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Conclusion

Large A/B viscous interactions can induce a slowing down of dynamical process in A/B compatible mixtures. We predict a large effect for small chains (unentangled regime) and large mutual viscosity ($\zeta_{AB} \gg \zeta_{AA}, \zeta_{BB}$). For long chains, viscous coupling is negligible and the conclusions of ref 2 are not modified.

Acknowledgment. We thank Professor L. Monnerie, who mentioned to us the possible importance of mutual friction.

Appendix

The full free energy including compressibility is

$$F_{\mathrm{cm}^3} = \frac{kT}{a^3}\left[\frac{\phi_A}{N_A}\log\phi_A + \frac{\phi_B}{N_B}\log\phi_B + \chi\phi_A\phi_B\right] + \frac{1}{2}E(\theta - \theta_0)^2$$

with

$$\phi_A = \mathcal{N}_A/(\mathcal{N}_A + \mathcal{N}_B + \mathcal{N}_v)$$

$$\phi_B = \mathcal{N}_B/(\mathcal{N}_A + \mathcal{N}_B + \mathcal{N}_v)$$

$$\theta = \mathcal{N}_v/(\mathcal{N}_A + \mathcal{N}_B + \mathcal{N}_v)$$

E, the compressibility modulus, is often much larger than $\chi kT/a^3$. Assuming viscous motions (no sound waves), the motion equations are

$$\dot{\phi}_A = -\mathrm{div}\, J_A = \Lambda_A\Delta^2(\mu_A - \mu_v)$$

$$\dot{\phi}_B = -\mathrm{div}\, J_B = \Lambda_B\Delta^2(\mu_B - \mu_v)$$

with $\mu_v = E(\theta - \theta_0)$. They lead to two modes:

(a) A fast mode

$$\frac{\dot{\phi}_A}{\Lambda_A} = \frac{\dot{\phi}_B}{\Lambda_B} = -Eq^2(\delta\phi_A + \delta\phi_B)$$

controlled by the *fast* species and describing relaxation toward optimal density.

(b) A slow mode

$$J_A = -J_B$$

describing mutual diffusion, for which

$$\nabla\mu_v = -\frac{\Lambda_A\nabla\mu_A + \Lambda_B\nabla\mu_B}{\Lambda_A + \Lambda_B} = -\nabla U \neq 0$$

as assumed in ref 5.

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Dynamic Viscoelastic Properties of Poly(styrenesulfonate) Latex

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Aqueous suspensions of monodisperse charged latex particles with very low concentrations of electrolyte form ordered structures, whose properties have been studied by many different methods.[1] Several investigations of polystyrene latices have revealed unusual viscoelastic properties with a finite yield stress and a substantial storage shear modulus in small oscillating deformations at frequencies both in the 50-kHz region[2-4] and from 0.05 to 350 Hz.[5,7] The storage of elastic energy in deformation is attributed to changes in electrostatic energy, and its dependence on particle volume fraction, salt concentration, and other variables has been calculated.[3,7-9] The frequency dependence of viscoelastic properties has been examined only for latices with quite high concentrations.[5,7]

We have now made measurements of storage shear modulus and dynamic viscosity (loss modulus divided by radian frequency) over a wide frequency range from 100 to 5700 Hz on a polystyrene–poly(styrenesulfonate) copolymer latex[10,11] which carries a considerably higher charge per particle and has a much lower concentration than investigated previously.

Materials and Methods

A latex of polystyrene copolymerized with poly(styrenesulfonate) was generously given us by Professor Norio Ise, Kyoto University. The concentration was 7.4% by volume; particle diameter was 100 nm and number of charges per particle was 2.7×10^4, determined as described previously by Ise et al.[10,11] To remove contaminating ions which would disturb the formation of the ordered structure, the suspension was treated with analytical grade mixed-bed ion-exchange resin (BioRad AG 501-X8, an equal mixture of Dowex 1-X8 and 50W-X8). Approximately 20 mL of the stock suspension was added to 50 mL of dry resin; the mixture was sealed and left to stand for several days. The resin was removed by filtering with an 8-μm Millipore filter and then three 5-mL aliquots of 15-MΩ deionized water were used to wash most of the latex from the resin. The resulting latex suspension was somewhat iridescent. A final deionization was accomplished by passing the suspension through an ion-exchange column (1-cm diameter, 40 cm long, AG501-X8 resin) with doubly deionized water. Central fractions, with high iridescence, for a total of 45 mL were pooled and used immediately for multiple-lumped resonator measurements. The latex concentration was 1.400 ± 0.004 w/w % (volume concentration 1.33%), determined gravimetrically. The conductance of water similarly treated was $1.1 \times 10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, corresponding to a KCl concentration of 8×10^{-6} M. At this very low electrolyte concentration, the ordered array of latex particles should be stable.

