

Morphology and Particle Size of Nanograde Polyurethane/Polyacrylate Hybrid Emulsions

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ABSTRACT: Poly(urethane acrylate) (PUA) composite particles were prepared by seeded surfactant-free emulsion polymerization. The aqueous polyurethane (PU) dispersions were used as seed particles. The diameters of the seed particles of the aqueous PU dispersions and PUA composite latexes were measured by dynamic light scattering. The microstructures of the PUA composite emulsion particles were observed by transmission electron microscopy. The influences of the amount of the hydrophilic chain extender, the types of initiators, and the PU/polyacrylate (PA) weight ratios on the diameters of the aqueous PU and composite emulsions were also studied. The results showed that the PUA composite emulsions formed a core-shell structure with PU as the shell and with PA as

the core. The diameter of the PU seed particles and the particle size of the PUA composite emulsions greatly depended on the amounts of the hydrophilic chain extender used in the preparation of the PU seed; when the hydrophilic chain extender concentration was 7.4%, the average diameter of the PUA composite emulsion particles showed the minimum value. The types of initiators and PU/PA weight ratios did not have a significant influence on the diameter of the PUA composite latex particles. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2030–2035, 2009

Key words: core-shell polymers; emulsion polymerization; particle size distribution; polyurethanes

INTRODUCTION

Aqueous polyurethane (PU) has recently experienced rapid development as an environmentally friendly material and has exhibited extensive application prospects in leather coatings, paper and textile finishes, cement additives, and other applications because of its excellent properties.^{1,2}

A hybrid aqueous resin is usually prepared with the interpenetrating polymer network technique, in which the core-shell emulsion is significantly important.^{3,4} There are some reports concerning a core-shell poly(urethane acrylate) (PUA) composite latex.^{3–7} Hirose and Kadowaki³ studied core-shell-type PUA hybrid emulsions containing reactive groups. In this type of emulsion, the shell part is composed of PU polymers containing pendent carboxylic groups and hydrazide end groups, and the core part is composed of acrylic copolymer containing ketone groups. Hirose et al.⁴ also reported preparing PUA hybrid emulsions by converting amphiphilic acrylic-PU graft copolymers (previously synthesized in non-aqueous media via the grafting of vinyl monomers to

partially vinyl-end-blocked PU) into aqueous emulsions, and these emulsions formed core-shell structures. Wu et al.⁵ reported that a PU dispersion and a PUA composite latex were synthesized and characterized with particle size analysis, gel permeation chromatography, Fourier transform infrared spectroscopy/attenuated total reflection, and dynamic mechanical analysis. The amounts of the solvent and dimethylol propionic acid used during the synthesis of the PU resin straightway affected the average particle size and stability of the aqueous PU dispersion. Mengnjoh and Frisch⁶ reported that full and pseudo-interpenetrating polymer networks of poly(2,6-dimethyl-1,4 phenylene oxide) (PPO) and a PUA were simultaneously synthesized and characterized with differential scanning calorimetry, ultimate mechanical property measurements, and electron microscopy. No evidence of phase separation was detected in the full or pseudo-PPO/PUA networks.⁶ It can be seen that research about the influence of reaction conditions such as the type of initiator on the morphology and particle size of nanograde PUA hybrid emulsions is limited.

In this study, an aqueous PU dispersion was prepared with carboxyl acid groups to make PU dispersible, and then a nanograde PUA composite latex was synthesized by a soap-free emulsion polymerization method with the PU dispersion as the

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TABLE I
Recipes for the PU Samples

