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ORIGINAL CONTRIBUTION

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High solids content latexes with low viscosity

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Abstract The effect of particle size distribution (PSD) on the solids content and viscosity of the multisized latex was investigated by blending mono-sized latexes and measuring their rheological properties. The results showed that the maximum packing (highest solids content) was observed at a weight fraction 80% of large particles with respect to total solids content for both bi-modal and tri-modal latexes, and the lowest viscosity was obtained when the ratio of large to medium to small particles was approximately 80/10/10 (by weight). A two-stage technique to prepare high solids multi-sized polymer latex was developed by using a polymer latex previously made as seed and by adding small amount of additional surfactants and/or second group of polymer particles. The PSD of the latex was optimized by varying the amount of the seed, the additional surfactants, and the second group of particles. Film forming latexes with high solids ($>65\%$) and low viscosity were obtained.

Key words High solids · Low viscosity · Latex

Introduction

The preparation of high solids content latexes is an area of great industrial interest and importance. High drying rates, low energy cost, and improved mechanical and rheological properties can be obtained with high solids contents. However, this topic has received very little attention in the literature in spite of its industrial importance. As a response to the growing interest expressed by industry, the amount of work in the technical literature on high solids content latex has increased in recent years. The most common way to achieve high solids is to produce a latex with a polydisperse particle size distribution (PSD) by using multistage polymerization [1–3] or some special emulsifiers [4, 5]. This allows us to create small particles that are situated in the voids between large particles, thereby increasing the maximum packing fraction of particles.

There are relatively few experimental or theoretical studies on multi-sized PSD latex. Kuo and Chen [6] studied emulsion polymerization using polymeric emulsifiers, and the emulsions obtained were found being a bimodal PSD, which was interpreted in terms of the formation of polymer aggregates. Masa et al. [7] investigated seeded semicontinuous emulsion polymerization, and reported that the secondary nucleation can take place when a large amount of emulsifier was used. Buckmann et al. [8] prepared a bimodal latex by mixing two mono-sized latexes, and studied the effect of the blend ratios on the rheology, the drying behavior, the MFT (minimum film-forming temperature), and the film water absorption of latex. Kim and Luckham [9] studied the rheological properties of bimodal polystyrene particles by measuring the elastic modulus, dynamic viscosity, and osmotic pressure as a function of blending ratios and total particle volume fraction. More recently, Chu et al. [10–13] prepared bimodal or trimodal polymer latexes by introducing additional surfactants during semi-continuous emulsion polymerization, and investigated the variation of particle sizes and size distribution, as well as the overall polymerization features. It was also demonstrated that the viscosity of latexes obtained depended strongly on the size distribution of particles and a minimum of viscosity was found at 20 wt% of small particles which corresponds to the highest particle packing.

In this article we first try to find the best PSD for a multi-sized polymer latex in order to achieve high solids and low viscosity. Then a two-stage technique was developed to prepare multi-sized high solids content latex by adding small amount of additional surfactants and/or second group of polymer particles. High solids (>65%) film forming latexes have been obtained.

Experimental

Technical-grade monomers were used in this work. Styrene (St, ACROS) contained 10–15 ppm *p-tert*-butylcatechol as inhibitor. Butyl acrylate (BA, ACROS) and methyl acrylate(MA, ACROS) contained 25–40 ppm *p-tert*-butylcatechol. Methacrylic acid (MAA, ACROS) contained 250 ppm methyl hydroquinone. 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.

Three monodisperse latexes were synthesized by seeded semi-continuous emulsion polymerization. The recipes for these latexes 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. 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 monomer, 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 latexes thus obtained are monodisperse [14], and Table 2 shows the particle sizes measured by quasielastic light scattering.

Multi-modal PSD latexes were prepared by two procedures. Procedure 1 was the general procedure using latex LP as the seed (or the first stage emulsion). Latex LP was charged into the reactor and some additional surfactants or/and second group of polymer particles (from the small mono-sized particles SP) were added in a single shot. The mixture was then heated to 80 °C and the monomers (St/BA/MAA = 65/32/3, wt/wt) and the solution of initiator (1 wt% based on monomers) were fed for 3 ~ 5 h (depending on the amount of monomers). After that, the reactor was maintained at 80 °C for another 2 h to complete the polymerization.