Measurements of storage (G') and loss (G'') shear moduli were made at 20.0 °C at frequencies ν of 102, 394, 986, 2380, and 5820 Hz by the Birnboim–Schrag multiple-lumped resonator[12] with a modified data acquisition and processing system described elsewhere.[13] This is a surface-loading instrument which measures the complex impedance per unit area at an oscillating surface.[14] Both the resonator and the housing were constructed of a titanium alloy.[15] They were washed for several days with deionized water until no increase in conductivity could be observed after water remained in the instrument overnight. The instrument was filled very slowly through a syringe with a needle diameter of 1.4 mm. Because of concern that the ordered latex structure might be disrupted by this procedure, measurements were made at intervals over a 2-day period to allow any disrupted structure to be reestablished. There was actually very little change with time. The results are reported as G' and the dynamic viscosity $\eta' = G''/\omega$, where ω is the radian frequency ($2\pi\nu$).

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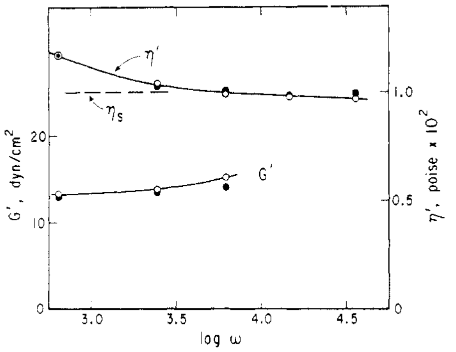

Figure 1. Plots of G' and η' (linear scales) against logarithm of frequency. Open circles, initial measurements (1-5 h after filling apparatus); black circles, after 2 days. Dashed line represents solvent viscosity.

Results and Discussion

The initial and final values of G' and η', differing almost negligibly, are plotted against log ω in Figure 1. There is very little frequency dependence in this range. In mechanical model terms, complete absence of frequency dependence would correspond to a Voigt element (spring and dashpot in parallel), which might represent a perfectly elastic structure with modulus G_e embedded in a viscous liquid with viscosity η_m. Actually, the combination of elastic and viscous stresses would depend on the coupling of the oscillating surface to both the ordered structure and the viscous medium, a feature discussed by Mitaku et al.[4] In our experiments, the latex particles appeared to adhere to the titanium surface and we assume that the coupling was good for both.

The slight change in G' and η' with frequency implies contributions from a relaxation spectrum H such that

$$G' = G_e + \int_{-\infty}^{\infty} [H\omega^2\tau^2/(1 + \omega^2\tau^2)]\, \mathrm{d} \ln \tau \tag{1}$$

$$\eta' = \int_{-\infty}^{\infty} [H\tau/(1 + \omega^2\tau^2)]\, \mathrm{d} \ln \tau + \eta_m \tag{2}$$

The internal consistency of the data can be tested by calculating H from the slopes of both G' and η' in Figure 1 with customary approximation relations.[16] The result at log ω = 3.39 gives H = 0.06 dyn/cm^2 from G' and 0.07 from η', in excellent agreement considering the very low slopes of these curves. The equilibrium static modulus G_e can be assigned an upper limit of 13 dyn/cm^2, but it is not clear whether there would be a further decrease at lower frequencies. The effective medium viscosity η_m is close to that of the solvent, η_s.

Comparisons with earlier measurements on polystyrene latices are not very useful because of the mostly much higher concentrations and lower per-particle charges in those studies. However, the data of Mitaku and collaborators on a latex with particle diameter 143 nm and 0.49 × 10^4 charges per particle extend to our low concentration, and interpolation gives $G' \simeq 40$ dyn/cm^2 there at 40 kHz (log ω = 5.4). This is similar in magnitude to ours and suggests that G' may continue to increase at higher frequencies. In flow measurements, Mitaku et al. noted a yield stress of the order of 1 dyn/cm^2. In our experiments, the maximum stress is estimated to be well below this value.

In the investigations cited,[2-6] η' was found to be similar in magnitude to η_s, the solvent viscosity. In our measurements, η' appears to approach η_s at higher frequencies. If the integral in eq 2 makes a finite contribution at our highest frequency, this implies that η_m, the effective viscosity of the medium, is somewhat less than η_s. However, that depends again on the degree of coupling of the ordered structure to the surface. Additional measurements at both higher and lower frequencies are needed to determine the nature of this very unusual type of viscoelasticity. The origin of the relaxation process corresponding to the small changes in G' and η' with frequency is of particular interest. Nevertheless, the model of an elastic structure embedded in a viscous medium serves well as a first approximation.

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Interfacial Profile between Coexisting Phases of a Polymer Mixture

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The structure of polymer interfaces between coexisting phases in binary (A, B) polymer mixtures has previously been analyzed in two limiting cases: (i) the limit where the two polymer chains can be treated as completely immiscible, so that the volume fraction ϕ of component A changes throughout the profile from $\phi = 0$ to $\phi = 1$,[1,2] and (ii) the critical region where the volume fractions ϕ_1 and ϕ_2 of the two coexisting phases become (nearly) identical.[3] In the present note, we study this problem at general volume fractions intermediate between these two limits.

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