Linear Viscoelasticity of Polymer Latices Containing PEO with Terminal Hydrophobes

Q.T. Pham[1], J.C. Thibeault[2], W. Lau[2], and W.B. Russel[3]

[1]Unilever Research, Edgewater NJ
[2]Research Laboratory, Rohm and Haas Co., Spring House PA
[3]Department of Chemical Engineering, Princeton U., Princeton NJ

SUMMARY: The rheology of polymer latices containing 35 kg/mole polyethylene oxide chains with C_{16} and C_{18} terminal hydrophobes is correlated by accounting for adsorption of polymer onto the particles and the viscoelasticity of the solution itself, indicating that direct interactions between the particles increase the low shear viscosity and introduce a power law spectrum of longer relaxation times.

Introduction

The rheology of latex dispersions containing triblock associative polymers depends primarily on the dynamics of the associated micellar solution in many cases, but can be affected profoundly, and perhaps adversely, by polymer-particle interactions that control the structure and stability of the dispersion[1,2,3]. Associative polymers adsorb onto polymer latices, forming dense layers that increase the hydrodynamic size of the particles and reduce the polymer concentration in solution. The former reduces the viscoelasticity of the solution, while the latter enhances contributions from hydrodynamic interactions between particles; however, neither affects the relaxation time, which remains that governing the response of the associated solution. On the other hand, attractions between adsorbed layers, e.g. due to bridging chains, both increase the stress and introduce much longer relaxation times. Thus the dispersion rheology depends qualitatively and quantitatively on the relative importance of the contributions from attractions between particles.

Previously[4,5,6,7] we reported on the rheology of narrow distribution polyethylene oxide (PEO) chains with C_{16} and C_{18} terminal hydrophobes in solution and in aqueous dispersions of poly(methylmethacrylate) (PMMA) latices. Both form adsorbed layers that couple with micelles in solution and adsorbed layers on other particles. At finite particle volume fractions ϕ we correlate the low shear viscosity of the dispersion normalized on that of the surrounding polymer solution with the effective volume fraction, which accounts for the adsorbed layer. The result indicates an effective no-slip boundary condition between adsorbed layer and

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micellar solution and direct associations between adsorbed layers that create a percolated network of particles. Thus, the enhancement of the dispersion viscosity and the viscoelasticity arises from the high viscosity of the polymer solution, the increased hydrodynamic volume of the particles, and direct interactions between adsorbed layers. Detailed analysis of the viscoelastic response to small amplitude oscillations relates a single relaxation time that controls the behavior at high frequency to the associated solution, as most expect, while the particles generate a power law distribution of longer relaxation times that dominate the low frequency response.

Here we review those results with emphasis on the effect of hydrophobe size, i.e. C_{16} (HDU) or C_{18} (ODU), for the same dialyzed PMMA latices (diameter $2a$=224 nm) and PEO backbones (35 kg/mole). The materials and methods are described in papers elsewhere[4,5,6,7], which also contain more complete references to the prior literature.

Adsorption[4)]

The adsorption isotherms for HDU, ODU, and PEO increase monotonically with the polymer concentration c_s in the aqueous phase and approach a plateau Γ_m at high concentration (Table 1) that increases with hydrophobe size, translating into a reduced area per chain for the larger hydrophobe. These plateaus are reached by solution concentrations of 0.05 wt% for HDU and 0.10 wt% for ODU.

Table 1: Adsorbed amounts and layer thicknesses[4)]

Polymer	Γ_m (mg/m^2)	$1/\sigma$ (nm^2/chain)	δ (nm)
ODU	2.69	21.6	26±5
HDU	1.79	32.4	18±6
PEO	0.90	64.9	10±4

Unmodified PEO also adsorbs on the latex particles, but at many points along its backbone, producing loops, trains, and tails with the tails governing the hydrodynamic thickness δ. The associative polymers adsorb into much denser and thicker layers (Table 1). The increase in δ with hydrophobe size is consistent with the notion that associative polymers adsorb via their hydrophobic endcap, essentially forming dense terminally-anchored brushes that stretch away from the surface due to excluded volume interactions. Since the interaction between a hydrophobe on the polymer chain and the surface affects adsorption, the larger

hydrophobes adsorb more strongly, form denser layers, and hence have a more stretched configuration.

