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EMULSIFICATION OF POLYMERS: EFFECT OF FINITE ADJUSTMENTS OF PARAMETERS

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ABSTRACT

Direct emulsifications of polystyrene (PS) and polyisobutylene (PIB) were conducted, where all the latices underwent homogenization after the initial mixing. The former utilized benzene as solvent, and removed it by vacuum distillation after homogenization; while the latter did not use solvent. Discernible variations in particle size were found by adjusting the polyoxyethylene chain length of nonionic surfactant, sodium dodecyl sulfate (SDS) content, the molecular weight (MW) of PIB, or the MW of poly(vinyl alcohol), as long as the viscosities of both the internal and external phases are located in an appropriate range. The prediction of particle size based on the external phase viscosity and Stokes' law seems closer to the experimental data than that based on the calculation of molecular areas of surfactants. For some latices, particles underwent coagulation during the vacuum-distillation process.

INTRODUCTION

The use of water-base coatings and adhesives is highly motivated because of environmental consideration. The direct emulsification of polymers provides an alternative technique for the preparation of latices of certain polymers, such as epoxy, polyester, polyurethane, cellulose derivatives, and stereoregular rubber, which cannot be prepared by emulsion polymerization [1, 2].

It was found [1] that in direct emulsification, important factors that control the particle size of the product latex may include: 1) the type of solvent or mixture of solvents used, 2) the viscosity of the polymer solution, 3) the chain length of the fatty alcohol, and 4) the ratio of the fatty alcohol to the surfactant in the mixed emulsifier combinations as well as the total concentration. However, the quantitative effect of each factor is not available.

Since latices prepared by direct emulsification usually have a large average particle diameter (1–10 μm), which can cause poor shelf stability and inferior film properties, the reduction of the average particle size of the latex produced could be very important [1].

Stokes' law shows that the rate of sedimentation can be reduced by raising the viscosity of the dispersing medium. Therefore, Stokes' law offers a route to determine the largest particle size that a latex can sustain without settling. According to Stokes' law:

$$\text{Rate of sedimentation} = (D^2/18\eta)(d_p - d_m)g \qquad (1)$$

where D is the particle diameter, η is the viscosity of the medium, d_p and d_m are the densities of the particles and the medium, respectively, and g is the gravitational constant. One criterion for the settling that has been given is that a sedimentation rate of 1 mm in 24 hours will be countered by the thermal convection currents and the Brownian motion in the latex [3]. By substituting this criterion, the largest particle size for polystyrene dispersed in water that will not settle on standing is 0.65 μm, and this proved to be consistent with experimental observation [4].

For an emulsification process to succeed, small droplets must be first obtained by mixing, and the coalescence of droplets must be prevented thereafter. There are many reports on this subject. Summaries of emulsification theory can be found in References 5–7.

There are three fundamental methods for preparing polymer latices by direct emulsification, i.e., solution emulsification [8–11], phase inversion [12–15], and self-emulsification [16–18]. In this study, solution emulsification was used to prepare polystyrene (PS) latex, where PS was dissolved in benzene (as the solvent) before dispersing it in water, and the solvent was removed by vacuum distillation after homogenization. On the other hand, the polyisobutylene (PIB) latex was prepared without using solvent, where low MW PIB ($<$2300) was mixed with fatty acid before dispersing it into an aqueous solution of poly(vinyl alcohol) (PVA), Triton X-100, and NaOH.

PS latex has been prepared by direct emulsification [4, 13] before. Saunders and Pelletier's formula [13] contained oleic acid and NaOH as emulsifier, and toluene as solvent, while Vanderhoff et al. [4] used SDS and cetyl alcohol (CA) as emulsifier, and benzene as the solvent. In both studies, crude latices were subjected to homogenization and vacuum distillation, consecutively. Vanderhoff et al. [4] reported that the final average latex particle size was less than about 0.5 μm.