PU sample	DMPA (wt %)	IPDI (mol)	PPG-1000 (mol)	PPG-2000 (mol)	DMPA (mol)	BDO (mol)
PU1	2.5	0.3	0.0725	0.0725	0.055	0.1
PU2	3.8	0.3	0.0625	0.0625	0.075	0.1
PU3	5.4	0.3	0.0525	0.0525	0.095	0.1
PU4	6.3	0.3	0.0475	0.0475	0.105	0.1
PU5	7.4	0.3	0.0425	0.0425	0.115	0.1
PU6	8.5	0.3	0.0375	0.0375	0.125	0.1
PU7	9.9	0.3	0.0325	0.0325	0.135	0.1

seed. Transmission electron microscopy (TEM) was used to characterize the core-shell structures of the hybrid emulsions. Dynamic light scattering was also employed to investigate the influence of the polymerization reaction conditions on the diameter and distribution of the composite emulsion particles. The correlations between the diameter of the particles and the microstructure were established. The average diameters of the hybrid emulsions were in the nanograde range, provided that the polymerization conditions were properly maintained.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI) was supplied by Huels AG Co. (Dusseldorf, Germany). Poly(propylene glycol)s (PPGs) with molecular weights of 1000 (PPG-1000) and 2000 (PPG-2000) were supplied by the 3rd Petrochemical Plant of Tianjin. Dimethylol propionic acid (DMPA), triethyl amine (TEA), 1,4-butanediol (BDO), dibutyl tin dilaurate (T-12), di-*n*-octyl phthalate (DOP), acetone, potassium persulfate (KPS), benzoyl peroxide (BPO), sodium bisulfite (SBS), methyl acrylate (MA), butyl acrylate (BA), and sodium dodecyl sulfate (SDS) were purchased from Peking Chemical Reagent Co.

PPG was dried at 70°C and 0.1 mmHg for 72 h before use. Acetone, DOP, and BDO were used after treatment with 4-Å molecular sieves for 72 h. IPDI, MA, and BA were distilled under reduced pressure. DMPA, TEA, T-12, KPS, BPO, SBS, and SDS were analytically pure grade and were used as received. Water was deionized and distilled, and the conductivity was below 1 µs/cm.

Preparation of the PU dispersion

The synthesis of the PU dispersion was carried out in a four-necked glass reactor equipped with a mechanical stirrer, a thermometer, a nitrogen inlet, and a condenser with a CaCl₂ drying tube. First, IPDI, PPG, DMPA, and a few drops of T-12 in a DOP solution were poured into the reactor, and the reactor mixture was kept at 60–80°C for about 3 h until the

NCO percentage dropped below 3.0. BDO was added, and the temperature remained constant for another hour. Then, the reactor was cooled below 40–45°C, and freshly dried acetone was added to bring down the viscosity of this PU prepolymer. The PU dispersion was obtained by high-shear-rate mixing of this PU prepolymer with an aqueous solution of TEA. The final PU dispersion had a solid concentration of 30% with a pH value of 8.5 after acetone was removed *in vacuo*. In the synthesis, the carboxylic acid group in the DMPA molecule was used to make the PU dispersible. The recipes are summarized in Table I.

Preparation of the PUA composite emulsion

The composite PUA latex was prepared by soap-free seeded emulsion polymerization with the previously synthesized anionic aqueous-based PU dispersion as the seed particle. A monomer mixture of MA and BA was used in the second stage of polymerization. The weight ratio of MA to BA in all mixture monomers was 1 : 1. The second stage of the soap-free seeded emulsion polymerizations was carried out with KPS, BPO, and KPS-SBS as the initiators at 80°C for 4 h separately. The recipes are summarized in Table II.

Characterization

Appearance

The colors, appearance, and agglomeration of the samples were visually observed.

Storage stability

The storage stability was determined by the time of agglomeration emergence. If an emulsion did not layer over 3 months, it was considered to be stable. Otherwise, it was regarded as unstable.

