Colloid Polym Sci 276:305–312 (1998)

ORIGINAL CONTRIBUTION

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Rheology of concentrated multi-sized poly(St/BA/MMA) latices

Received: 22 November 1996
Accepted: 26 November 1997

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Abstract Four monodisperse latices with particle size of 75, 135, 340 and 477 nm were synthesized. The rheological properties of mixture of the monodisperse latices were investigated as a function of blending ratio, and compared with those of multimodal latices, in a range of shear rate from 0.2 to 100 s^{-1}. The maximum packing (highest solid contents) was observed at a weight fraction 80% of large particles with respect to total solids contents for both bimodal and trimodal latices, and the lowest viscosity was obtained when the ratio of large to medium to small particles was approximately 80/10/10 (by wt.). It was also demonstrated that this minimum in the viscosity is not strongly dependent on the actual size of each kind of particles present in the multimodal latices.

Key words Rheology – multi-sized – high solid content – latex

Introduction

The rheological properties of latices have been the subject of numerous investigations in recent years [1–5]. Although the majority of the experimental and theoretical studies were based on monosized latices, the effect of the particle size distribution on rheology is of great practical importance, as well as fundamental interest. It is well recognized that the maximum packing fraction of the monodisperse particles can be increased by a bimodal or multimodal particle size distribution (PSD). Thus, a polydisperse dispersion might show a lower viscosity at the same volume fraction of particles, or an equivalent viscosity at a higher solids content than the monodisperse latex. The most extensive experimental and theoretical works [6–10] have been focused on mixture of glass spheres with sizes ranging from 10 to 200 mm suspended in viscous media. For these non-Brownian binary mixtures, the volume dependence of the viscosity can be fitted using an equation developed by Quemada [11] using ϕ_m as a fitting parameter:

$$\eta_r = [1 - \phi/\phi_m]^{-2} , \tag{1}$$

where η_r is the relative viscosity, ϕ is the volume fraction and ϕ_m the volume fraction at maximum packing (i.e. the volume fraction at which the viscosity becomes intinite). This expression is similar to the Krieger–Dougherty equation [8, 12]

$$\eta_r = \eta/\eta_0 = [1 - \phi/\phi_m]^{-[\eta]\phi_m} \tag{2}$$

which provides good fit of viscosity as a function of concentration for sterically stabilized polystyrene latices [5, 13]. Here η is the viscosity of the dispersion, η_0 is the viscosity of the media and $[\eta]$ the intrinsic viscosity (= 2.5 for hard sphere).

The viscosity of a concentrated polymer latex is a complex function of many parameters such as the PSD, particle shape, concentration and multibody thermodynamic and hydrodynamic interparticle interactions. Due to this complexity, relatively few experimental and theoretical studies have been carried out on the flow behavior of multisized polymer latex in spite of its practical importance. Rodiguez [14] investigated the steady shear viscosity of binary mixture of crosslinked polystyrene particles (84 and 141 nm) dispersed in bromoform and found a minimum in the viscosity at a small particle weight fraction of 35%. Kim et al. [15] studied the rheological properties of bimodal polystyrene particles (204 and 1400 nm) by measuring the elastic modulus, dynamic vicosity and osmotic pressure as a function of the composition and total particle volume fraction. It was found that at a volume fraction of about 40% a small change in the ratio of the small and large particles caused a large variation in elastic modulus. The lowest elastic modulus and osmotic pressure were obtained at around 20 vol% of small particles, which corresponds to the highest packing fraction. Buckmann et al. [16] studied the rheology, MFT, drying behavior and film absorption of water on bimodal latices obtained by blending two latices with different particle sizes (50 and 340 nm). It was also demonstrated that the viscosity, MFT and drying time showed a minimum at a 80/20 (large/small, by weight) blend ratio. It was recognized that at this ratio the small particles fill the voids of a large particle system so that the whole system has a minimum void volume.

In this paper, we report the rheological properties of bimodal and trimodal latices obtained by blending three monosized styrene/butyl acrylate/methacrylic acid copolymer latices, a type of latex widely used in the coating industry. The effect of particle size and size distribution on the viscosity and the maximum packing fraction were studied. In addition, the rheology of several high solid content trimodal polymer latices was compared with that of the corresponding latices obtained from blending the monosized latices.