The preparation of PIB (or butyl rubber) latex by direct emulsification has been reported before [19, 20]. Hunter et al. [19] used oleic acid, KOH, PVA, and Triton X-100 as emulsifier, and the butyl rubber used had a molecular weight (MW) of 35,000 to about two million. In the other study [20], a fatty acid metal salt or Na or NH_4 salts of nonylphenyl ether of polyoxyethylene sulfate and related compounds were used. After the removal of hexane, the final latex contained 55% solids.

In this study, mixed emulsifier systems containing sodium dodecyl sulfate (SDS), CA, and polyoxyethylene nonylphenyl ether (Pannox) with different oxide numbers were used. Attempts were made to obtain a quantitative scheme for the effects of the polyoxyethylene chain length of Pannox, the viscosities of both the continuous phase and the droplet phase, and the droplet coalescence during vacuum distillation.

EXPERIMENTAL PROCEDURES

Materials

PS was obtained by bulk polymerization of styrene, and the number-average molecular weight ($\overline{M}_n$) of it as determined by GPC was 37,000. PIB (3 samples with $\overline{M}_n$ of 900, 1290, and 2300, respectively) was provided by Amoco Chemical Company. Nonionic surfactants, Pannox (polyoxyethylene nonylphenyl ether) series, were offered by Pan Asia EOD Chemical Corporation, and Triton X-100 (polyoxyethylene octylphenyl ether with EO number of 9.5) was given by Rohm and Haas Company. SDS (reagent grade) was used as the anionic surfactant. Water was double distilled. Chemicals were reagent grade and used without further purification.

Emulsification

The emulsification of PS was conducted at 63°C. PS was dissolved in benzene, and the solution was then added to an aqueous solution in which SDS, CA, and Pannox had been dissolved beforehand. The mixture was then stirred at 300 rpm for 30 minutes, followed by homogenization using a Polytron Homogenizer (Model PTA 20s) at 4500 rpm for 3 minutes twice with a 2-minute intermission. The operation of the homogenizer combines cavitation and mechanical shearing action. The solvent (benzene) was removed by vacuum distillation at 110 mmHg absolute and 50°C for 11 hours. The recipes for all runs are listed in Table 1.

The emulsification of PIB was carried out at 63°C without using solvent. The recipes are shown in Table 2. Poly(vinyl alcohol) (PVA), Triton X-100, and NaOH were dissolved in water by stirring at 300 rpm for 30 minutes. PIB was mixed with oleic acid and stirred at 300 rpm for 30 minutes. The latter solution was added to the previous one, stirred at 300 rpm for 30 minutes, followed by homogenization in a similar way as that described in the preceding paragraph.

Characterizations

Both particle diameter and solid content of latex were determined before and after the homogenization process, and during the vacuum distillation. The solid content of samples was determined gravimetrically. Values of average particle diameter for most latices were measured by dynamic light scattering (DLS, Photal 3000/3100) and by a transmission electron microscope (TEM, Jeol JEM-200CX). For samples with larger diameters (>0.8 μm), the average particle diameter was deter-

TABLE 1. Recipes for the Emulsification Runs of Polystyrene

	A series				B series			C series			
Parameter	A1	A2	A3	A4	B1	B2	B3	C1	C2	C3	C4
PS, g	18.75	18.75	18.75	18.75	60.0	60.0	60.0	18.75	18.75	18.75	18.75
H_2O, g	222.0	222.0	222.0	222.0	140.0	140.0	140.0	222.0	222.0	222.0	222.0
SDS, g	1.20	1.20	1.20	1.20	2.40	1.60	0.80	1.20	1.20	1.20	1.20
CA, g	2.10	2.10	2.10	2.10	4.20	4.20	4.20	2.10	2.10	2.10	2.10
Benzene, g	56.25	56.25	56.25	56.25	60.0	60.0	60.0	56.25	37.50	28.13	18.75
Pannox, g	0.75	0.75	0.75	0.75	—	—	—	0.75	0.75	0.75	0.75
EO no.	50	40	22	19	—	—	—	50	50	50	50
HLB_{Pannox}	18.1	17.7	16.2	15.8	—	—	—	—	—	—	—
HLB_{mix}	15.7	15.6	15.4	15.3	15.2	11.8	7.2	—	—	—	—