TEM observation

The PUA composite latex particle morphology was observed with a Hitachi H-800 transmission electron

TABLE II
Recipes for the PUA Composite Emulsions

PUA sample	PU seed dispersion (g)					Initiator (g)			Monomer (g)			PU/PA weight ratio
	PU3	PU4	PU5	PU6	PU7	KPS	BPO	KPS-SBS	MA	BA	H ₂ O	
PUA1	25					0.05			3.75	3.75	17.5	1/1
PUA2		25				0.05			3.75	3.75	17.5	1/1
PUA3			25			0.05			3.75	3.75	17.5	1/1
PUA4				25		0.05			3.75	3.75	17.5	1/1
PUA5					25	0.05			3.75	3.75	17.5	1/1
PUA6			25				0.05		3.75	3.75	17.5	1/1
PUA7			25					0.05	3.75	3.75	17.5	1/1
PUA8			15			0.05			5.25	5.25	24.5	1/2.3
PUA9			35			0.05			2.25	2.25	10.5	1/0.4

microscope (Hitachi, Japan) after staining with 1–2% (wt %) phosphotungstic acid (PTA) in a water solution, which was adjusted strictly to pH 6.5 with 0.1N NaOH in a water solution in advance.

Particle size analysis

Particle size distribution curves of the aqueous PU dispersion and PUA composite latex were measured with the particle size analyzer of a dynamic light scattering instrument (Brookhaven Co., Holtsville, NY).

RESULTS AND DISCUSSION

TEM observation

Figure 1 shows some TEM photographs of the PUA composite latexes obtained from stable composite emulsions of PUA1 [Fig. 1(a)], PUA3 [Fig. 1(b)], PUA5 [Fig. 1(c)], PUA6 [Fig. 1(d)], PUA7 [Fig. 1(e)], PUA8 [Fig. 1(f)], and PUA9 [Fig. 1(g)]. These composite emulsion systems were all core-shell-structured spheres. In these core-shell particles, the darker region of the outer layer was PU domains,

