Characterization

Rheological properties of the suspensions were measured by using a HAAKE (model CV20) parallel disk rheometer at 23°C. Samples were prepared just before the experiments. A new sample was used in each experiment. Oscillatory shear and steady shear experiments were conducted on samples with 0, 10, 20, and 30% glass beads. The oscillatory shear experiments involved steps that were needed to determine the linear viscoelastic region and to validate the "no slip at the wall" assumption.

In determining the linear viscoelastic region, the frequency was kept constant at 1 rad $\cdot$ s^{-1}, and the strain amplitude was varied between 5 and 50%. A constant gap height of 1 mm was used and the storage modulus, G', the loss modulus, G'', and the complex viscosity, η^*, were measured as functions of the strain amplitude.

After determining the linear viscoelastic region, experiments were performed by using different gap heights of 1.0, 1.5, and 2.0 mm and keeping the strain amplitude constant at 10%. The storage and loss moduli, and the complex viscosity were measured as functions of the frequency in the range of 0.63 to 29.1 rad $\cdot$ s^{-1}. In the steady shear experiments, gap heights of 1.0, 1.5, and 2.0 mm were used to check the "no slip at the wall" assumption. The steady shear viscosity was measured in the shear rate range of 0.177–2.578 s^{-1}. The duration of the experiments were chosen long enough so that the values of the viscosities measured were the steady-state ones.

RESULTS AND DISCUSSION

Oscillatory Shear Experiments

Figures 1–3 show the results of the experiments involving the determination of the linear viscoelastic range. As seen from these figures, the oscillatory shear properties G', G'', and η^* are not strongly dependent on the strain amplitude, γ_0, in the range of 5–50% strain. This is in contrast to the behavior of highly concentrated systems (e.g., Doraiswamy and coworkers[12] found that G', G'',
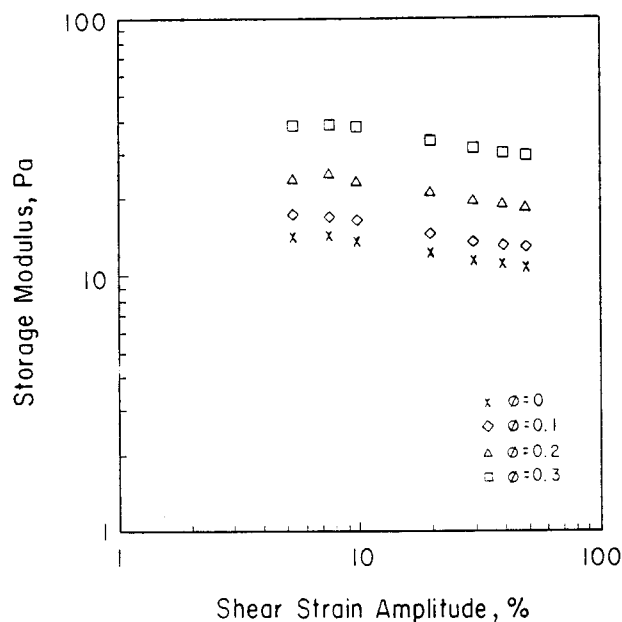
Figure 1 Effect of shear strain amplitude on storage modulus for suspensions with 0, 10, 20, and 30% glass beads at the gap height of 1 mm.
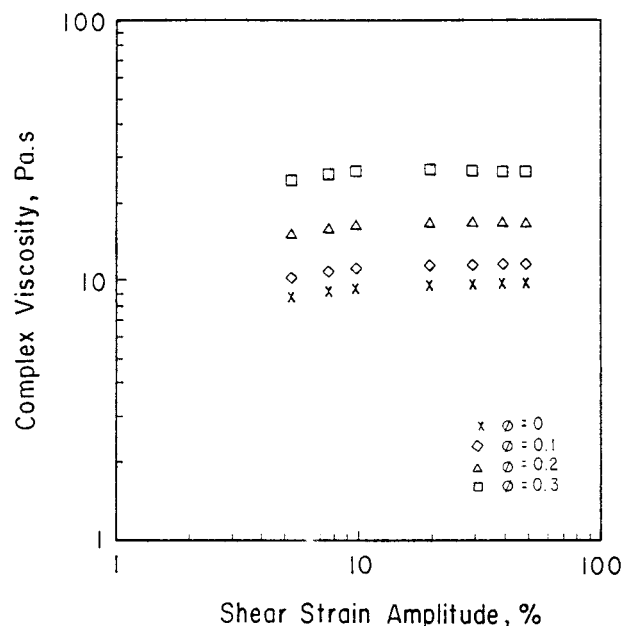