TABLE 2. Recipes for the Emulsification Runs of PIB

Parameter	D series				
	D1	D2	D3	D4	D5
PIB, g	60.0	60.0	60.0	60.0	60.0
$\overline{M}_n$	920	920	920	1290	2300
η, cP (63°C)	1340 ± 150	1340 ± 150	1340 ± 150	3890 ± 600	29,000 ± 5400
H_2O, g	140.0	140.0	140.0	140.0	140.0
Oleic acid, g	3.15	3.15	3.15	3.15	3.15
Triton X-100, g	3.15	3.15	3.15	3.15	3.15
NaOH, g	0.50	0.50	0.50	0.50	0.50
PVA, g	2.70	2.70	2.70	2.70	2.70
MW	15,000	22,000	100,000	100,000	100,000
% hydrolyzation	87.5 ± 1.5	98.5 ± 1.5	87.5 ± 1.5	87.5 ± 1.5	87.5 ± 1.5
η, cP (aq, 63°C)	24.6 ± 0.5	36.9 ± 4.1	102 ± 12	102 ± 12	102 ± 12
D_n, μm	0.71 ± 0.09	0.65	0.53	1.01 ± 0.08	1.15
D_w/D_n	1.05	1.06	1.09	1.07	1.01

mined by using a Centrifugal Automatic Particle Analyzer (CPA, Horiba Capa-300).

The viscosities were measured by using a rotational viscometer, Brookfield, Model RVT/DV-II, where the rotation speed was set at 10 rpm.

RESULTS AND DISCUSSION

Stable latices were obtained via direct emulsification by using the recipes shown in Tables 1 and 2. The average particle diameters of latices prepared by the process are comparatively larger than those obtained by the emulsion polymerization process. Some latices have a particle size distribution (D_w/D_n) below 1.1, but some may be as large as 10.0, depending on the conditions under which the latices were made.

Effect of Polyoxyethylene Chain Length of the Polyoxyethylene Nonylphenyl Ether

Direct emulsification of polystyrene was performed using a mixture of SDS, CA, and Pannox surfactants (i.e., polyoxyethylene nonylphenyl ether) as the stabilizer for the latex. By increasing the ethylene oxide (EO) number of Pannox (Recipes A1-A4, Table 1), both the number-average particle diameter (D_n) of latex after vacuum distillation and the surface tension of aqueous solution of the stabilizer mixture decreased, as shown in Fig. 1. This indicates that Pannox surfactants with a higher EO number have higher efficiency in emulsification. The range of data spread is quite large, i.e., the particle size varies from 0.79 to 5.60 μm and the effect of the EO number of Pannox on the particle size is great enough to be discernible in this case.

The HLB (hydrophile lipophile balance) value of the Pannox surfactants increases as the EO number increases. In other words, the particle size decreases as the HLB value increases. Calculation of HLB for individual surfactants was based

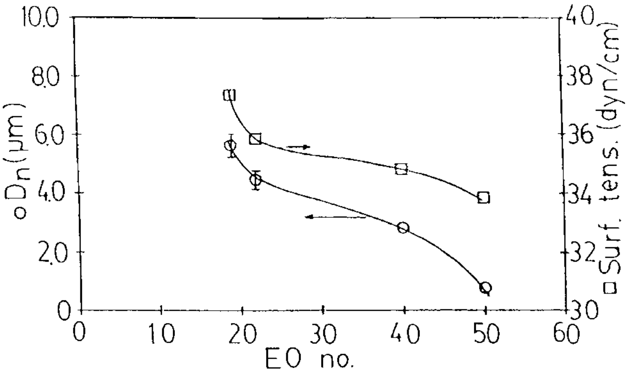

FIG. 1. EO number of the Pannox surfactant on both the final latex particle size (D_n) of PS and the surface tension of the corresponding aqueous solution of stabilizer mixture.