Table 2 Particle sizes of latexes by QELS

Latex	Dp (nm)	Dispersity
SP	75	0.017
MP	135	0.022
LP	477	0.043

Procedure 2 is described at the beginning of the second part of results and discussions. This procedure, which led to bimodal PSD, was only used for the latexes concerning the results in Figs. 3, 4, and 5.

The particle size and size distribution of these latexes was measured using a centrifuger-quasielastic light scattering method [14]. The latex was first fractionated by centrifugation, and the different populations of particle were separated. The size of these particles was subsequently measured by quasielastic light scattering (QELS), and the mass fractions of the different sized particles were determined gravimetrically.

The solids content of all the latexes was determined gravimetrically. In order to determine the best PSD of the multi-sized latex, the latex blends were concentrated under vacuum in order to obtain higher solids contents. The volume fraction of the particles was calculated from the total solids, using a measured polymer density of 1.05 g/cm^3. The viscosity of latex was measured on a SUCK V10 rheometer at 21 °C.

Results and discussions

Effect of PSD on viscosity and solids content of latex

It is well recognized that the maximum packing fraction of a polymer latex can be increased by a bimodal or multi-modal PSD. Thus, a multi-sized latex might show a lower viscosity at the same, or even higher, solids content than a mono-sized latex. As can be seen from Table 3, the mono-sized latex shows a viscosity of 1953 mPa·s at solids content of 65%, while the tri-modal latex with a similar composition and solids content only shows a viscosity of 84 mPa·s.

In order to optimize the PSD of latex, the mono-sized latexes were blended and then concentrated under vacuum in order to obtain higher solids content. The viscosity of latex was measured. The maximum packing fraction of particles ϕ_m and the maximum solids content obtainable S_m were calculated by the Krieger-Dougherty equation [15, 16]:

$$\eta_r = \eta/\eta_0 = [1 - \phi/\phi_m] - [\eta]\phi_m$$

where η_r is the relative viscosity, η_0 is the viscosity of the media, ϕ is the volume fraction, ϕ_m is the volume

Table 1 Recipes for the polymerization of the mono-sized latexes

Run	St (g)	BA (g)	MAA (g)	NOS25 (g)	HV25 (g)	APS (g)	H_2O (g)	Solids 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	67	32	1	0.27	1.56	0.67	90.8	53%

Table 3 Effect of PSD on viscosity of latex

Latex	Particle size (nm) and PSD (in weight)			Solids content (%)	Viscosity (mPa·s)
	Large	Medium	Small		
LP concentrated	477 (100%)	0 (0%)	0 (0%)	65.1	1953
LP-40–4	531 (82.1%)	91 (5.7%)	38 (12.2%)	65.0	84.4

fraction at maximum packing (i.e., the volume fraction at which the viscosity becomes infinite), and $[\eta]$ the intrinsic viscosity (=2.5 for hard sphere).

It should be indicated that ϕ here is the effective volume fraction of particle (including the hydrated layer on particle surface). ϕ_m was obtained from a plot of $\eta^{1/2}$ vs ϕ and extrapolation to $1/\eta^{1/2}=0$ [17, 18]. ϕ_m is almost independent of the particle size. However, the maximum solids content obtainable (S_m) differs significantly with the particle size because of the presence of the hydrated layer.

Figure 1 presents the ϕ_m and S_m of the bimodal latexes as a function of blending ratios. It could be seen that the bi-modal latexes show a higher ϕ_m or S_m than the mono-sized ones in all the blending ratios, and a maximum volume fraction (or solids content) was found to be 80 wt% of the large particles with respect to total solids. In our previous paper [13] it was shown that the packing fraction of particles could be further increased when a third component was introduced into the bimodal systems. As shown in Fig. 4 of [13], the S_m of tri-modal latexes was always more than 72.5 wt% of large particles between 75% and 85% in total solids. The highest packing fraction was found at weight blending ratios of around 10/10/80 (small/medium/large).

