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ORIGINAL CONTRIBUTION

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Preparation of heterogeneous film from core-shell composite polymer particles produced by the stepwise heterocoagulation method with heat treatment

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Abstract Core-shell composite polymer particle consisting of a hydrophilic core and hydrophobic shell was produced by the stepwise heterocoagulation of small cationic styrene-butyl acrylate-methacryloyoxyethyl trimethylammonium chloride terpolymer particles onto a large anionic methyl methacrylate-ethyl acrylate-methacrylic acid terpolymer particle (LP), which was proposed by the authors in 1990. In order to prepare a film from such a core-shell composite polymer emulsion, the shell content was controlled by changing the diameter of LP and by increasing the methacrylic acid content in LP.

Key words Film – emulsion polymerization – core-shell – stepwise heterocoagulation – heterogeneous structure

Introduction

Emulsion polymers are widely used in film state. Film forming ability and film property are affected by both bulk property of base polymer and particle morphology [1]. In the process of seeded emulsion polymerization, if the phase separation within composite polymer particles consisting of hydrophobic and hydrophilic polymers, which contact with water, proceeds until a thermodynamic equilibrium state, the core-shell particles which consist of a hydrophobic core and hydrophilic shell should be produced [2]. However, in many cases the phase separation obeys kinetic control because of high viscosity within particle, and often results in peculiar morphologies [3–9].

In previous articles [10, 11], we suggested the stepwise heterocoagulation method in which many small cationic polymer particles were adsorbed onto one large anionic polymer particle to form anomalous composite polymer particle having an uneven surface. Moreover, utilizing this method, the core-shell composite polymer particles having a rigid hydrophilic core and a soft hydrophobic shell were produced [12]. As described above, it is difficult to produce such particles by the seeded emulsion polymerization. When such a core-shell composite polymer emulsion is cast, since the heterogeneous structure should be maintained in the process of the film formation [13], the hydrophobic shell acts as a continuous phase and the hydrophilic core plays as a discontinuous phase in the film.

In this article, the effect of the shell content which is controlled by changing the particle size and methacrylic acid content (MAA) of large polymer particle on film formation will be discussed.

Experimental

Materials

Methyl methacrylate (MAA), ethyl acrylate (EA), MAA, butyl acrylate (BA) and styrene (S) were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Methacryloyoxyethyl trimethyl ammonium chloride (QDM, Nitto Chem. Ind. Co.) was used without further purification. Analytical grade potassium persulfate (KPS) and 2,2′-azobis (2-amidinopropane)

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hydrochloride (V-50, Wako Pure Chem. Ind. Ltd.), as initiators were recrystallized. Commercial grade nonionic polyoxethylene sorbitan monooleate (Tween 80, Kao Atlas Corp.), analytical grade hydrochloric acid (HCl) and potassium hydroxide (KOH) were used as received. Deionized water was distilled before use.

Preparation of polymer particles

All polymerizations were carried out at 70 °C for 24 h in a glass reactor equipped with a condenser, mechanical stirrer and nitrogen inlet. Large anionic MMA-EA-MAA terpolymer (P(MMA-EA-MAA)) particles were produced by emulsifier-free emulsion terpolymerization. Small cationic S-BA-QDM terpolymer (P(S-BA-QDM)) (47.5/49.5/3.0, molar ratio) particles with 90 nm in diameter (SP) and small anionic S-BA-MAA terpolymer (P(S-BA-MAA)) (47.5/49.5/3.0, molar ratio) particles with 270 nm in diameter (SP-MAA) were produced by emulsion terpolymerization under conditions listed in Table 1. The glass transition temperatures (T_g) of LP, SP and SP-MAA were calculated to be 70, 17 and 17 °C, respectively, according to Fox equation [14].