Viscosity[4,6)]

The PMMA dispersions thickened with HDU or ODU generally exhibit a Newtonian viscosity at sufficiently low shear rates, shear thickening at intermediate shear rates, and thinning at high shear rates. The shear thickening is amplified relative to that of the neat solution, while the thinning is less abrupt. The dispersion viscosity increases monotonically with polymer concentration and is comparable to the neat solution, but can decrease with the addition of particles.

Since the viscosity of the dispersion is largely controlled by that of the solution, HDU produces less viscous dispersions than ODU. This makes the contributions to the viscosity from the attractive interactions between particles mentioned above more evident and causes shear thinning at substantially lower shear rates (0.04–0.2 s^{-1}) for the higher volume fractions. Thus, at high polymer concentration (c_p>3 wt%) the dispersion viscosity gradually decreases over all accessible shear rates. For c_p<1.5 wt%, the viscosity is Newtonian at intermediate and high shear rates (10-1000 s^{-1}), but can increase at very low shear rates, producing an apparent dynamic yield stress. The latter can be suppressed by (i) preshearing at a high shear rate (100 s^{-1}) before measuring at low shear rates or (ii) performing the steady shear sweep from high to low shear rates. At the same conditions we observe visually weak flocculation, apparently due to reversible bridging, suggesting a percolation network that increases the apparent viscosity but can be easily destroyed by high shear.

Table 2: Apparent intrinsic viscosities and Huggins coefficients of dispersions[4,6)]

Polymer	$[\eta]$	k_h
ODU	2.3 ±0.6	3.2 ±0.4
HDU	2.4 ±0.6	3.1 ±1.2

Thus the hydrophobe size affects the rheology of the dispersions through the viscosity of the associated solution, the amount of adsorbed polymer, and the associations between the particles. To understand the situation more fully we start by examining the effect of polymer and particle concentrations on the low shear viscosity through a simple correlation that accounts separately for these three effects. The challenge is to account for the fact that the low shear viscosity η_o increases monotonically with ϕ at high c_p but decreases abruptly with ϕ

at low to moderate c_p. Therefore, we rescale the volume fraction as $\phi_{eff}=(1+\delta/a)^3\phi$, to account for the adsorbed layer, and adjust the polymer concentration to $c_s=[c_p(1-\phi)-\Gamma_m\phi]/(1-\phi_{eff})$, recognizing that adsorption removes polymer from solution. For simplicity Γ_m and δ are assumed constant at the values in Table 1 for all concentrations. The low shear viscosity η_s of the HDU and ODU solutions is related to the solution concentration c_s by empirical expressions of the form[5)]

$$\frac{\eta_s}{\mu} = 1 + [\eta_s] c_s \exp\left(\frac{k_s [\eta_s] c_s}{1 + c_s / c_O}\right) \tag{1}$$

where μ is the water viscosity at 25°C. Then plotting the data according to

$$\frac{\eta_O}{\eta_s(c_s)} = 1 + [\eta]\phi_{eff} \exp\left(k_h [\eta]\phi_{eff}\right) \tag{2}$$

produces intrinsic viscosities and Huggins coefficients (Table 2) for the dispersions containing the two associative polymers that are indistinguishable within experimental error. The values of $[\eta]\approx 2.5$ coinciding with the no-slip limit indicate effective coupling between the coated particles and polymer solution, while the $k_h\approx 3$ exceed significantly the hard sphere limit of unity. The latter strongly suggests reversible associations between the adsorbed layers. The comparable $[\eta]$ and k_h for ODU and HDU demonstrate that the hydrophobe size does not change the nature of the interactions between particles and polymers.