Figure 3 Effect of shear strain amplitude on complex viscosity for suspensions with 0, 10, 20, and 30% glass beads at the gap height of 1 mm.

and η^* were inversely proportional to γ_0). It may be concluded that the samples used in our study are linear viscoelastic up to 50% strain. The reproducibility of the data was affected by sample uniformity and torque value. The torque values measured for small strain amplitudes were at the

Figure 2 Effect of shear strain amplitude on loss modulus for suspensions with 0, 10, 20, and 30% glass beads at the gap height of 1 mm.

lower end capability of the torque measuring device, therefore small deviations from the constant values existed at small strain amplitudes. The oscillatory experiments showed better reproducibility at high strain amplitudes and high frequencies, due to higher torques involved. However, samples may exhibit fracture at high strain amplitudes, thus an intermediate strain amplitude of 10% was chosen for the experiments that followed.
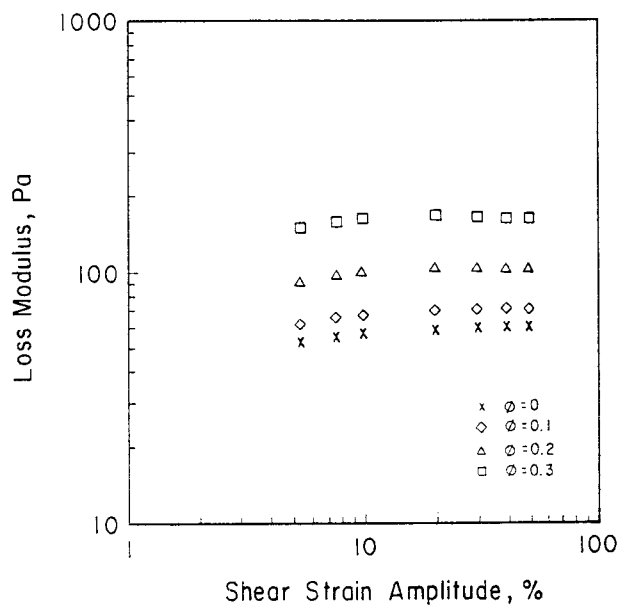
Figures 4–6 show some of the results of the experiments on samples with 30% glass beads that were done to validate the "no slip at the wall" assumption. Similar experiments were conducted for the samples containing 0, 10, 20, and 30% glass beads. The results for all concentrations were similar [i.e., the properties measured (G', G'', and η^*) were independent of the gap height in the range of gap heights studied]. This proves that the samples did not exhibit slip at the wall under the conditions studied. Yilmazer and Kalyon[5] observed that the rheological properties of a highly concentrated (60% by volume) suspension did depend on the gap height, indicating that slip at the walls of the parallel disk rheometer occurred. Lack of slip at the wall in our experiments is thought to occur due to the low filler contents studied. At low and moderate filler contents, the particles may move over each other during flow so that a velocity gradient may exist
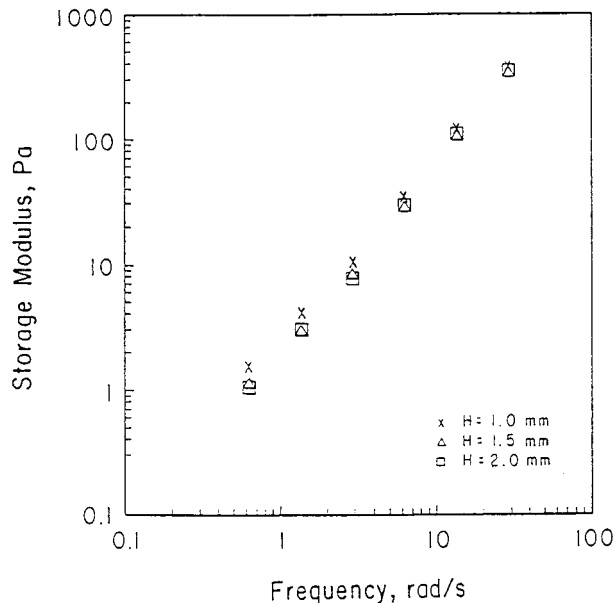
Figure 4   Effect of gap height on storage modulus as a function of frequency at gap heights of 1, 1.5, and 2 mm.