Production of core-shell composite polymer particle (CSP)

CSPs were produced by utilizing the stepwise heterocoagulation method with heat treatment as described in the previous paper [12]. The heat treatment was carried out at 70 °C for 48 h for each sample. The shell content was designated to Eq. (1) as the weight percentage of SP in CSP which was determined gravimetrically after unadsorbed SPs were removed by centrifuging at 6000 rpm (4000 g) for 30 min at the end of the heat treatment. The degree of coverage of LP surface by SPs was designated to Eq. (2) as the percentage (P_c) of the experimental number (N) of SPs adsorbed by one LP against the theoretical number ($N_{\max}$) which is calculated according to Eq. (3) [15].

$$\text{Shell content } (\%) = \text{SP}/(\text{LP} + \text{SP}) \times 100 \tag{1}$$

$$P_c(\%) = (N/N_{\max}) \times 100 \tag{2}$$

$$N_{\max} = (2\pi/\sqrt{3}) \times [(D_{\mathrm{LP}} + D_{\mathrm{SP}})/D_{\mathrm{SP}}]^2 \tag{3}$$

Table 1 Recipes of emulsion polymerizations[a] for the preparation of cationic small P(S-BA-QDM) particles and anionic small P(S-BA-MAA) particles

Ingredient molar ratio		SP	SP-MAA
		P(S-BA-QDM) 47.5/49.5/3.0	P(S-BA-MAA) 47.5/49.5/3.0
BA	(g)	13.3	13.3
S	(g)	10.4	10.4
MAA	(g)		0.543
QDM	(g)	1.34	
KPS	(g)		0.125
AIBA	(g)	0.125	
Tween 80	(g)	1.25	1.25
H_2O	(g)	100	100
$D_n^{b)}$	(nm)	92	270

[a] N_2; 70 °C; 24 h.
[b] Number-average diameter measured by dynamic light scattering spectroscopy.
Abbreviations: S, styrene; BA, butyl acrylate; MAA, methacrylic acid; QDM, methacryloyoxyethyl trimethyl ammonium chloride; KPS, potassium persulfate; AIBA, 2,2′-azobis (2-amidinopropane) hydrochloride; Tween 80, polyoxyethylene sorbitan monooleate.

ζ-potential and particle size

The ζ-potential of the particles was measured in 10 mM KCl with a laser Electrophoresis Zeta-potential Analyzer (Otsuka Electronics Inc., Model LEZA-600). The particle size in each step of the stepwise heterocoagulation was determined by dynamic light scattering spectroscopy (Otsuka Electronics Inc., Model DLS-700).

Film formation

Films with a dry thickness of about 0.3 mm were prepared from SP and CSP emulsions on a release-paper (4 × 4 cm) at 45 °C, and from LP emulsion and blend emulsion of LP and SP-MAA on a glass plate (5 × 5 cm) at 80 °C.

Heat distortion temperature

The strain of films (breadth, 2.0 mm; primary length, 10 mm; thickness, about 0.3 mm), at the bottom of which a 4.1 g weight was hung, was measured as a function of temperature at a heating rate of 1 °C/min in silicon oil. For convenience, the temperature at which the strain increased remarkably was defined as the heat distortion temperature.

Viscoelastic property

Dynamic mechanical spectroscopic studies were carried out under shear conditions with a DMS (Instrument Corp., itk DVA-220S) at 10 Hz and at a heating rate of 6 °C/min.

Results and discussion

Controlling shell content

LPs with different diameters (D_n) were prepared under the polymerization conditions listed in Table 2. D_n decreased with a decrease in the monomer concentration and with an increase in the initiator concentration. Three kinds of LPs were used to produce CSPs by the stepwise heterocoagulation method with heat treatment.