TABLE 3. The Largest Particle Sizes That Will Not Settle on Standing, Calculated from Eq. (1)

	η, cP		
	24.6	36.9	102
D_n, μm	0.72	0.89	1.47

on the equation provided by Davies [21]. The mixed HLB values, HLB_{mix}, for stabilizer mixtures were computed by using

$$HLB_{mix} = \Sigma(HLB_i)W_i \tag{2}$$

where W_i is the weight fraction of each surfactant in the stabilizer mixture.

For the emulsion polymerization of styrene, it has been suggested that the suitable HLB range is 13-16 [22]. However, the range was located between 15.3 and 15.7 for the direct emulsification process of PS in Series A, and between 15.2 and 7.2 for Series B in this study. Factors other than surface activity could be more important.

Effect of Viscosity of External Phase

According to Stokes' law, increasing the viscosity of the external phase can reduce the rate of sedimentation and favor the stabilization of droplets.

Values for the largest particle size of latices that will not settle on standing were calculated based on Stokes' law with a criterion for the sedimentation rate of 1 mm in 24 hours, and they are shown in Table 3. A higher viscosity in the external phase allows the larger particles to be sustained without settling, which allows for a further reduction of particle size in the process.

In the presence of CA, the viscosity of SDS aqueous solution increases rapidly, as shown in Fig. 2. It has been reported [23-25] that a mixture of SDS and CA can form compact envelopes surrounding the droplets. This is important in preventing

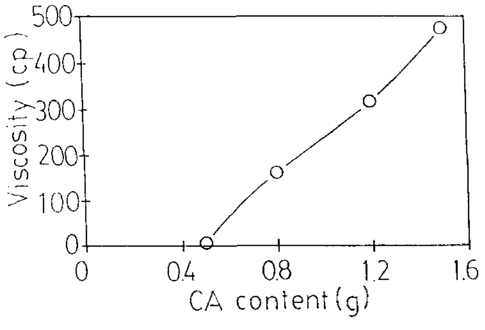

FIG. 2. Variation of viscosity for the aqueous solution of mixed surfactants as a function of CA content (SDS/H_2O = 0.30 g/55 g) at 25°C and 10 rpm.

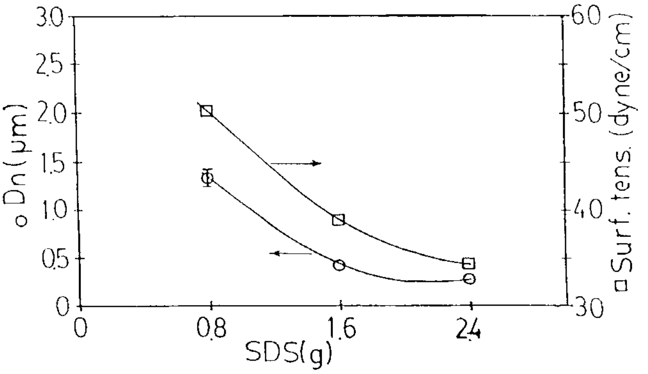

FIG. 3. The SDS content vs the final latex particle size (D_n) of PS and the surface tension of the corresponding aqueous solution of surfactants in the presence of 4.2 g of CA (Recipes B1-B3).

the coalescence of droplets. Therefore, it was not surprising to find that SDS was not effective for direct emulsification in the absence of CA.

It is obvious that once the external phase is thickened with the addition of CA, the minor stabilizing effect of ionic surfactant (e.g., SDS) can be demonstrated. As shown in Fig. 3, both the particle size of latex and the surface tension of stabilizer aqueous solution decrease with increasing SDS content (Recipes B1-B3).

In the emulsification of PIB (Recipes D1-D3), increasing the viscosity of the external phase from 24.6 to 102 cP [i.e., increasing the MW of PVA from 1.5 × 10^4 (Recipe D1) to 10 × 10^4 (Recipe D3)] made the latex particle size decrease from 0.71 to 0.53 μm, as shown in Fig. 4. The experimental particle size data (Table 2) are rather close to the predicted data in Table 3. The predictions based on the external phase viscosity is closer to the experimental data than those based on the molecular areas of the surfactants. The latter will be discussed later. Note also that an increase in the MW of PVA can provide better protection to the droplets.