Figure 1 compares the correlation (lines from Eqn (2)) with the full set of data for ODU. For $c_p\geq 2$ wt%, the high solution viscosity η_s and increased particle interaction k_h maintain a high dispersion viscosity η_o that increases monotonically with ϕ_{eff}. For $c_p=1.5$ wt%, addition of particles reduces η_o more than an order of magnitude below the original solution viscosity, while for $c_p<1$ wt% η_o becomes independent of the polymer concentration and increases slightly with ϕ_{eff}. Though qualitatively correct, the correlation describes η_o poorly in this regime, perhaps because these concentrations fall within the two-phase regime for the solution[8)]. Alternatively, the values of η_o lower than predicted for $c_p<1.5$ wt% suggest adsorption of more polymers at high ϕ than indicated by measurements at dilute ϕ. Note that

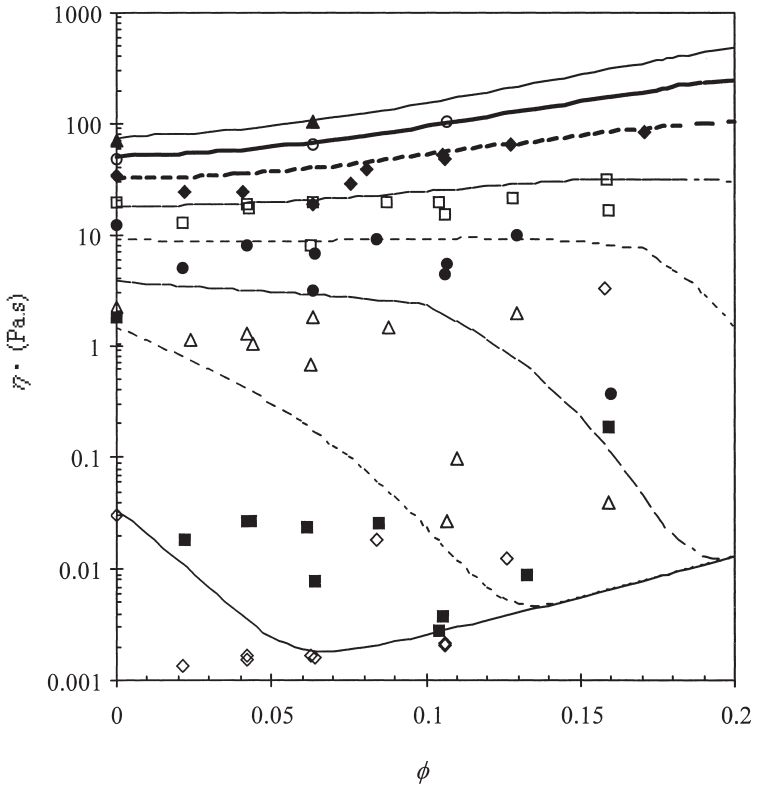

Figure 1: Low shear viscosities of dispersions as function of total ODU concentration and particle volume fraction[4]. Solid and dashed lines are calculated from the correlation (2) and correspond to the polymer concentrations: c_p= 0.5 wt% (◊), 1.0 wt % (■), 1.5 wt% (Δ), 2.0 wt % (■), 2.5 wt% (□), 3.0 wt% (◆), 3.5 wt% (○) 4.0 wt% (▲).

the correlation and data coincide rather well beyond the upturn in the lowest curve, when solution polymer is almost entirely depleted and particles with adsorbed layers interact in a dilute solution with the viscosity of pure water.

One might define the thickening efficiency as $\eta_o(\phi,c_p)/\eta_o(\phi,0)$, the ratio of the viscosity of the dispersion with associative polymer to that of a neat dispersion at the same volumefraction, as calculated from Eqn (2) with k=1, $[\eta]$=2.5, and c_p=0. Either ODU or HDU at c_p>2 wt% increases the dispersion viscosity by several orders of magnitude. The thickening effect is drastically diminished for c_p=1.5 wt% and the ratio becomes $O(1)$ for c_p<1 wt%, consistent with the correlation and the effect of adsorption.