Figure 6   Effect of gap height on complex viscosity as a function of frequency at gap heights of 1, 1.5, and 2 mm.

in the sample. However, at high filler contents, if the fillers cannot move over each other, the sample may slip at the wall showing very little or no deformation inside.[6]

The viscoelastic properties G', G'', and η^* are shown as functions of the frequency in Figures 7–9 for all of the filler contents studied. The stor-
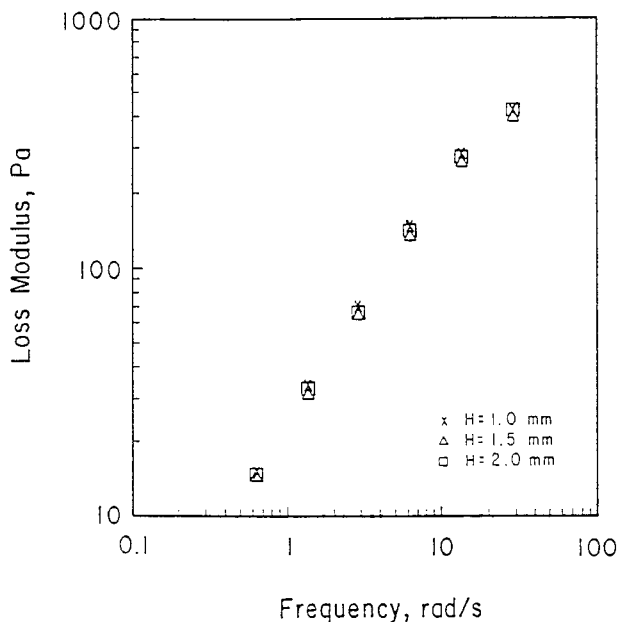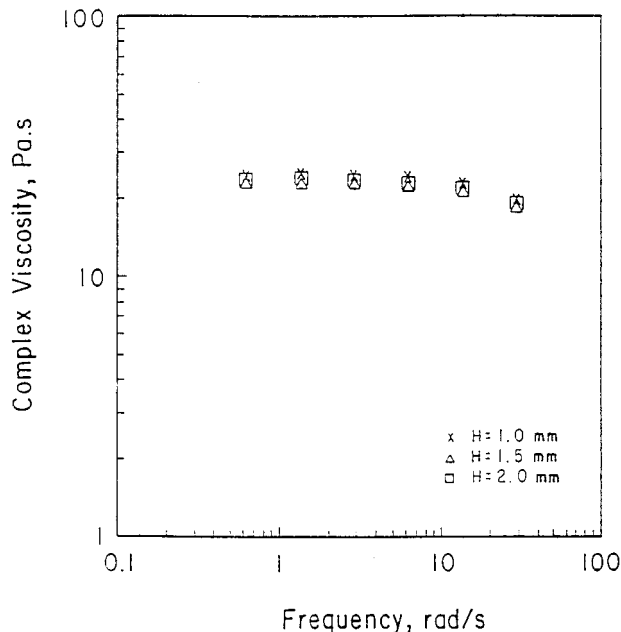
age and loss moduli increase with the frequency. However, the complex viscosity remains constant with increasing frequency, indicating that the suspensions are Newtonian in this frequency range.
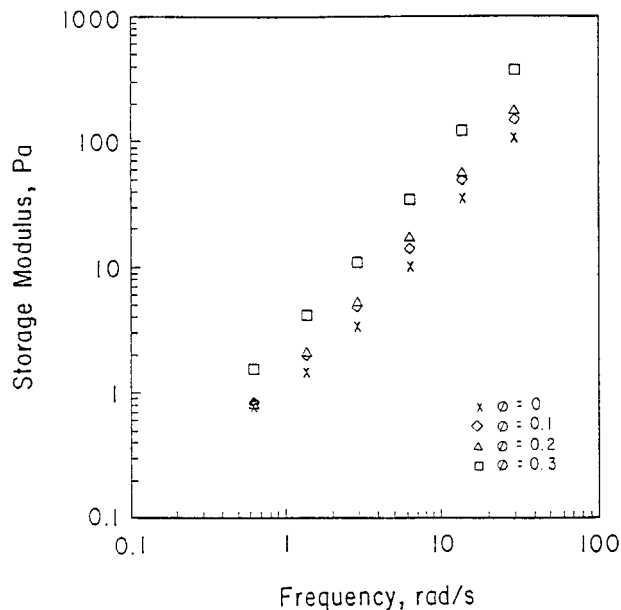

Figure 5   Effect of gap height on loss modulus as a function of frequency at gap heights of 1, 1.5, and 2 mm.