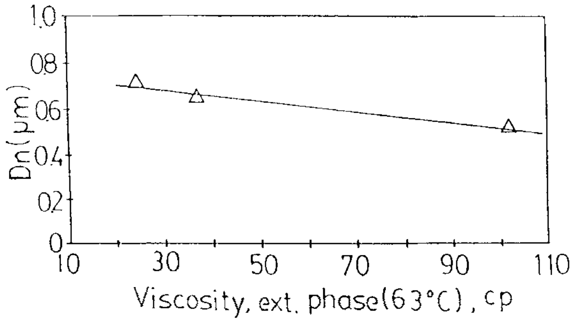

FIG. 4. Viscosity of the external phase vs the final latex particle size (D_n) of PIB (Recipes D1-D3).

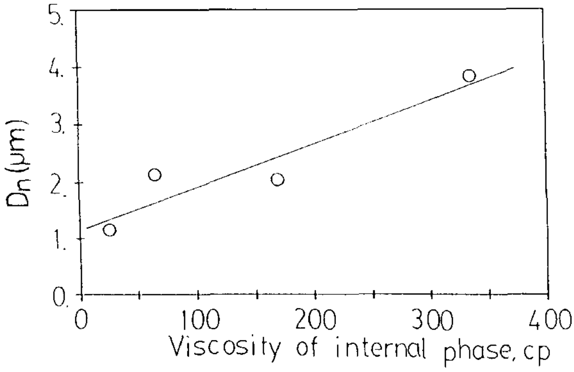

FIG. 5. Viscosity of the internal phase vs the final latex particle size (D_n) of PS (Recipes C1-C4), where the viscosity of the external phase = 12.3 cP.

Effect of Viscosity of Internal Phase

It has been suggested [4] that the viscosity of the internal phase should be less than 10,000 cP when direct emulsification is conducted.

In order to study the effect of changing the internal phase viscosity on the latex particle size, different amounts of solvent were added to the polymer to vary the internal phase viscosity. See Recipes C1-C4. Figure 5 shows that the particle size decreases as the viscosity of the internal phase decreases while keeping the viscosity of the external phase constant (i.e., 12.3 cP).

As the MW of PIB is increased, the viscosity of the bulk polymer increases, as shown in Table 2 (Recipes D3-D5). Figure 6 shows that the final latex particle size increases rapidly and then levels off as the viscosity of PIB increases. The internal phase has been reduced by adding oleic acid. The oleic acid is also acting as an emulsifier, which contributes an additional stabilization effect.

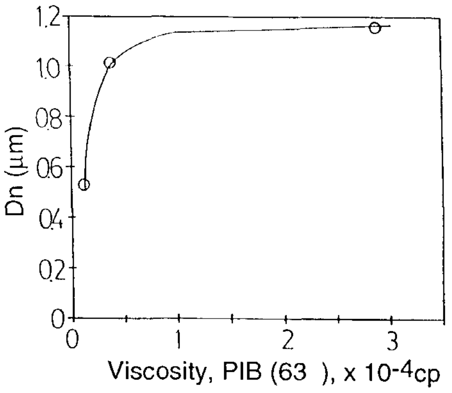

FIG. 6. Viscosity of PIB vs the final latex particle size (D_n) of PIB (Recipes D3-D5).

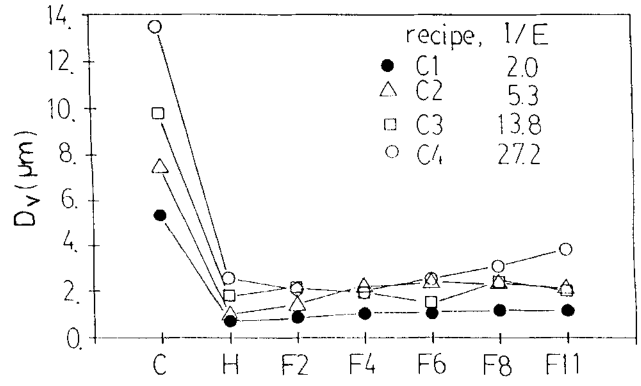

FIG. 7. Variations of volume-average particle diameter (D_v) of latices (Recipes C1–C4) during the emulsification and posttreatment process (C: before homogenization, H: after homogenization, F*n*: after *n* hours of distillation, and I/E: viscosity ratio of internal phase to external phase) (viscosity of external phase was 12.3 cP).