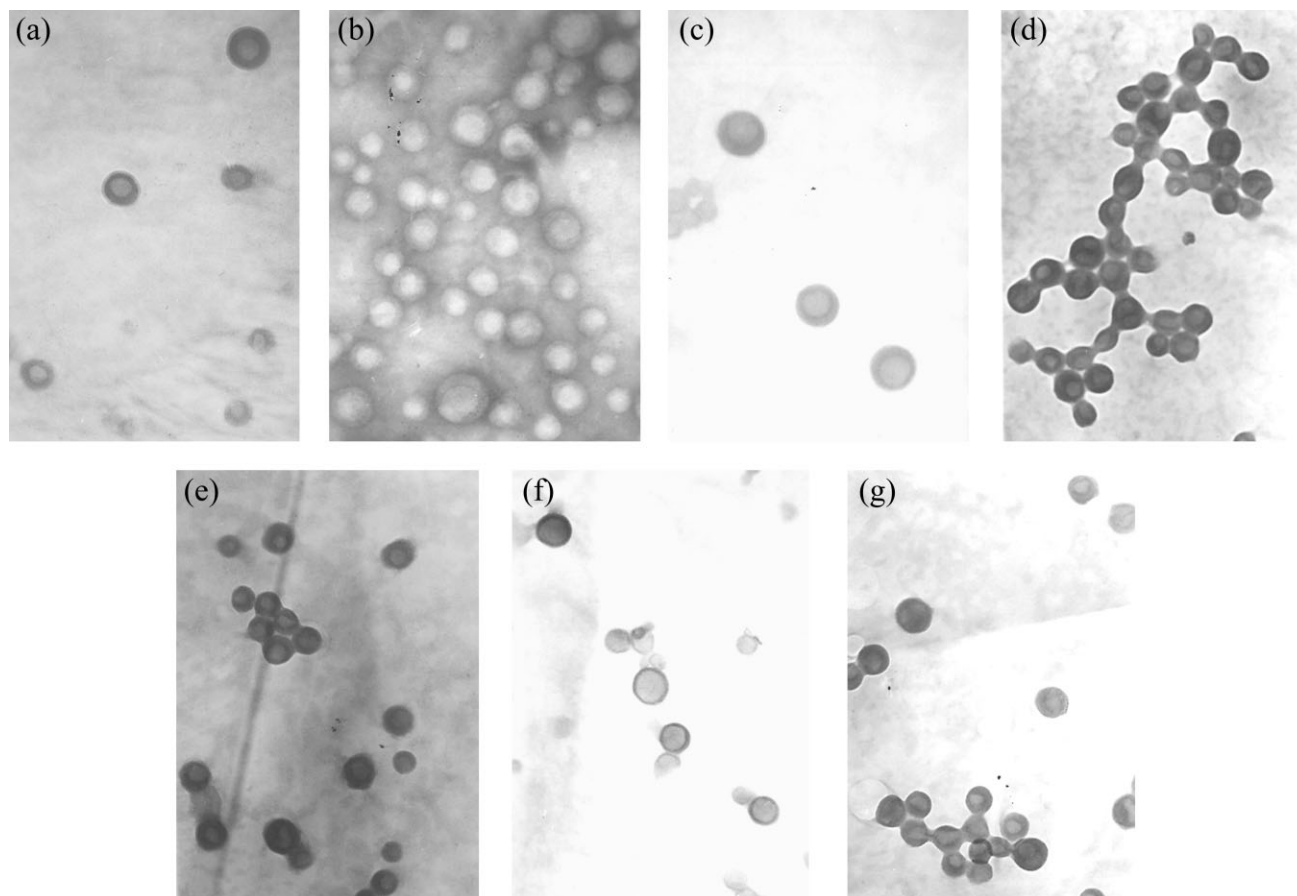


Figure 1 TEM photographs of (a) PUA1, (b) PUA3, (c) PUA5, (d) PUA6, (e) PUA7, (f) PUA8, and (g) PUA9.

TABLE III
Effect of the DMPA Level on the Properties of the PU Dispersions

PU sample	DMPA (wt %)	Solid content (%)	pH	Appearance	Storage stability	Average diameter (nm)
PU1	2.5	30	8.5	White emulsion	Not stable	Precipitation
PU2	3.8	30	8.5	White emulsion	Not stable	216.8
PU3	5.4	30	8.5	Slightly blue emulsion	Stable	146.7
PU4	6.3	30	8.5	Slightly blue emulsion	Stable	98.3
PU5	7.4	30	8.5	Blue emulsion	Stable	60.2
PU6	8.5	30	8.5	Blue emulsion	Stable	48.5
PU7	9.9	30	8.5	Translucent solution	Not stable	40.0

and the lighter region in the core was polyacrylate (PA). On the one hand, the electronic cloud density around the PU chains was higher than that around PA because PU had greater polarity in comparison with that of the PA chains. On the other hand, PTA staining was pH-dependent,⁸ and the solubility of PTA in ester was much higher than in water under acidic conditions; the solubility of PTA in water was higher than in ester under slightly basic conditions because PTA mainly existed in the form of sodium phosphotungstate. The core-shell structure could be observed in terms of the difference in the solubility of PTA in different substances.⁸ This result was also in good agreement with results reported previously.^{3,4} The more hydrophilic chains in the amphiphilic PUA composite system were selectively located in the shell region, and the hydrophobic chains were concentrated in the core region of the emulsion particles in the course of the phase-inversion process. In addition, the core-shell structure with PA as the core and with PU as the shell was proved with X-ray photoelectron spectroscopy.⁹

Effect of the DMPA level on the properties of the PU dispersion

The effect of the DMPA level on the properties of the PU dispersion is shown in Table III. With an increase in the amounts of DMPA, the storage stability of the aqueous PU increased except for PU7; the appearance of the PU dispersion changed from a

white emulsion to a solution; and the average diameter of the PU dispersion particles decreased.