Experimental

Technical-grade monomers were used in this work. Styrene (St. ACROS) contained 10–15 ppm p-tert-butylcatechol as inhibitor. Butyl acryloate (BA, ACROS) and Methyl acrylate (MA, ACROS) contained 25–40 ppm p-tert-butylcatechol. Methacrylic acid (MAA, JANSSEN CHIMICA) contained 250 ppm MEHQ. Ammonium persulfate (APS, MERCK), sodium hydroxide (PROLABO), emulsifier HV25 (polyoxyethylene alkylphenyl ether from SCHERING) and NOS25 (sodium salt of sulfated polyoxyethylene alkylphenyl ether from SCHERING) were also used as received. Deionized water was used throughout the work.

Four monodisperse latices were synthesized by seeded, semi-continuous emulsion polymerization. The recipes for these latices are given in Table 1. Polymerizations were carried out in a 1 l glass reactor equipped with a reflux condenser, an anchor stirrer, sampling device, nitrogen inlet and two feed inlet tubes. The seed (7.5% of the total monomers, initiator and 25% of the total surfactants as well as water) was charged into the reactor under nitrogen atmosphere, heated to 70 °C, maintained at that temperature for 15 min for latex SP, MP and 1.5 h for latex LP-1, LP-2. The reactor was then heated to 80 °C and the monomer feed was introduced. The feed was divided into two streams. The first was a pre-emulsion of the monomers, surfactant and water. The second was an aqueous solution of the initiator. The flow rates of these streams were adjusted so that the addition of both streams was complete after 5 h. The polymerization was then continued in batch for another 2 h. The latices thus obtained are monodisperse [17], and Table 2 shows the particle sizes measured using quasielastic light scattering (QELS).

Multimodal PSD latex, refered as TM1, TM2, TM3 and TM4 were obtained from ELF ATOCHEM.

The particle size and size distribution was measured using a centrifuger-quasielastic light scattering method [17]. The latex was first fractionated by centrifugation, and the different populations of particle were separated. The size of these particles was subsequently measured quasielastic light scattering (QELS), and the mass fractions of the different sized particles were determined gravimetrically. The particle sizes and size distributions obtained by this method are reported in Table 3.

The solid contents of all the latices were determined gravimetrically. In order to obtain a wide range of solids,

Table 1 Recipes for the polymerization of the monodisperse latices

Run	St	BA	MAA	NOS25	HV25	APS	H_2O	Solid content [%]
SP	67.4	32.4	0.2	4.4	5.1	0.67	110	50
MP	66	33	1	2.5	2.2	0.6	104	50
LP-1	66	32.5	1.5	0.69	1.76	0.61	90.8	53
LP-2	67	32	1	0.27	1.56	0.67	90.8	53

Table 2 Particle sizes of lattices by QELS

Latex	D_p [nm]	Dispersity
SP	75	0.017
MP	135	0.022
LP-1	340	0.004
LP-2	477	0.043

the latex (or latex blends) was diluted with deionized water to obtain low volume fractions, or concentrated under vacuum in order to obtain higher solids contents. The volume fraction of the particles was calculated from the total solid, using a measured polymer density of 1.05 g cm^{-3}.

The rheological measurements were performed on a SUCK V10 (Germany) Rheometer. A coaxial cylinder with a mobile cup of radius of 20 cm and a fixed bob of radius of 18.5 cm was used. Measurements were carried out over a range of shear rate from 0.2–100 s^{-1}. The value of the latex viscosity at the shear rate 10 s^{-1} was used for calculating the absorbed layer thickness δ and the maximum packing fraction ϕ_m. All the measurements were made at 21 °C.

Results and discussion

Figure 1 shows the viscosity profiles of the monodisperse lattices, and of their mixtures at various concentrations. All the latices displayed the typical flow behavior found in nonflocculated concentrated colloidal dispersions [18]: a Newtonian plateau at low shear rates followed by shear thinning at intermediate rates. The high-shear Newtonian plateau was not found because of the limitation of shear rate range of the rheometer. For the least concentrated latex, the flow behavior appears to be Newtonian; which can be explained by the weak interparticle interactions. Because of the high surface charge density, the dominant colloid chemical force between particles is electrostatic repulsion, and the Brownian motion of the particle is suppressed. At low shear stress, the particles assume positions in a three-dimensional structure. Under shear however, the three-dimensional latex structure is destroyed, and in its place one would expect that the particles would arrange themselves in layers parallel to the planes of constant shear. When the concentration of latex is reduced, this repulsive force was less important and the effects of the structure became rheologically insignificant.