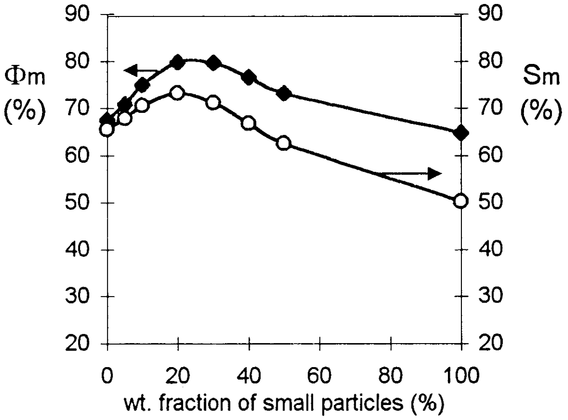

Fig. 1 Maximum volume fraction ϕ_m and maximum solids S_m as a function of wt. fraction of the smaller particles in binary mixture of latex SP and LP

The results above are based on the blends of mono-sized latexes. In order to confirm the suitability of these results for latex synthesized, the rheology of four tri-modal latexes synthesized was compared with those from blending. Table 4 and Fig. 2 present such a comparison. Although the individual particle sizes of these pairs of latexes are different, they show very similar viscosity and flow behavior when the size distribution and total solids are close. However, a small change of the PSD greatly changes the viscosity of latex. As shown in Fig. 2B, a variation of wt% of large particles from 85 wt% to 90 wt% increases the viscosity significantly. Furthermore, it is interesting to note that the latexes synthesized showed a rather stronger shear-thinning behavior than the blended ones, especially at low shear rates. This may be explained by higher level of MAA in the composition of synthesized latex as compared with the blends. Usually, the shear-thinning increases with increasing amount of MAA in composition because of the enhancement of interparticle interactions.

Table 4 Comparison of particle sizes and PSD of latexes obtained from blending and synthesis

Latex	Particle size (nm)			PSD in weight (large/medium/small)	Solids content (%)	Viscosity mPa·s[b]
	Large	Medium	Small			
LP-50–3* Diluted	549	101	55	80.5/9/10.5	64.8	150
LP-50–2.1[a]	586	128	42	91/4/5	68.0	824
Blend 1	477	135	75	81/9.5/9.5	64.3	140
Blend 2	477	135	75	90/4/6	68.4	879
Blend 3	477	135	75	85/10/5	67.8	404

[a] See second part of this paper for the syntheses of the latex
[b] Viscosity at the shear rate 10 s^{-1}

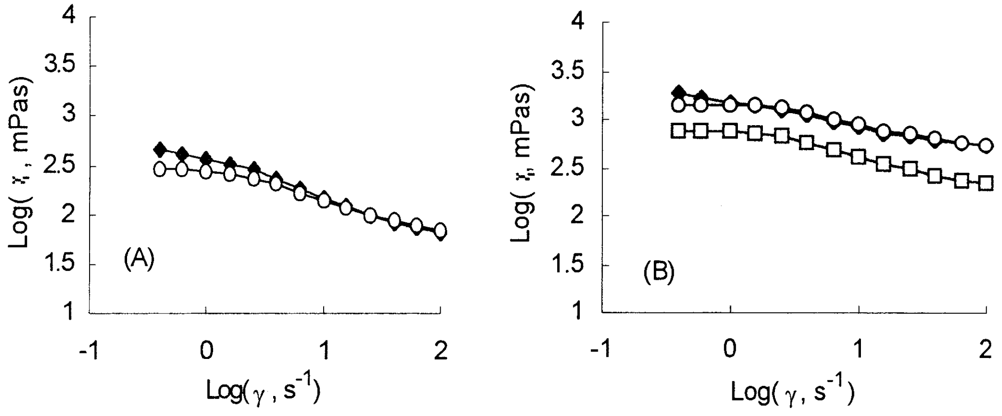

Fig. 2A, B Comparisons of rheology of technical and blended latexes: **A** ◆ LP-50–3, ○ blend 1; **B** ◆ LP-50–2.1, ○ blend 2, □ blend 3

Multi-sized latexes prepared by secondary nucleation

It is common knowledge that the nucleation takes place when the concentration of free surfactant in an emulsion polymerization system is over critical micelle concentration. Thus, a second population of particles can be generated by adding some additional surfactants during polymerization. Figure 3 is the microphotograph of a typical bimodal latex obtained in this way. The composition of polymer is the same as latex LP. Once 70% of monomers were introduced, 3.5% (based on the weight of monomers) of additional surfactants (NOS25 + HV25) was added in a single shot. As can be seen in Fig. 4, the calculated surfactant surface coverage S decreased from 78% to 50% before the addition of additional surfactants, assuming that all the surfactant molecules were absorbed on the surface of particles. When the additional surfactants were introduced, the particles were over-stabilized, and much of the surfactant was left in the serum, which results in the generation of new particles. Figure 5 shows the evolution of the sizes of both large and small particles.