The dispersion of PU in water depended on the hydrophilic carboxyl acid group. The quantity of DMPA actually affected the hydrophilic/hydrophobic ratios. When the amounts of the hydrophilic groups increased, the average diameter decreased. This was in good agreement with previous results.⁵

In addition, when the amount of DMPA was 9.9%, PU precipitated from the aqueous solution in a short time with an increase in the measured cycle times; when the dynamic light scattering method was used, a stable diameter distribution curve was difficult to produce. This might be due to the fact that when there are too many hydrophilic groups, PU will change from a state such as a micelle to the verge of a solution state;¹⁰ stable seed particles do not exist, so a stable distribution curve is difficult to experimentally generate.

Effect of the DMPA level on the properties of the PUA composite emulsion

The effect of the DMPA level on the properties of the PUA composite emulsion is shown in Table IV. When other conditions were the same, with an increase in the amounts of DMPA (e.g., samples PUA1, PUA2, PUA3, PUA4, and PUA5), the average diameter of the PUA composite emulsion particles first decreased and then increased, and it was lowest when the DMPA concentration was 7.4%. This might

TABLE IV
Effect of the DMPA, Initiator, and PU/PA Levels on the Properties of the PUA Emulsions

PUA sample	DMPA in the PU dispersion (wt %)	Solid content (%)	pH	Appearance	Storage stability	Average diameter (nm)
PUA1	5.4	20	7.5	White emulsion	Stable	140.8
PUA2	6.3	20	7.5	White emulsion	Stable	104.7
PUA3	7.4	20	7.5	Blue emulsion	Stable	89.8
PUA4	8.5	20	7.5	White emulsion	Stable	112.8
PUA5	9.9	20	7.5	White emulsion	Stable	143.6
PUA6	7.4	20	7.5	Blue emulsion	Stable	77.9
PUA7	7.4	20	7.5	Blue emulsion	Stable	81.0
PUA8	7.4	20	7.5	Blue emulsion	Stable	81.6
PUA9	7.4	20	7.5	Blue emulsion	Stable	87.8

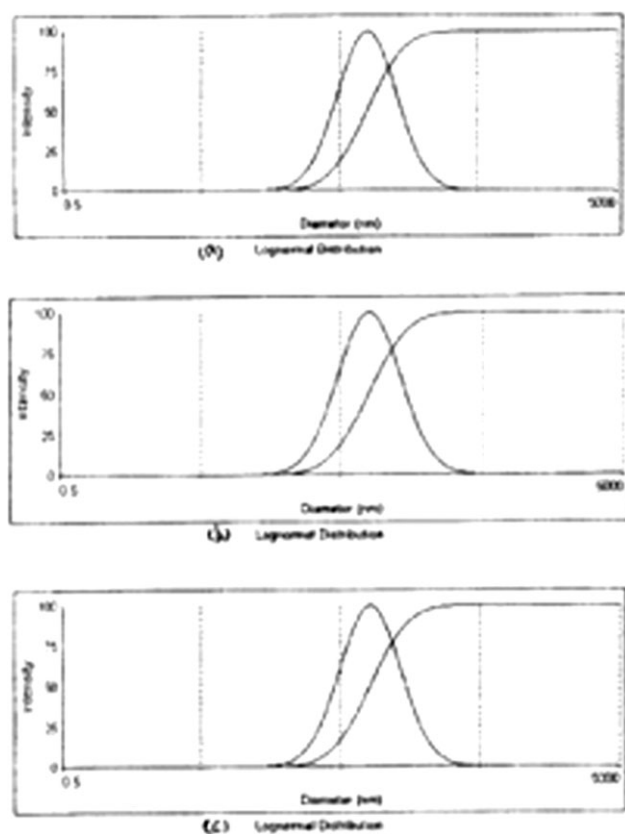


Figure 2 Particle size distribution curves of the PUA emulsions with different initiators: (a) KPS ($D = 78.2$ nm, $P = 0.274$), (b) BPO ($D = 77.9$ nm, $P = 0.294$), and (c) KPS-SBS ($D = 81.0$ nm, $P = 0.285$).

be attributed to the simultaneous influence of the surface activity and the viscosity of the system.