Table 3 shows the effects of D_n of LP on SP/(LP + SP), P_c and film formation from CSP. The film formation was carried out at 45 °C at which the core consisting of LP does not melt, but the shell consisting of SPs does. As D_n of LP decreased, SP/(LP + SP) value increased, whereas P_c value gradually decreased from 34 to 16%. As D_n decreased from 1000 (LP3-1) to 343 nm (LP3-3), ζ-potential value of LP3 ~ 3 decreased from −46 to −15 mV. It seems that the decrease in the ζ-potential reduces P_c value. In the case of CSP emulsions produced using LP3-1 and LP3-2, SP/(LP + SP) values were, respectively, 11 and 18%, and a continuous film could not be prepared at 45 °C. Whereas, in the case of that using LP3-3, in which SP/(LP + SP) value was 24%, a continuous film was prepared at 45 °C, although it had some cracks at the surface. These results suggest that the shell content of 24% is near to the minimum value for preparing the film at 45 °C. On the other hand, in the film formation at 45 °C from the blend emulsion of LP3-3 and SP, a continuous film could not be prepared even at the SP content of 50%. These suggests that SPs constituting the shell operate much more effectively to make a continuous film than those in the blend emulsion.

Table 4 shows recipes for preparing LPs having different MAA contents. The ζ-potential value at pH 9 increased from −30 to −52 mV with an increase in the MAA content from 3 to 7 mol% while they had similar D_n values.

Table 2 Recipes of emulsifier-free emulsion polymerizations[a] for the preparation of anionic large P(MMA-EA-MAA) (66.5/30.5/3.0, molar ratio) particles with different sizes

		LP3-1	LP3-2	LP3-3
MMA	(g)	21.2	10.6	10.6
EA	(g)	9.8	4.9	4.9
MAA	(g)	0.82	0.41	0.41
KPS	(g)	0.064	0.032	0.064
Water	(g)	128	128	256
$D_n^{b)}$	(nm)	1000	576	343

[a] N_2; 70 °C; 24 h.
[b] Number-average diameter measured by dynamic light scattering spectroscopy.
Abbreviations: MMA, methyl methacrylate; EA, ethyl acrylate; MAA, methacrylic acid; KPS, potassium persulfate.

Table 3 The effects of D_n of LP in the LP/SP core-shell composite particles on SP/(LP + SP), P_c and film formation

		LP3-1	LP3-2	LP3-3
$D_n^{a)}$	(nm)	1000	576	343
ζ-potential at pH 9[b]	(mV)	−46	−30	−15
SP/(LP + SP)[c]	(%)	11	18	24
$P_c^{d)}$	(%)	34	29	16
Film formation[e]		No	No	Yes

[a] Number-average diameter measured by dynamic light scattering spectroscopy.
[b] Measured by Laser Electrophoresis Zeta-potential Analyzer.
[c] Determined gravimeterically.
[d] Calculated according to Eqs. 2 and 3.
[e] Dried at 45 °C.
Abbreviations: D_n, number-average diameter; LP, P(MMA-EA-MAA); SP, P(S-BA-QDM); P_c, the percentage of the experimental number of SPs adsorbed by one LP against the theoretical number.

Table 4 Recipes of emulsifier-free emulsion polymerizations[a] for the preparation of anionic larg P(MMA-EA-MAA) particles with different MAA contents

molar ratio		LP3-2 66.5/30.5/3.0	LP5 64.0/31.0/5.0	LP7 61.0/32.0/7.0
MMA	(g)	10.6	14.3	24.4
EA	(g)	4.9	7.5	12.8
MAA	(g)	0.41	1.42	2.41
KPS	(g)	0.032	0.047	0.079
Water	(g)	128	160	159
$D_n^{b)}$	(nm)	576	690	580
ζ-potential[c] at pH 9	(mV)	−30	−42	−52

[a] N_2; 70 °C; 24 h.
[b] Number-average diameter measured by dynamic light scattering spectroscopy.
[c] Measured by Laser Electrophoriesis Zeta-potential Analyzer.
Abbreviations: MMA, methyl methacrylate; EA, ethyl acrylate; MAA, methyacrylic acid; KPS, potassium persulfate.