Figure 7   Storage modulus as a function of frequency for suspensions with 0, 10, 20, and 30% glass beads at the gap height of 1 mm.
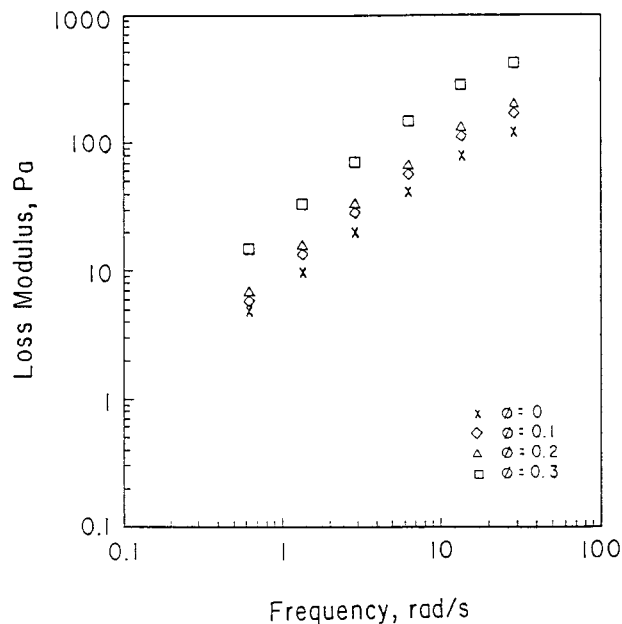
Figure 8 Loss modulus as a function of frequency for suspensions with 0, 10, 20, and 30% glass beads at the gap height of 1 mm.

Steady Shear Experiments

In the steady shear experiments, a constant shear rate was applied and the torque was measured as a function of time. The viscosity, η, was calculated from
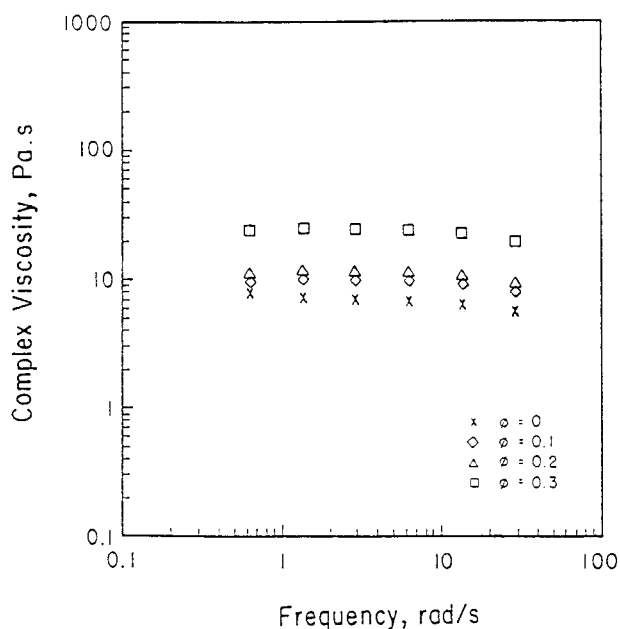