With an increase in the number of the hydrophilic carboxyl acid groups, the hydrophilic/hydrophobic ratios increased, the number of seed particles also increased, but the average diameter of the composite emulsion decreased; at the same time, the viscosity of the system also increased. In the second stage of emulsion polymerization, the rate of diffusion of the monomer into the nuclei decreased because of the greater viscosity and easy conglomeration of smaller particles to form bigger particles, so the average diameter of the composite emulsion increased.

When the DMPA concentration was less than 7.4%, the average diameter decreased with an increase in the amount of DMPA; this might have contributed to the lower number of hydrophilic carboxyl acid groups. When the DMPA concentration was higher than 7.4%, the average diameter increased with the DMPA level, and this was mainly contributed by the system viscosity. When the DMPA concentration was about 7.4%, the amount of carboxyl acid groups was greater, and the viscosity of the system was not too much, so the average diameter of the PUA composite emulsion particles was lowest.

When the DMPA concentration was 9.9%, although the particle distribution curve of the PU dispersion was difficult to obtain, the particle distribution curve of the corresponding PUA composite emulsion could be stabilized. This shows that PUA was a stable emulsion system. The seed PU played the role of a surfactant. The average diameter of the PU dispersion was about 40 nm by nephelometry, and the average diameter of the PUA composite emulsion was about 114.4 nm. This was in good agreement with the regular rule: the average diameters of core-shell emulsions increase with increases in the amounts of the second-stage monomers.

Effect of the initiator on the particle size of the PUA composite emulsion

The effects of different types of initiators on the particle size of the PUA composite emulsion are shown in Figure 2. D means diameter, and P means polydispersity. Figure 2(a–c) was obtained from PUA3, PUA6, and PUA7, respectively. Water-soluble (KPS), solvent-soluble (BPO), and oxidation-reduction (KPS-SBS) initiators were used, respectively, and PU5 (DMPA concentration = 7.4%) was used as the seed.

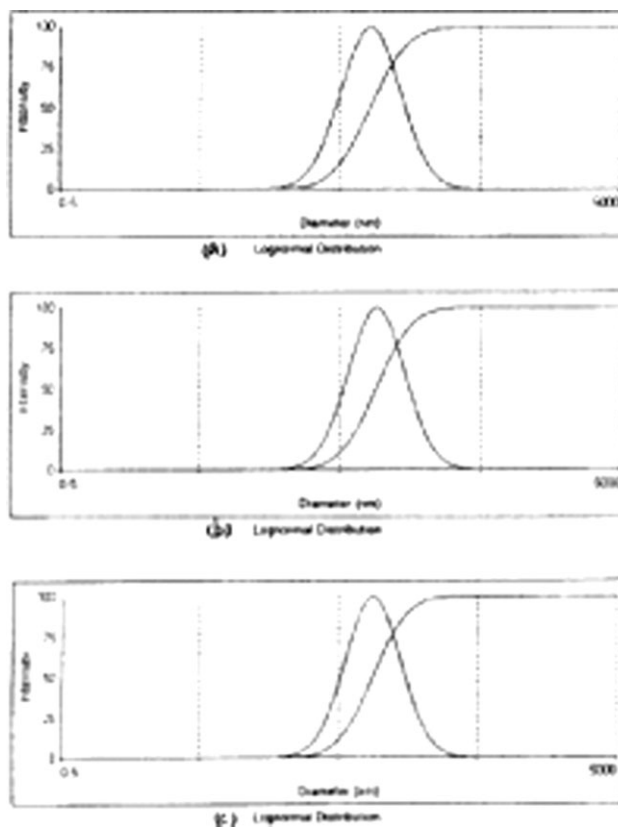


Figure 3 Particle size distribution curves of the PUA emulsions with different PU/PA weight ratios: (a) 1 : 2.3 ($D = 81.6$ nm, $P = 0.269$), (b) 1 : 1 ($D = 89.8$ nm, $P = 0.238$), and (c) 1 : 0.4 ($D = 87.8$ nm, $P = 0.235$).