The fraction of the thickening due to the solution viscosity alone is

$$f = \frac{\eta_s(c_s(\phi))}{\mu} \Big/ \frac{\eta_o(\phi, c_p)}{\eta_o(\phi, 0)}, \tag{3}$$

with the remainder (1-f) due to the increased hydrodynamic size of and direct interactions between the particles. For HDU with c_s>0, f decreases from 1 to 0.4 as ϕ increases for 0.04<ϕ<0.2 with less influence of polymer concentration. Thus, at low ϕ the solution viscosity dominates and f→1; but with increasing ϕ the increased hydrodynamic volume and interactions with k_h>1 reduce f. Overall, ODU and HDU thicken latex dispersions by the same mechanisms, though the lower solution viscosity with HDU reduces the dispersion viscosity.

Linear Viscoelasticity[6,7)]

In solutions of triblock associative polymers the dominant relaxation time increases exponentially with hydrophobe size and depends only weakly on concentration, while the high frequency modulus increases algebraically with hydrophobe size (through the effect on micellar aggregation number) and roughly quadratically on concentration[5)]. The product of these quantities determines the low shear viscosity. The addition of particles introduces the additional sources for stresses discussed briefly above, which bring along a quite different spectrum of relaxation times.

Thus the viscoelasticity of the dispersions deviates from the simple Maxwellian behavior of the solution by exhibiting multiple relaxation modes. The loss G'' and storage G' moduli still increase with polymer concentration c_p, but increasing the particle volume fraction alters the low frequency asymptote of the latter from $G'\sim\omega^2$ for the solution to $G'\sim\omega$ at intermediate ϕ and sometimes $G'\sim\omega^0$. This effect is more pronounced for HDU than for ODU, since the high frequency relaxation is weaker and the crossover for G' and G'' generally lies beyond the range (ω>200 rad/s) of the RFS II rheometer.

Our decomposition of the viscoelastic response recognizes that the rapid relaxation of the associated solution controls at high frequency, while the slower particle dynamics introduce a power law spectrum of relaxation times at low frequency, suggesting

$$R(\lambda) = G_\infty' \lambda_m \delta(\lambda - \lambda_m) + G_o \left(\frac{\lambda_o}{\lambda}\right)^n H(\lambda_o - \lambda) \tag{4}$$

with $R(\lambda)$ the relaxation spectrum and $\delta(x)$ and $H(x)$ the Kroenecker delta and Heaviside step function, respectively. The moduli follow from

$$G' = \int R(\lambda) \frac{(\omega\lambda)^2}{1+(\omega\lambda)^2} \frac{d\lambda}{\lambda} \qquad G'' = \int R(\lambda) \frac{\omega\lambda}{1+(\omega\lambda)^2} \frac{d\lambda}{\lambda}. \tag{5}$$

For most of the compositions examined the power law slope approaches unity (n=1), though n<1 with HDU at some high ϕ. The remaining parameters G'_∞, H_o, λ_m, λ_l, and λ_o are obtained by systematically fitting the moduli to the data. While not beyond question, the process does yield parameters that offer some insight into the underlying mechanisms are argued below.

The high frequency modulus of the dispersion $G'_\infty(c_p,\phi)$ generally increases with c_s but falls somewhat below that for the solution $G'_\infty(c_s,0)$ except at the highest ϕ_{eff}. As expected from the solution behavior, the relaxation time λ_m controlling the dissociation process is shorter for HDU (4-5 ms) than for ODU (10-15 ms) and varies on weakly with ϕ_{eff}. Curiously for HDU our estimates for the dispersions are significantly shorter than for the neat solution and increase with ϕ_{eff}, probably suggesting that extrapolation required at high frequency to be less accurate with the low frequency relaxations. However, in all cases the differences between the quantities characterizing the dispersion and those determined earlier for the solutions are $O(1)$ or less. There may be systematic variations but the scatter in the data prevents any interpretation.