Figure 9 Complex viscosity as a function of frequency for suspensions with 0, 10, 20, and 30% glass beads at the gap height of 1 mm.
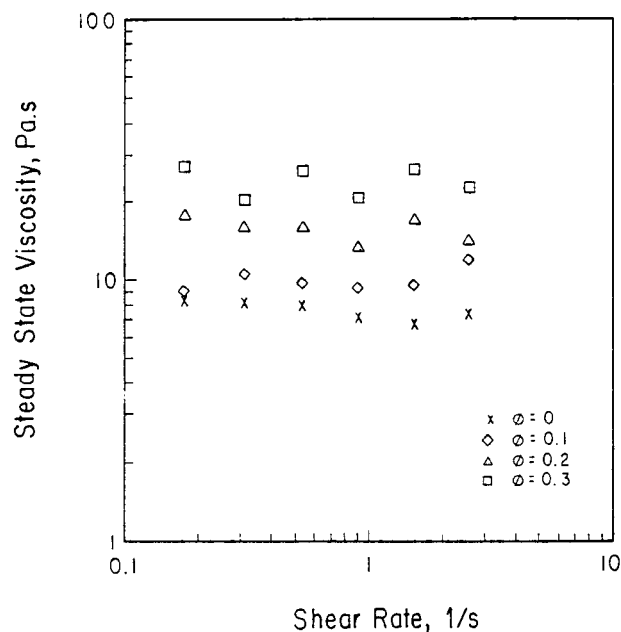

Figure 10 Steady-state shear viscosity as a function of shear rate for suspensions with 0, 10, 20, and 30% glass beads at the gap height of 1 mm.

$$\eta = \frac{(T/2\pi R^3)}{\dot{\gamma}}\left[3 + \frac{d\,\ln(T/2\pi R^3)}{d\,\ln\dot{\gamma}}\right] \qquad (1)$$

where T is the torque, R is the radius of disks, and $\dot{\gamma}$ is the shear rate at the edge of the disk.[21] The results shown in Figure 10 indicate that the suspensions are Newtonian, thus eq. (1) reduces to

$$\eta = \frac{2T}{\dot{\gamma}\pi R^3} \qquad (2)$$

The concentration dependence of the steady shear viscosity of suspension has been the subject of several studies. Kamal and Mutel,[1] Metzner,[2] and Khan and Prud'homme[3] summarized some of the literature available on this subject.

The relative viscosity, η_r, is defined as

$$\eta_r = \frac{\eta}{\eta_0} \qquad (3)$$

where η_0 is the viscosity of the matrix material measured at the same shear rate. The relative viscosity is assumed to be independent of the shear rate and is studied as a function of the filler content in several theories formulated. Figure 11 shows η_r as a function of the filler content at various shear rates. At each filler content, an
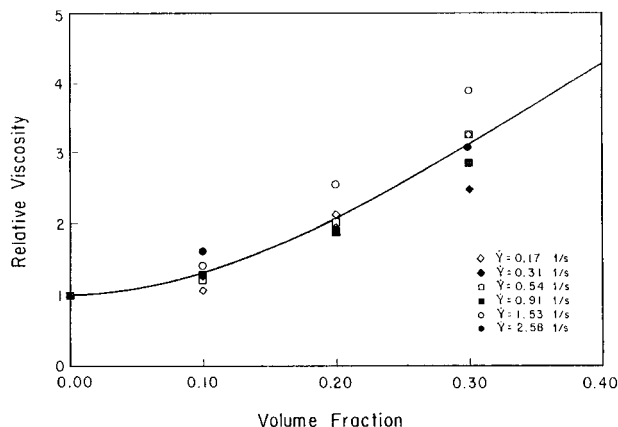
Figure 11 Relative viscosity as a function of volume fraction of glass beads at various shear rates. Curve represents the average values of all the shear rates.

average value of η_r is calculated for all the shear rates studied. Thus, it is assumed that

$$\eta_r = f(\varnothing) \tag{4}$$

where $f(\varnothing)$ is the average indicated in Figure 11 and is used in the analysis that follows.

Figures 7–9 show that G', G'', and η^* can be shifted vertically. The deviations due to experimental errors are somewhat large for G' at very small frequencies due to small torque values. Thus, it is proposed to express G', G'', and η^* as

$$G' = G'_0 f(\varnothing) \tag{5}$$

$$G'' = G''_0 f(\varnothing) \tag{6}$$

$$\eta^* = \eta^*_0 f(\varnothing) \tag{7}$$

where G'_0, G''_0, and η^*_0 are the storage modulus, the loss modulus, and the complex viscosity of the polymer matrix. Figure 12 shows $G'/f(\varnothing)$ and $G''/f(\varnothing)$ calculated using the experimental values in Figures 7 and 8 and the $f(\varnothing)$ given in Figure 11. Similar results were found for $\eta^*/f(\varnothing)$, but they are not included in Figure 12 for clarity. The results are satisfactory, indicating that, for these systems, the interactions between the particles are small and G', G'', and η^* can be written as independent functions of the frequency and the filler content. Similarly, η can be formulated as an independent function of the filler content and the matrix viscosity as implied in eqs. (3) and (4) and shown in Figure 11.