Table 5 The effects of MAA content in LP on SP/(LP + SP), P_c and film formation

MAA (mol. %)		LP3-2	LP5	LP7
		3	5	7
SP/(LP + SP)[a]	(%)	18	23	37
P_c[b]	(%)	29	49	50
Film formation[c]		No	Yes	Yes

[a] Determined gravimeterically.
[b] Calculated according to Eqs. 2 and 3.
[c] Dried at 45 °C.
Abbreviations: MAA, methacrylic acid; LP, P(MMA-EA-MAA); SP, P(S-BA-QDM); P_c, the percentage of the experimental number of SPs adsorbed by one LP against the theoretical number.

Table 5 shows the effects of MAA content of LP on SP/(LP + SP), P_c and film formation from CSP emulsion. With the increase in the MAA content, SP/(LP + SP) increased from 18 to 37%, and P_c values increased from 29 to 50%. These effects were different from those with decreasing D_n of LP, in which SP/(LP + SP) increased but the P_c value decreased. Continuous films were prepared at 45 °C from CSP emulsions produced using LP5 and LP7, although the former had some cracks at the surface of which SP/(LP + SP) value was 23%.

Mechanical properties of film produced by CSP emulsion

Figures 1 and 2 show dynamic mechanical spectra of films, respectively, from the blend emulsion of LP7 and SP-MAA and from the CSP emulsion consisting of LP7/SP, where the weight percentages of SP-MAA/(LP + SP − MAA) in the blend emulsion and SP/(LP + SP) in CSP were almost the same. In the blend emulsion film, there were two peaks of tan δ at about 30° and 70 °C, due to T_g values of SP-MAA and LP7 phases, respectively. The peaks of tan δ of the films cast from SP and LP7 emulsions appeared, respectively, at about 30° and 105 °C (data were omitted). The difference of tan δ between the films cast from the blend emulsion of LP7 and SP-MAA and from LP7 emulsion may be caused by diffusion of a part of SP molecules into LP7 phase during film formation at 80 °C because the mobility of SP molecule is much higher than that of LP molecule, which reduce T_g of LP phase. Whereas in the CSP emulsion film there was one peak of tan δ at about 30 °C due to T_g of SP, but no peak due to T_g of LP. In the blend emulsion film in Fig. 1, E′ decreased markedly above 75 °C, whereas in the CSP emulsion film in Fig. 2, it decreased gradually. These suggest that in the latter film the ionic boning interaction operates at the core/shell interfacial layer between two kinds of polymers which contain the carboxyl groups and the quaternary ammonium groups, respectively.

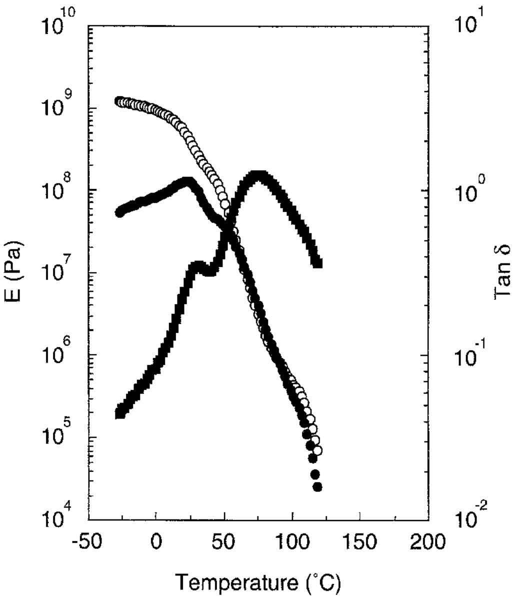

Fig. 1 Mechanical spectra of the film cast from blend emulsion (65/35, w/w) of P(MMA-EA-MAA) (61/32/7, molar ratio) and P(S-BA-MAA) (47.5/49.5/3.0, molar ratio). ○, shear storage modulus; ●, shear loss modulus; ■, loss tangent