The volume dependence of viscosity of concentrated dispersions can be predicted using the Krieger–Dougherty expression [Eq. (2)]. The maximum packing fraction can be obtained from a plot of $1/\eta^{1/2}$ versus ϕ and extrapolation to $1/\eta^{1/2} = 0$ [5, 13]. For latex SP ($D_p = 75$ nm), the maximum packing fraction ϕ_m was 0.645, while for latex MP ($D_p = 135$ nm) and latex LP-1(340 nm) ϕ_m was found to be 0.678 and 0.682, respectively, which is near the theoretical close packing volume fraction (0.68 for body-centered cubic, and 0.64 for random packing).

Given that there is always a absorbed layer on the particle surface of latex, the particle volume fraction ϕ should be replaced by ϕ_{eff}, in order to fit the viscosity to the Krieger–Dougherty equation. From ϕ_{eff}, and ϕ the absorbed layer thickness δ was calculated using for ϕ_{eff}, and ϕ the following expression:

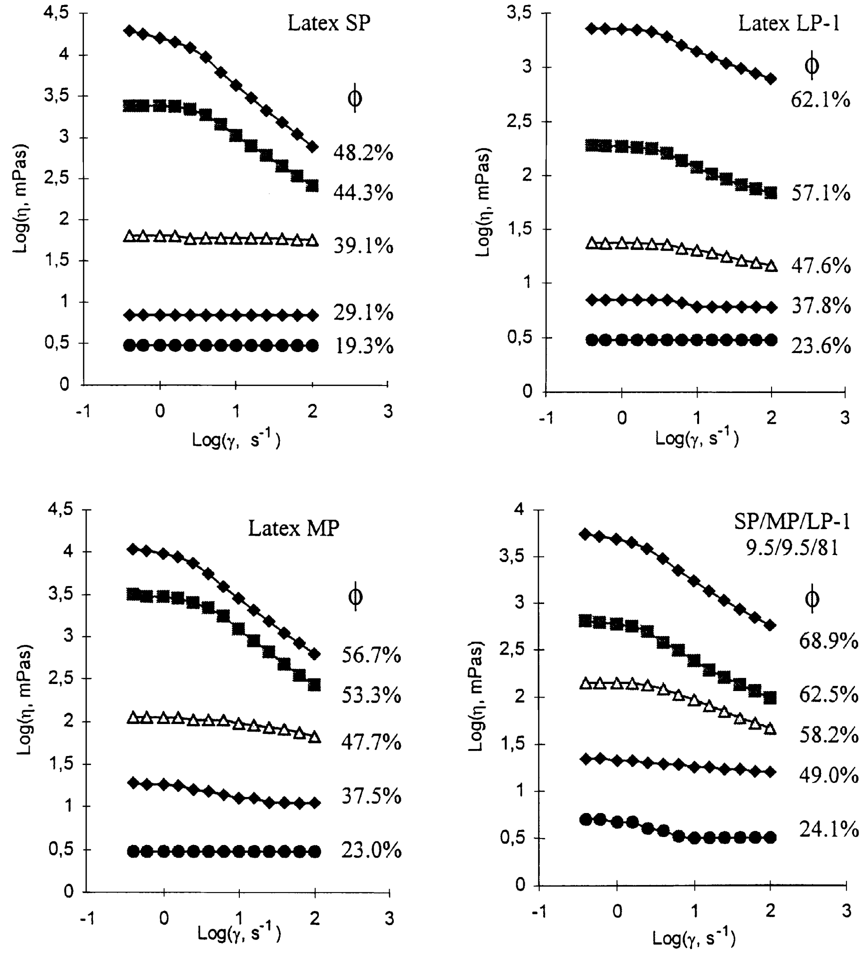
$$\phi_{\mathrm{eff}} = \phi(1 + \delta/R)^3 , \qquad (3)$$

where R is the particle radius. Figure 2 shows the variation of η_r versus ϕ_{eff} for the three monodisperse latices. The values of δ used to fit the experimental points to the Eq. (2) are given in Table 4. The results show that δ decreases gradually with increase of volume fraction, which is caused clearly by the compression of the absorbed layer when the concentration of the latex is increased. δ was also observed to increase with increasing size particle. These tendencies agree reasonably well with the results of Liang and of Prestidge [5, 13], although the δ values found in this work were much more smaller. The lower δ values may be explained by the fact that the surfactants used in this work have a low molecular mass and that low amount of