The other characteristic time λ_l denotes the transition or crossover between the discrete and power law relaxation regimes. For ODU λ_l=0.10±0.02 s, but for HDU it decreases from 0.1 to 0.01 with increasing c_p and ϕ_{eff}. Either trend could be an artifact of the fitting process. If this cutoff time scale for the power law spectrum arises from diffusion of the particles, then $\lambda_l=\ell^2/D_o=6\pi\eta_s a\ell^2/kT$. This implies the relevant length scale to be ℓ=O(5 nm), which is somewhat smaller than the micellar dimensions.

The strength of the power law spectrum is set by $H_o\lambda_o$ for n=1, which has units of Pa-s and represents the product of a modulus and relaxation time. For both associative polymers this quantity shows little systematic dependence on c_s for c_s > 1.5 wt% but increases monotonically almost three orders in magnitude for ϕ_{eff} = 0.05 to 0.35 with a form

$$H_o\lambda_o = \begin{cases} (150 \pm 13 \text{ Pa}\cdot\text{s})\phi_{eff}^{3.3\pm0.7} & \text{for ODU} \\ (50 \pm 20 \text{ Pa}\cdot\text{s})\phi_{eff}^{3.3\pm0.7} & \text{for HDU} \end{cases}, \tag{6}$$

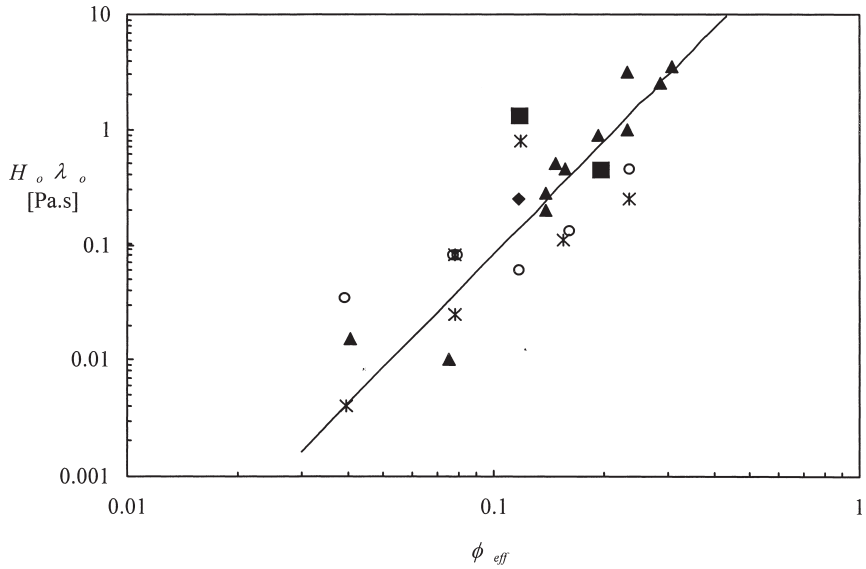

Figure 2: Strength of power law spectrum as function for effective volume fraction for different ODU concentrations: c_p = 1.5 wt% (✚), 2.0 wt% (✳), 2.5 wt% (○), 3.0 wt% (▲), 3.5 wt% (■), 4.0 wt% (◆).

as illustrated in Figure 2 for ODU.

Both the power law spectrum itself and this dependence on volume fraction signify structure for the dispersion in the vicinity of a gelation or percolation transition. Indeed, a variety of studies with weakly aggregated dispersions detect elastic moduli that vary as ϕ^n with n=3-4. Therefore, the magnitudes observed for the product $H_o\lambda_o$ should be compared to the characteristic energies and relaxation times for the dispersion. The formation of large clusters or chains of particles without macroscopic phase separation of the dispersions suggests an attraction of roughly kT, which translates into an energy density of $3kT/4\pi a^3$ = 0.74 Pa. The diffusion time of an individual particle, $a^2/D_o=6\pi\eta_s a^3/kT$, is 6 ms in water but ranges from 6-60 s in 2-4 wt% HDU or 60-600 s in 2-4 wt% ODU. The product, which reduces to $9\eta_s/2$, is 4.5-45 Pa-s for HDU or 45-450 Pa-s for ODU and compares well with the prefactors in (7). This scaling is further tested by plotting $H_o\lambda_o/\eta_o(c_s)$ versus ϕ_{eff} for ODU in Figure 3; the points for HDU would scatter about those shown. The variation with polymer concentration is still substantial, but the prefactor associated with the "best fit" is now close to the 9/2 expected. While not proving the scaling, this does establish the consistency of our observations with expectations. Thus the volume fraction dependence is attributable to the