Relaxation Times Distribution

Boltzmann Superposition Principle describing linear viscoelastic behavior can be given as

$$\tau(t) = \int_{-\infty}^{t} G(t - t')\dot{\gamma}(t') \, dt' \tag{8}$$

where τ is the shear stress, $G(t)$ is the linear relaxation modulus, and $\dot{\gamma}$ is the shear rate.

The most popular approach to describe the behavior of polymer solutions, and melts in linear viscoelastic experiments is the generalized Maxwell model. The function used in this model is

$$G(t - t') = \sum_{i=1}^{N} G_i \exp[-(t - t')/\lambda_i] \tag{9}$$

where G_i is the relaxation modulus and λ_i the relaxation time. They are determined as N pairs from discrete experimental data.

From oscillatory shear experiments, the model parameters (G_i, λ_i) can be determined by using the following equations[22]:

$$G'(w_j) = \sum_{i=1}^{N} G_i \frac{(w_j\lambda_i)^2}{1 + (w_j\lambda_i)^2} \tag{10}$$

$$G''(w_j) = \sum_{i=1}^{N} G_i \frac{(w_j\lambda_i)}{1 + (w_j\lambda_i)^2} \tag{11}$$

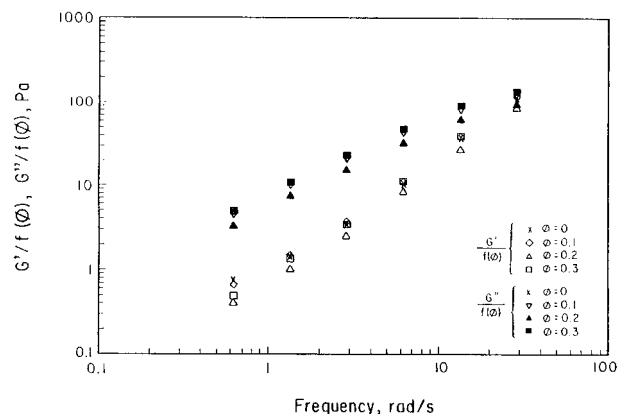Here, w_j refers to the experimental frequency.

Figure 12 Shifted values of storage and loss moduli as a function of frequency for different filler contents.
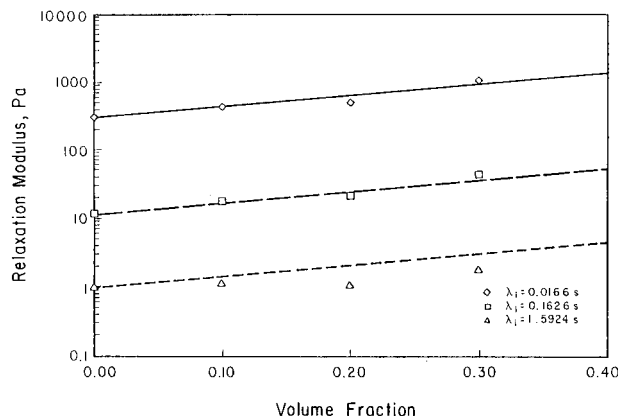
Figure 13 Relaxation modulus and relaxation time as functions of volume fraction of glass beads. Lines represent theoretical values calculated from eq. (13).

In this study, the linear least-squares method[20] was used to obtain the relaxation time and the relaxation modulus. N sets of model parameters (G_i, λ_i) were determined by using the experimental sets of data $[G'(w_j), G''(w_j)]$ with eqs. (10) and (11) given previously.

Logarithmically distributed N values of λ_i were chosen within the range of experimental frequencies. The values of λ_i were taken as $1/w_j$ within the experimental frequency range. The least-squares principle was applied to determine the values of G_i.[20] The following sum in eq. (12) was calculated:

$$\sum_{j=1}^{M}\left[\left(\sum_{i=1}^{N}\frac{1}{G'(w_j)}\,G_i\,\frac{(w_j\lambda_i)^2}{1+(w_j\lambda_i)^2}-1\right)^2\right.$$
$$\left.+\left(\sum_{i=1}^{N}\frac{1}{G''(w_j)}\,G_i\,\frac{w_j\lambda_i}{1+(w_j\lambda_i)^2}-1\right)^2\right]=S \quad (12)$$

The sum of the squares of the errors, S, can be minimized by differentiating S with respect to each G_i. The equations obtained from the differentiation can be solved numerically[23] by using singular value decomposition, which is available as a software package program.