Table 3 Particle size and size distribution of trimodal latices

Latex	Particle size [nm]			Size distribution	(Large/middle/small)
	Large	Middle	Small	In weight	In number
TM-1	531	91	38	82/6/12	1/14.5/399
TM-2	549	101	55	80.5/9/10.5	1/18/130
TM-3	538	121	36	89/4/7	1/4/263
TM-4	586	128	42	91/4/5	1/4.2/149

Fig. 1 Latex viscosity as a function of shear rate. The particle volume fractions are indicated at the end of lines



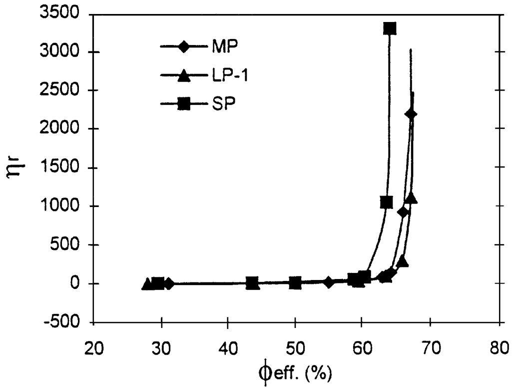


Fig. 2 Relative viscosity of latex versus effective volume fraction. Solid lines are drawn using the Krieger–Dougherty equation

surfactants was used in the formulation, while the polystyrene latex was stabilized sterically by grafted poly (ethylene oxide) chains in the previously cited works.

It can also be seen from Table 4 that when the latices were concentrated, δ tends to about the same value regardless of any differences in particle sizes. Therefore, one can estimate ϕ_m of a multi-sized latex from Eq. (2) by assuming an appropriate value of δ. In order to do that, the latex must be concentrated to a high volume fraction in order to obtain a relative similar value of δ for all the particles.

Tables 5 and 6 show the results of this type of calculation for a δ of 3.8 nm. The maximum solids contents S_m (corresponding to ϕ_m) are also presented in these Tables. In Fig. 3, the ϕ_m of the bimodal latices are plotted as a function of blending ratios. For mixtures of both SP/LP-2 latices and MP/LP-2 latices, a maximum volume fraction (or solid content) was found at 80% wt. fraction of the large particles w.r.t. total solid. No maximum volume fraction was observed for the mixture of SP/MP latices because of the insignificant difference in the sizes of the two kinds of particles. If one compares Fig. 3A with B, it can be seen that the binary mixture with SP shows a higher

Table 4 Absorbed layer thickness δ calculated by Eqs. (2) and (3)

Latex P ($D_p = 75$ nm)				Latex MP ($D_p = 135$ nm)				Latex LP-1 ($D_p = 340$ nm)			
η_r	ϕ	ϕ_{eff}	δ [nm]	η_r	ϕ	ϕ_{eff}	δ [nm]	η_r	ϕ	ϕ_{eff}	δ [nm]
3292	48.2	64.1	3.7	2185	56.7	67.1	3.9	1108	62.1	67.1	4.4
815	45.3	63.5	4.5	946	53.3	66.6	5.2	292	59.9	65.8	5.4
83.1	40.8	60.3	5.2	141	49.6	64.1	6.0	93.1	57.1	63.4	6.0
49.2	39.1	58.7	5.4	85.4	47.7	62.9	6.5	33.1	52.2	59.4	7.5
6.2	29.1	43.6	5.4	9.6	37.5	50.0	6.8	16.2	47.6	54.9	8.3
2.7	19.3	29.6	5.7	2.8	23.0	31.2	7.2	5.8	37.8	43.8	8.6
								2.5	23.6	28.0	10.0