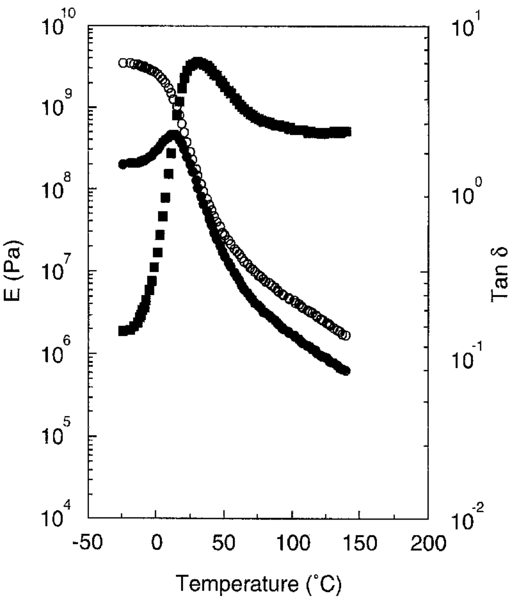

Fig. 2 Mechanical spectra of the film cast from P(MMA-EA-MAA) (61/32/7, molar ratio)/P(S-BA-QDM) (47.5/49.5/3.0, molar ratio) core-shell (63/37, w/w) composite emulsion produced by the stepwise heterocoagulation method with heat treatment. ○, shear storage modulus; ●; shear loss modulus; ■, loss tangent

Figure 3 shows heat distortion curves of the films prepared from LP7, SP, SP-MAA and CSP emulsions and

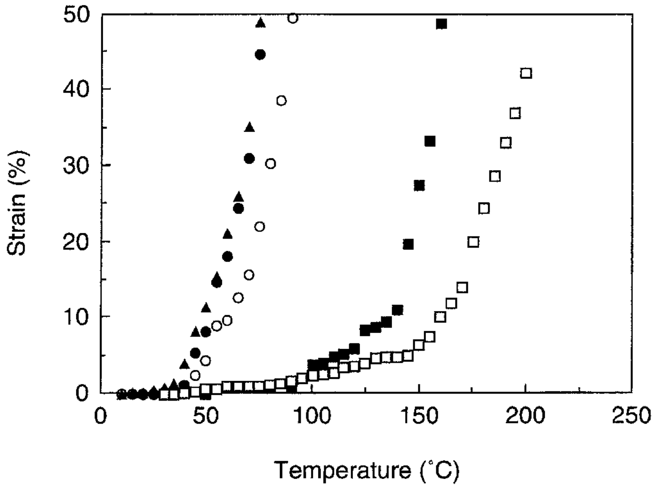

Fig. 3 Heat distortion curves of the films: ■, P(MMA-EA-MAA) (61/32/7, molar ratio) emulsion; ○, P(S-BA-QDM) (47.5/49.5/3.0, molar ratio) emulsion; ▲, P(S-BA-MAA) 47.5/49.5/3.0, molar ratio) emulsion; □, P(MMA-EA-MAA)/P(S-BA-QDM) core-shell (63/37, w/w) composite emulsion produced by the stepwise heterocoagulation method with heat treatment; ●, blend emulsion (65/35, w/w) of P(MMA-EA-MAA) and P(S-BA-MAA)

from blend emulsion of SP-MAA and LP7 (35/65, w/w). The heat distortion temperature of the blend emulsion film was almost the same, about 50 °C, as those of SP and SP-MAA films. That for LP7 film was about 130 °C. On the other hand, the heat distortion temperature of the CSP film was about 150 °C. Such a high heat distortion temperature of the CPS film also suggests that the ionic bonding interaction operates in the interfacial layer between SP and LP in the CPS. A similar result was obtained in the film prepared from composite polymer particles which consisted of two kinds of polymer molecules having opposite charges each other, which were produced by a seeded emulsion polymerization [16].

From these results, it is concluded that a continuous film having a heterogeneous structure in which hydrophilic and hydrophobic parts, respectively, consist of discontinuous and continuous phases can be prepared from the core-shell composite polymer particle having a hydrophilic shell and a hydrophobic core produced by the stepwise heterocoagulation method with heat treatment.

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