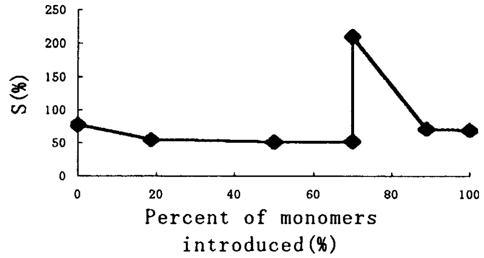

Fig. 4 Evolution of the calculated surfactant surface coverage (S) as a function of time. S = area covered by surfactant/surface area of particles. The molecular absorption area Ap = 160 Å^2 for NOS25 and 110 Å^2 for HV25

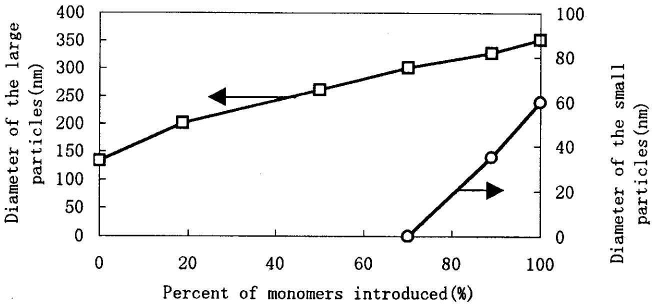

Fig. 5 Evolution of particle sizes of bimodal latex

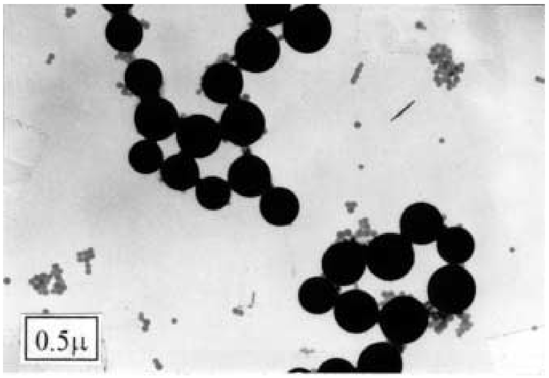

Fig. 3 TEM microphotographs of a typical bi-modal latex

In order to investigate secondary nucleation and optimize the PSD of multi-sized polymer latex, the mono-sized latex LP was used as the starting latex (seed) and a varying amount of surfactant was introduced. The polymerization was carried out by drop-wise addition of monomers. In the first series of experiments, the amount of monomers added was fixed (weight of monomers/latex LP in solids = 40/60) and the amount of surfactant was varied from 0% to 4% based on total solids. As seen in Table 5, an increase in the amount of additional surfactants causes the diameter of large particles, the diameter of middle particles, and the amount (weight) of large particles to decrease, but the amount of both the

Table 5 Effect of the amount of additional surfactants on properties of final latexes

Run	Additional surfactants (NOS25 + HV25)	Monomers/ latex LP (weight in solids)	PSD and particle size (Large/ Medium/Small)	Properties of final latex		
				Solids content (%)	Viscosity (mPa·s)[a]	Coagu-lum (%)
LP-40–4	4.0%	40/60	82/6/12 (531/91/38 nm)	65.0	84.4	0
LP-40–2.5	2.5%	40/60	89/4/7 (538/121/36 nm)	64.0	79.6	0
LP-40–1.25	1.25%	40/60	93/4/3 (549/130/36 nm)	63.3	96.6	0
LP-40–0	0%	40/60	Coagulate			

[a] Viscosity at shear rate 10 s^{-1}

small and medium particles to increase. Without the addition of additional surfactants, no secondary nucleation was found and emulsion was coagulated during polymerization. Comparing Table 5 with the results of the first part, it seems that a 4% addition of additional surfactants (Run LP-40–4) gives the best PSD.