Table 5 Calculated ϕ_m and S_m of bimodal latices by assuming $\delta = 3.8$ nm

Latex	Ratio of particles [by wt.]	η_r	ϕ [%]	ϕ_{eff} [%]	ϕ_m [%]	S_m [%]
LP-2/SP	100/0	4315	64.0	67.1	67.6	65.6
	95/5	462	64.7	68.8	71.0	67.9
	90/10	469	67.0	72.2	75.0	70.7
	80/20	323	68.2	75.4	79.8	73.2
	70/30	1077	68.0	77.2	79.6	71.2
	60/40	1139	64.2	74.7	76.6	66.9
	50/50	646	59.6	71.1	73.2	62.6
	0/100	3292	48.2	64.4	64.8	50.3
LP-2/MP	100/0	4315	64.0	67.1	67.6	65.6
	90/10	538	66.6	70.7	73.0	69.9
	80/20	238	67.5	72.6	77.1	72.9
	70/30	785	68.3	74.3	76.7	71.5
	60/40	223	62.7	69.0	72.7	67.4
	40/60	508	60.3	67.9	69.8	63.2
	0/100	2185	56.7	66.8	67.5	58.5
MP/SP	100/0	2185	56.7	66.8	67.5	58.5
	80/20	1285	54.3	65.7	66.6	56.3
	70/30	1946	54.5	66.8	67.6	56.4
	0/100	3292	48.2	64.4	64.8	50.3

Table 6 Calculated ϕ_m and S_m of trimodal latices by assuming $\delta = 3.8$ nm

Latex	Ratio of particles [by wt.]	η_r	ϕ [%]	ϕ_{eff} [%]	ϕ_m [%]	S_m [%]
LP-2/MP/SP	85/10/5	785	69.8	75.1	77.6	73.2
	85/5/10	777	70.3	76.2	78.9	73.8
	75/17.5/7.5	531	69.4	75.9	79.2	73.5
	75/7.5/17.5	831	70.6	78.3	81.3	74.3
	81/9.5/9.5	1077	71.7	78.0	80.5	75.0
LP-1/MP/SP	85/10/5	592	66.3	71.4	73.7	69.7
	85/5/10	454	65.8	71.3	74.0	69.4
	75/17.5/7.5	754	66.3	72.5	74.6	69.4
	75/7.5/17.5	562	65.0	72.1	74.6	68.4
	81/9.5/9.5	723	67.4	73.4	75.7	70.6

ϕ_m than that with MP at same blending ratios. It seems that the small particles fill the voids of large particles more effectively than those between the medium sized particles. This behavior was also observed in rheology of concentrated suspensions using binary mixtures of glass beads [19].