The average diameters and particle distribution curves of all three PUA composite emulsions were analogous. The different types of initiators did not have a significant influence on the average diameter and the distribution curves of the PUA composite emulsion. This was because whether the initiator was a water-soluble, solvent-soluble, or oxidation-reduction type, in the process of polymerization, only the sites of initiation and the polymerization temperatures were different, and no new nuclei formed, so the distribution curves of the three types of PUA composite emulsions using different initiators were analogous.

There are additional advantages. BPO is a solvent-soluble initiator; it cannot initiate emulsion polymerization when SDS is used as the surfactant; but it can initiate the emulsion polymerization reaction when aqueous PU is used as the seed and there are no surfactants in the system. This is because PU forms into nuclei that contain more hydrophobic chain segments in the core and more hydrophilic chain segments in the surface of the seed particles; BPO can stably exist in the hydrophobic area of PU, so BPO can initiate the polymerization reaction of acrylate monomers.

Effect of the PUA weight ratios on the particle size of the PUA composite emulsion

The effects of the PUA weight ratios on the particle size of the PUA composite emulsions are shown in Figure 3(a–c). They were obtained from PUA8, PUA3, and PUA9 samples, respectively.

When the PU/PA ratio was greater than 1 : 1, the average diameters of the PUA composite emulsions increased with an increase in the amounts of the acrylate monomers. This was in good agreement with the regular rule.

The average diameter of the composite emulsion with a PU/PA ratio of 1 : 2.3 was less than that with the other two PU/PA ratios. This may be due to the fact that when the PU/PA ratio is too low, the surface area of particles cannot be entirely covered by the hydrophilic carboxyl groups. Therefore, some of the acrylate polymers precipitate from the emulsion, and this leads to the actual amounts of PA in the PUA composite emulsion particles decreasing. Therefore, the average diameter decreased when the PU/PA ratio was 1 : 2.3. The distribution curves of the three kinds of composite emulsions with different PU/PA ratios did not show significant changes.

In addition, the average diameters of the three PUA composite emulsion systems using different PU/PA ratios were larger than those of the PU seed

dispersions. This is also in good agreement with the regular rule.

CONCLUSIONS

The PUA composite emulsion prepared by soap-free seeded emulsion polymerization formed a core-shell structure in aqueous media with PU as the shell and with PA as the core.

With an increase in the amount of DMPA, the average diameter of the PU dispersion particles decreased. When the amount of DMPA was 9.9%, a stable diameter distribution curve by the dynamic light scattering method was difficult to generate, but the particle distribution curve of the corresponding PUA composite emulsion could be stabilized.

When other conditions were kept the same, with an increase in the amount of DMPA, the average diameter of the PUA composite emulsion particles first decreased and then increased, and the lowest values were found when the DMPA concentration was 7.4%.

With the PU seed dispersion (DMPA = 7.4%) and KPS, BPO, and KPS-SBS as initiators, the particle distribution curves of all three PUA composite emulsions were analogous. The types of initiators did not have much influence on the particle size and distribution of the PUA composite emulsion.

With the PU seed dispersion (DMPA = 7.4%) and different PU/PA weight ratios, when the PU/PA ratio was greater than 1 : 1, the average diameters of the PUA composite emulsions increased with an increase in the amounts of the acrylate monomers. The average diameter of the composite emulsion was less than that of the composite emulsions with the two other PU/PA ratios when the PU/PA ratio was 1 : 2.3. The polydispersity of the three PUA composite emulsions did not show significant changes.

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