It is interesting to note in Table 5 that the PSD of latexes obtained shows a tri-modal distribution. This could be explained by the polydispersion of the second population of particles, caused by the flocculation of small particles. In order to compare more clearly the results among different experiments, a second fractionation by centrifugation has been conducted for the secondarily generated particles. This fractionation is also the reason why the size of the smallest particle fraction is independent of the amount of additional surfactant.

In the second series of experiments, the amount of additional surfactants was 4% or 3%, but the amount of monomers added was changed from 30% to 50% in total solids. The results are shown in Table 6. As expected, the diameters of the three groups of particles increase as the quantity of the monomers increases. Due to the fact that the small particles have a larger surface, the small particles grow faster than the larger ones. As a result, the fraction of the large particles decreases with the increase of monomers. Thus, one can get an ideal PSD using relatively lower level of surfactant by increasing the quantity of monomers. However, latex will probably coagulate when the solids content is over 68%.

It can be seen from the results above that run LP-50–3 shows the best PSD and highest solids content. Because the presence of large amounts of surfactant are undesirable in terms of latex applications, we try to reduce the amount of additional surfactants in third series of experiments. Table 7 gives the results. As expected, the percentage of large particles decreases with

Table 6 Effect of the amount of monomers on properties of final latexes

Run	Additional surfactants (NOS25 + HV25)	Monomers/latex LP (weight in solids)	PSD and particle size (Large/Medium/Small)	Properties of final latex		
				Solids content (%)	Viscosity (mPa·s)[a]	Coagulum (%)
LP-30–4	4.0%	30/70	89/1/10 (507/91/26 nm)	61.7	66.2	0
LP-40–4	4.0%	40/60	82/6/12 (531/91/38 nm)	65.0	84.4	0
LP-50–3	3.0%	50/50	80.5/9/10.5 (549/101/55 nm)	66.2	77.8	∼0.5
LP-57–4	4.0%	57/43	Coagulate			

[a] Viscosity at shear rate 10 s^{-1}

Table 7 Effect of the amount of additional surfactants on properties of final latexes

Run	Additional surfactants (NOS25 + HV25)	Monomers/ latex LP (weight in solids)	PSD (Large/ Medium/ Small)	Properties of final latex		
				Solids content (%)	Viscosity (mPa·s)[a]	Coagulum (%)
LP-50–3	3.0%	50/50	80.5/9/10.5	66.2	77.8	∼0.5
LP-50–2.1	2.1%	50/50	91/4/5	68.0	525	∼0.5
LP-50–1.25	1.25%	50/50	92/6/2	66.8	138	∼1
LP-57–3	3%	57/43	Coagulate			

[a] Viscosity at shear rate 10 s^{-1}

decreasing amount of surfactant. Another consequence of the reduction of the amount of surfactant is that more coagulum will be produced during polymerization, which is unfavorable for production of latex. If we added more monomers to latex LP-50–3 (run LP-57–3 in Table 7), latex coagulated at the end of polymerization because of higher solids content and a departure from the best PSD.

It is very important to use a mixture of anionic surfactant and nonionic surfactant in order to obtain high solids latex with no or little coagulum. As shown in Table 8, particles were insufficiently stabilized and a great deal of coagulum was formed with only anionic surfactant, while the absence of anionic surfactant was unfavorable for the secondary nucleation. It seems that the exact ratio of anionic/nonionic surfactant did not have a significant effect on the secondary nucleation provided their mixture was used.

Effect of introduction of second group of particles on properties of latex

It is also possible to prepare multi-sized polymer latex by adding some smaller-sized polymer particles to a polymerization system. Figure 6 is the microphotograph of a typical bimodal latex obtained by this mode. The composition of polymer is the same with latex LP. When 50% of monomers was introduced, 11%(based on the weight of monomers) of smaller polymer particles (latex SP, Dp = 75 nm, mono-sized) was added in a single shot. The final latex has a bi-modal PSD with 60.5% of large particles (Dp = 398 nm) and 39.5% of small particles (Dp = 169 nm).