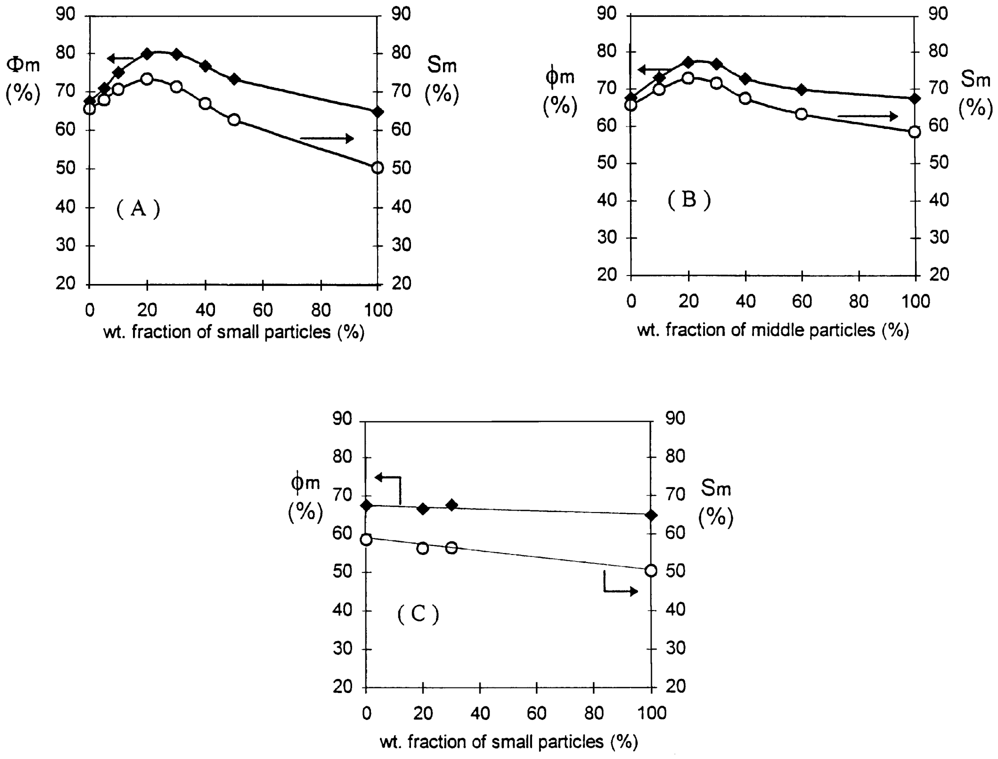


Fig. 3 Maximum volume fraction ϕ_m and maximum solid S_m as a function of wt. fraction of the smaller particles in binary mixtures (A) mixture of SP/LP-2 latices; (B) mixture of MP/LP-2 latices; (C) mixture of SP/MP latices

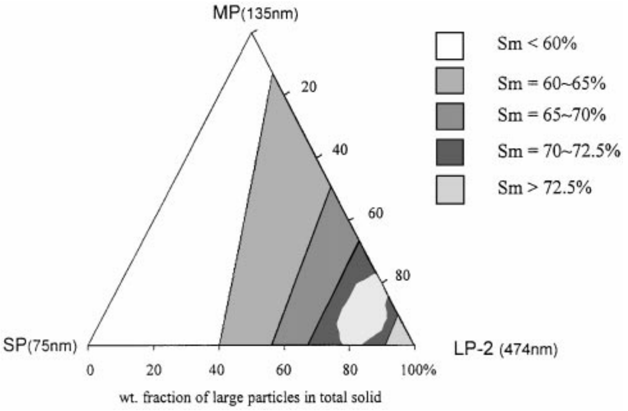


Fig. 4 Maximum solid obtainable (Sm) as a function of particle size distribution of trimodal latices (LP-2/MP/SP)

Table 6 shows the results of the trimodal systems, and it can be seen that the introduction of a third component further increases the particle packing. At wt. fraction of large particles between 75% and 85% in total solid, ϕ_m was always more than 77.5% and S_m more than 73%. The change of the ratio of small particles/medium particles at same wt. fraction of large particles seems to have no noticeable effect on the ϕ_m and S_m. The highest packing fraction was found at wt. blending ratio of around 10/10/80 (small/medium/large). Figure 4 shows a ternary diagram which summarizes the above results.

When latex LP-2 was replaced by LP-1, i.e., when the size of large particles in trimodal latex was reduced, similar results was obtained. The highest volume fraction was also observed at blending ratio of around 80/10/10 (large/medium/small), as shown in Table 6. In case of LP-1, a lower ϕ_m was obtained, compared to that found for of LP-2, which indicates a significant effect of the size of large particles (or ratio of large/small) on the rheology of latex.

Figure 5 shows the comparisons between the trimodal latices obtained both from blending and those coming from ATOCHEM. Although the individual particle sizes of these pairs of latices are different, they show very similar viscosity and flow behavior when the size distribution and total solid are close. However, a small change of the PSD greatly changes the viscosity of the latex. As can be seen from Fig. 6, a variation of wt.% of large particles from 85% to 90% increases significantly the viscosity. Furthermore, it is interesting to note that the latices (TM1-4) showed a much stronger shear-thinning behavior than the blended ones. This may be explained by small changes in their composition as compared with the blends.