Relaxation times and moduli determined from oscillatory shear data are shown in Figure 13 for the filler contents studied. The relaxation modulus increases with decreasing relaxation time and increasing filler content.

Equations (5) through (7) and the Maxwell model imply that the relaxation moduli, $G_i(\lambda_i, \varnothing)$, can be represented as separable functions of the filler content, $\varnothing$, and the relaxation time, λ_i

$$G_i(\lambda_i, \varnothing) = G_{i,0}(\lambda_i)\,f(\varnothing) \quad (13)$$

In equation (13), $G_{i,0}(\lambda_i)$ is the relaxation modulus of the matrix as a function of λ_i. The values of $G_i(\lambda_i, \varnothing)$ obtained from $G_{i,0}(\lambda_i)$ and $f(\varnothing)$ are also shown in Figure 13 as the lines. The satisfactory agreement indicates that, for this noninteracting system, the relaxation moduli are modified by $f(\varnothing)$ as indicated in eq. (13).

Finally, the Cox–Merz rule is tested for these suspensions. The Cox–Merz rule states that

$$\eta = \eta^* \quad \text{at} \quad \dot{\gamma} = w \quad (14)$$

Experimental data are shown in Figure 14 at $\dot{\gamma} \to 0$ and $w \to 0$, indicating the applicability of the Cox–Merz rule for these suspensions with noninteracting particles.

The analysis pertaining the Boltzmann superposition principle can be cross-checked as follows. The steady shear viscosities $\eta(\dot{\gamma} \to 0)$ can be calculated from

$$\eta(\dot{\gamma} \to 0) = \sum\lambda_i G_i \quad (15)$$

The values of $\eta(\dot{\gamma} \to 0)$ calculated from eq. (15) are also shown in Figure 14 supporting the analysis.

CONCLUSIONS

Rheological properties of suspensions of glass beads in a Newtonian fluid (hydroxyl-terminated polybutadiene) were characterized by oscillatory and steady shear experiments. The linear vis-
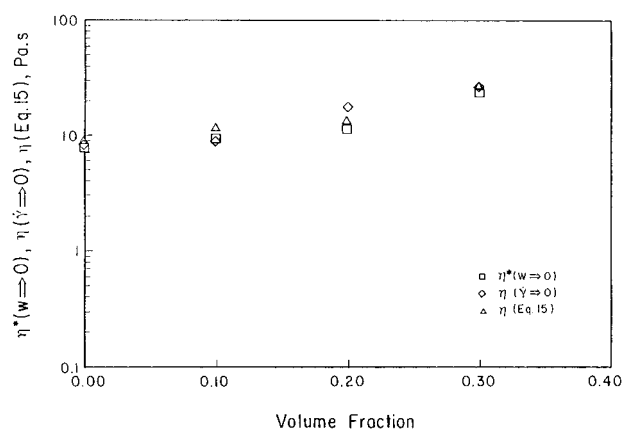

Figure 14 Viscosities for very low values of frequency and very low values of shear rate and the values calculated from eq. (15) as functions of the filler content.

coelastic range in oscillatory shear experiment was determined. The samples showed linear viscoelastic behavior up to a strain amplitude of 50%. Then, a strain amplitude of 10% was chosen for the rest of the oscillatory shear experiments. The occurrence of slip at the wall was checked by using multiple gap separations between the disks. It was found that the samples did not show any slip at the wall. For all of the suspensions, it was observed that the storage modulus, loss modulus, and complex viscosity were increasing with increasing filler content. Relaxation spectra [i.e., $G_i(\lambda_i, \varnothing)$] were calculated by using oscillatory shear data. $G_i(\lambda_i, \varnothing)$ decreased with λ_i, but increased with the filler content. The functions G', G'', and η^* can be expressed as separable functions of the filler content and the frequency. Similarly, the relaxation moduli, $G_i(\lambda_i, \varnothing)$, were formulated as separable functions of the filler content and the relaxation modulus of the matrix material. The previously mentioned function of the filler content is the same as the relative viscosity function referred to in the literature.

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