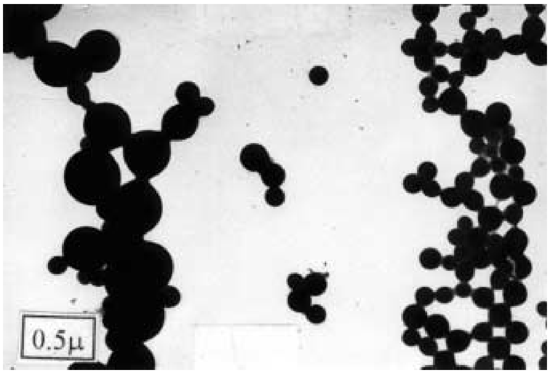

Fig. 6 Typical bi-modal latex obtained by adding second group of particles

Although multi-sized latexes could be prepared by introducing some additional surfactants, as previously described, some disadvantages exist for this method. The presence of too much surfactant is always unde-

Table 8 Effect of the type of additional surfactants on properties of final latexes

Run	Additional surfactants	Monomers/ latex LP (weight in solids)	PSD (Large/ Medium/Small)	Properties of final latex		
				Solids content (%)	Viscosity (mPa·s)[a]	Coagulum (%)
LP-40–2.5	NOS25 1.25%	40/60	89/4/7	64.0	79.6	0
	HV25 1.25%	40/60	89/4/7	64.0	79.6	0
LP-40–2.5A	NOS25 2.0%	40/60	89/5/6	64.4	72	0
	HV25 0.5%	40/60	89/5/6	64.4	72	0
LP-40–2.5B	NOS25 2.5%	40/60	84.5/3.5/12	51.0	16	~15
LP-40–2.5C	HV25 2.5%	40/60	93.5/5.5/1	Coagulate		

[a] Viscosity at shear rate 10 s^{-1}

Table 9 Effect of the introduction of second group of polymer particles on properties of final latexes

Run	Amount of second group of polymer particles	Additional surfactants (NOS25 + HV25)	Monomers/ latex LP (weight in solids)	PSD and particle size (Large/Medium/Small)	Properties of final latex		
					Solids content (%)	Viscosity (mPa·s)[a]	Coagulum (%)
LP-40–0.3	0%	0.3%	40/60	100/0/0 (509/0/0 nm)	61.3	78	~0.5
LP-40–0.3P	10%	0.3%	40/60	83/17/0 (546/122/0 nm)	55.6	15	~4
LP-50–2.1	0%	2.1%	50/50	91/4/5 (586/128/42 nm)	68.0	525	~0.5
LP-50–2.1P	5%	2.1%	50/50	86.5/10.5/3 (584/121/43 nm)	68.1	161	~0.2
LP-57–3	0%	3.0%	57/43	Coagulate			
LP-57–2.1P	10%	2.1%	57/43	83/14/3	68.6	153	~1.0
LP-57–2.7P	15%	2.7%	57/43	79/17/4	69.1	155	~1.0

[a] Viscosity at shear rate 10 s^{-1}

sirable in application of latex, whereas a well-adapted PSD often could not be obtained when a low amount of surfactant was used. In order to overcome this difficulty, a second group of particles with smaller particle size was added to the polymerization system following the addition of additional surfactants. Table 9 shows the comparisons. The first pair of experiments (LP-40–0.3 and LP-40–0.3P) shows that the coagulation was notably aggravated by the introduction of a second group of particles if not enough surfactant was present. This behavior may be explained by the increase of particle surface and the reduction of surfactant surface coverage. Comparing runs LP-50–2.1 and LP-50–2.1P, it is obvious that the introduction of second group of polymer particles had no noticeable effect on particle size of three groups of particles, but increased significantly the amount of the medium particles and hence optimized the PSD of latex. Without the addition of second group of particles, polymerization with 57% of monomers (LP-57–3) leads to coagulation. Therefore latex with high solids content and low viscosity could be prepared by combining the addition of a second group of particles and a small quantity of additional surfactants.

Conclusions

The viscosity of the bimodal and trimodal latexes was studied as a function of the blending ratios of the monodisperse latexes. The maximum packing fraction of particles was calculated by the Krieger-Dougherty equation. The results show that the maximum packing (or highest solids) occurs at a weight fraction of 80% of large particles with respect to total solids content for both bimodal and trimodal latexes. The best PSD for a trimodal latex to obtain the maximum packing was found to be around 80/10/10 (large/medium/small particles by weight).

The possibility of preparing high solids film-forming latexes was also studied through the addition of small amount of additional surfactants and/or second group of particles. The results show that low viscosity, coagulum free latexes with more than 65% solids content can be obtained whereas the maximum solids content obtainable by means of the conventional emulsion polymerization was limited to around 60%.

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