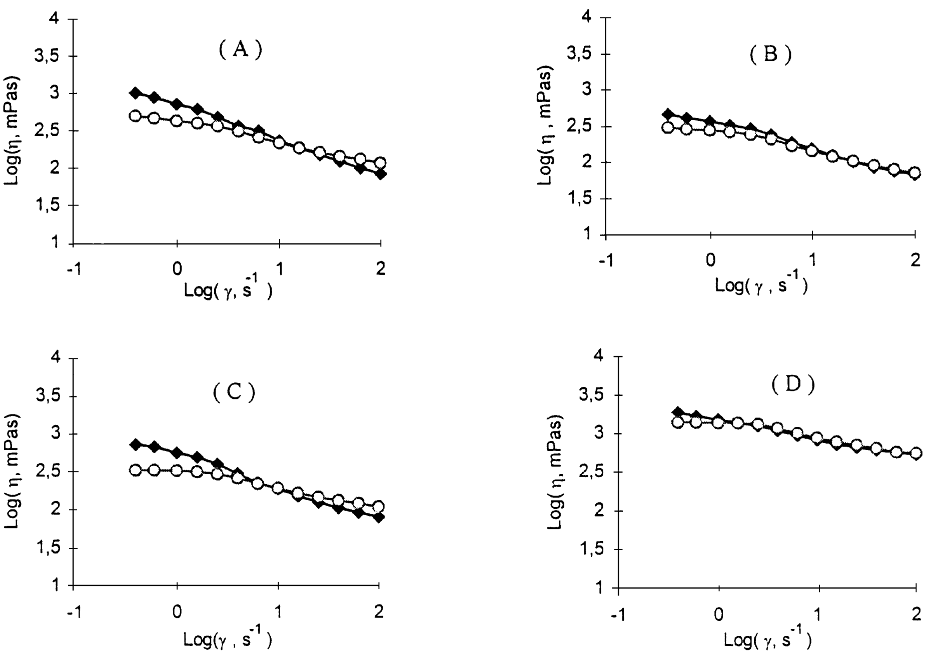


Fig. 5 Comparison of latices obtained from blending and synthesis with same PSD and total solid content. (A): (◆) TM-1, solid content = 65.10%; large/middle/small = 82/6/12; (○) LP-2/MP/SP = 85/5/10, solid content = 65.4%. (B): (◆) TM-2, solid content = 64.8%; large/middle/small = 80.5/9/10.5; (○) LP-2/MP/SP = 81/9.5/9.5, solid content = 64.3%. (C): (◆) TM-3, solid content = 64.0%; large/middle/small = 89/4/7; (○) LP-2/MP/SP = 90/4/6, solid content = 64.5%. (D): (◆) TM-4, solid content = 68.0%; large/middle/small = 91/4/5; (○) LP-2/MP/SP = 90/4/6, solid content = 68.4%

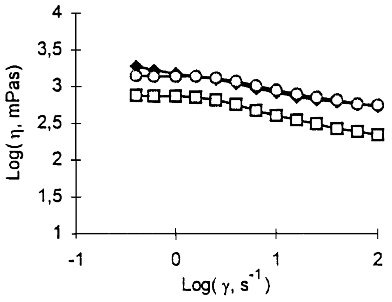


Fig. 6 Comparison of latices obtained from blending and synthesis with same total solid content but a different PSD. (◆) TM-4, Solid content = 68.0; large/middle/small = 91/4/5; (○) LP-2/MP/SP = 90/4/6, solid content = 68.4%. (□) LP-2/MP/SP = 85/10/5, solid content = 67.8%

Conclusions

The rheological measurements presented here were used to investigate particle interactions by measuring the value of the surface absorbed layer thickness δ. For St/BA/MAA copolymer latices stabilized by low molecular mass surfactant, the δ values were found to be in the range of 4–10 nm, depending on the concentration of latex and the size of particle.

The viscosity of the bimodal and trimodal latices was studied as a function of the blending ratios of the monodisperse latices. The maaximum packing fraction of particles was calculated by Krieger–Dougherty equation. The results show that the maximum packing (or highest solid) occurs at a wt. fraction of 80% of large particle w.r.t. total solids content for both bimodal and trimodal latices. The best PSD for a trimodal latex to obtain the maximum packing was found to be around 80/10/10 (large/middle/small particle by wt.).

A comparison of the synthesized and blended trimodal latices revealed that the two latices had a very close viscosities and rheological behavior when their PSD and total solids content were the same, even if the particle sizes of the two latices were different. Thus the results obtained from the mixture of monodisperse latices can be used to optimize the synthesis of multimodal PSD latex.

Acknowledgements The authors are indepted to ELF ATOCHEM for support and the permission to publish that work.

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