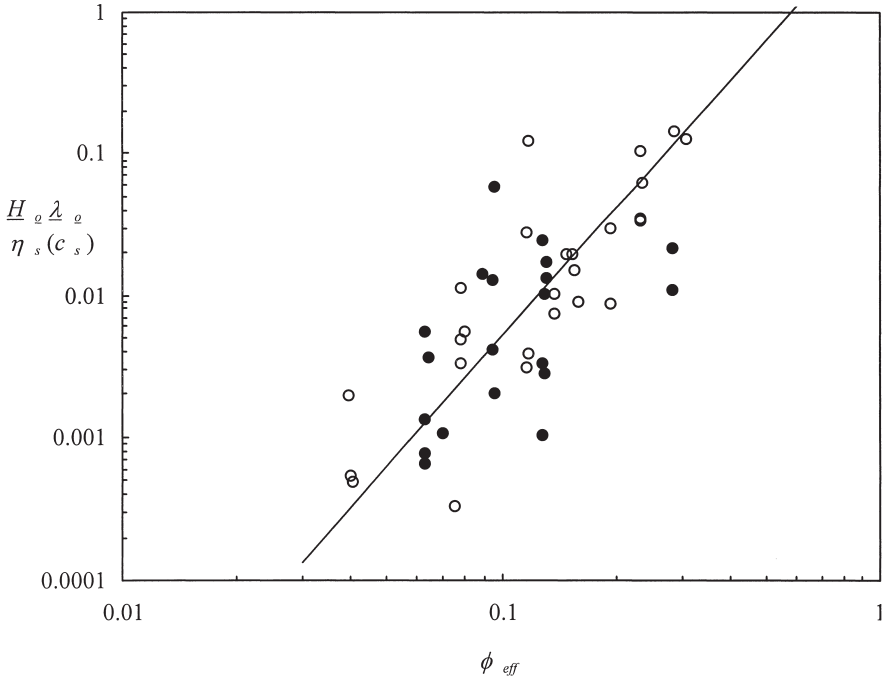

Figure 3: Strength of power law spectrum scaled on corresponding solution viscosity for HDU[6] (●) and ODU[7] (o) with the solid line representing the power law fit.

structure of percolating systems and the magnitude to diffusion of particles in the polymer solution.

Conclusions

Here we offer correlations quantifying the effects of associative polymer on the rheology of latex dispersions in terms of the viscoelasticity of the associated solution, the amount and layer thickness arising from adsorption of polymer onto the particles, and the volume fraction of particles. Adsorption of associative polymers generates spheres of larger hydrodynamic volume that couple weakly with one another through the adsorbed layers, thereby complicating the dispersion rheology. The low shear viscosity depends on both the interparticle interactions and the associations in solution. Despite stronger adsorption that depletes the solution more than HDU, ODU still produces the higher solution viscosity and, hence, the higher dispersion viscosity. The Huggins coefficients and intrinsic viscosities that

correlate the low shear viscosities of the dispersions indicate similar interactions between particles and with the polymer solution for ODU and HDU. Likewise, the viscoelasticity for both reveals a combination of the single rapid relaxation governed by the associated solution and a power law spectrum of slower relaxations arising from reversible couplings between particles. The power law spectrum appears to be controlled by diffusion of the particles in the associated solution and, therefore, also scales on the solution viscosity. Nonetheless the couplings between particles are more noticeable with the HDU in both steady shear and linear viscoelastic measurements.

Acknowledgments

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