Particle Coalescence during Vacuum Distillation

The homogenization process is important to the direct emulsification process, since the crude latex particles are quite large (i.e., 5.35–13.5 μm, as shown in Fig. 7) after the initial mixing. Latices might easily experience further coalescence and sedimentation. Homogenization offered a key operation in reducing particle size to close to 0.65 μm, a critical size that will not to settle on standing. The chance for latices to coagulate or settle during the solvent-removal process is, therefore, substantially minimized.

The homogenization condition used in this study has been carefully chosen by trial-and-error. The condition used proved to be effective in reducing the particle size to the appropriate range. To facilitate comparison with other effects, the conditions were kept constant throughout the study.

TABLE 4. Molecular Area (A_m) of Each Surfactant Molecule on Polystyrene [26]

Surfactant	A_m, Å^2
SDS	47[a]
Pannox EO no.:	
12	54
19	76
40	101
50	171

[a] Also Ref. 27.

TABLE 5. Comparison of the Predicted Minimum Particle Diameter ($D_{\min}$) and the Experimental Data ($D_{n,\text{expt}}$, number-average particle diameter after vacuum distillation)

	Recipe					
	B1	B2	B3	A1	A2	A4
$D_{\min}$, μm	0.15	0.22	0.34	0.071	0.076	0.071
$D_{n,\text{expt}}$, μm	0.28	0.43	1.33	0.79	2.8	5.6

Solvent was removed by the vacuum-distillation process, during which particles might coalesce. This led to an increase in particle size. On the other hand, if coalescence is not present, particle size may be reduced because the swelling of particles is reduced by the removal of solvent. A high internal viscosity or a larger particle size may induce further coalescence if not enough particle protection is provided during the solvent-removal process.

Some recipes (such as Recipes B1 and B2) did show obvious reductions in particle size. Obviously, no coalescence occurred during the process and the stabilizers offered enough stabilization to particles to prevent particle coalescence. However, in some recipes (C1-C4), coalescence occurred during the vacuum-distillation process and the value of volume-average particle diameter (D_v) increased. As shown in Fig. 7, values of D_v at the end of distillation are larger than those before distillation. In addition, the fluctuation of particle size was smaller for recipes (such as C1) with a lower viscosity in the internal phase and a smaller D_v before the distillation process.

Data of molecular area (A_m) of each surfactant on polystyrene have been determined by the soap-titration method by our group [26] and others [27], as shown in Table 4.

A prediction of the minimum particle diameter ($D_{\min}$) for a latex prepared by direct emulsification was made. It was assumed that the total particle surface area is occupied by the surfactants (SDS and Pannox) and that no free surfactants are available elsewhere. The predicted data and the experimental results are compared in Table 5. The experimental data are much larger (twofold to eightyfold) than the $D_{\min}$. This was also manifested by the considerably large particle coagulation that occurred during the dispersing process.

CONCLUSIONS

Increasing the viscosity of the external phase or reducing the viscosity of the internal phase decreases the particle size. When the viscosity of the external phase is high enough, the increase in the PEO chain length of a nonionic surfactant or in the SDS content can lead to smaller latex particles. The variation in the MW of PIB or of PVA affects the viscosity of the corresponding phase, and therefore the particle size of the latex. The homogenization process exerts a crucial effect on reducing the particle size. The predicted error based on the external phase viscosity was more acceptable than that based on the molecular areas of the surfactants. For some latices, the particle size increases during the vacuum-distillation process.

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