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SHORT COMMUNICATION

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Analysis of stepwise heterocoagulation for the preparation of soft core/hard shell composite polymer particles

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Abstract The stepwise heterocoagulation of small cationic hard particles (SPs) onto a large anionic soft particle (LP) for the preparation of soft core/hard shell composite polymer particles was examined using dynamic light scattering and spectrophotometry. The effects of the pH value, the emulsifier content which was pre-added to the LP emulsion, and the heat treatment time on the covering of a LP by SPs, and the stability of the heterocoagulated emulsion were clarified.

Key words Particle – blend – latex – heterocoagulation – emulsion polymerization – morphology

Introduction

In previous articles [1, 2] we suggested a novel technique for preparing core-shell composite polymer particles by depositing many cationic small particles (SPs) with a glass transition temperature (T_g) of 100 °C onto an anionic large particle (LP) with a T_g of 70 °C, followed by heat treatment. As seen in Fig. 1, both LPs and SPs have two kinds of charge which are derived from the monomer and the initiator. The anionic ζ potential value of the LP is very low at pH 3 and increased remarkably with an increase in pH value to the alkaline region, because of ionization of the carboxyl group of methacrylic acid copolymer. On the other hand, the cationic ζ potential value of the SP is almost independent of pH because the main cationic charges are due to the quaternary ammonium of methacryloyoxyethyl trimethyl ammonium chloride (QDM) copolymer, though amidino end groups such as a V-50 initiator fragment ionized at pH 3. As shown in Fig. 2, the technique which was named the "stepwise heterocoagulation method" consists of four steps: (1) emulsion blend, (2) soft heterocoagulation, (3) hard heterocoagulation, and (4) separation

Step 1: LP and SP emulsions are mixed in a stable colloidal state without coagulation at room temperature. In order to obtain this stable blend emulsion, nonionic emulsifier is added to a LP emulsion and the pH of each emulsion is adjusted to pH 3 before the blend [1].

Step 2: Heterocoagulation due to the enhancement of electrostatic attraction between LP and SP is caused by adjusting the pH to an alkaline region, in which the number of cationic surface charges of SP mainly derived from the quaternary ammonium groups is almost unchanged, whereas the number of anionic surface charges of LP is increased by ionization of the carboxyl group. In this step, since SPs attracted around LP do not directly touch the LP surface because of a nonionic emulsifier, they can be redispersed by readjusting the pH to 3. Therefore, this step is named "soft" heterocoagulation.

Step 3: The soft heterocoagulated particle (HP) is treated at a temperature which is higher than the T_g of LP and near the cloud point of the nonionic emulsifier, and results in a "hard" HP in which SPs cannot be redispersed even by readjusting the pH to 3 because they directly touch the LP surface.

Step 4: The individual HPs are obtained by removing unheterocoagulated free SPs with centrifugation due to the size difference between the HP and the SP.

Furthermore, we prepared spherical hard core/soft shell composite polymer particles in which core and shell should be derived from LP and SPs, respectively, regardless of the difference in hydrophilicities of the two kinds of polymer with heat treatment at a temperature above the T_g of SP [3, 4]. Ottewill and coworkers

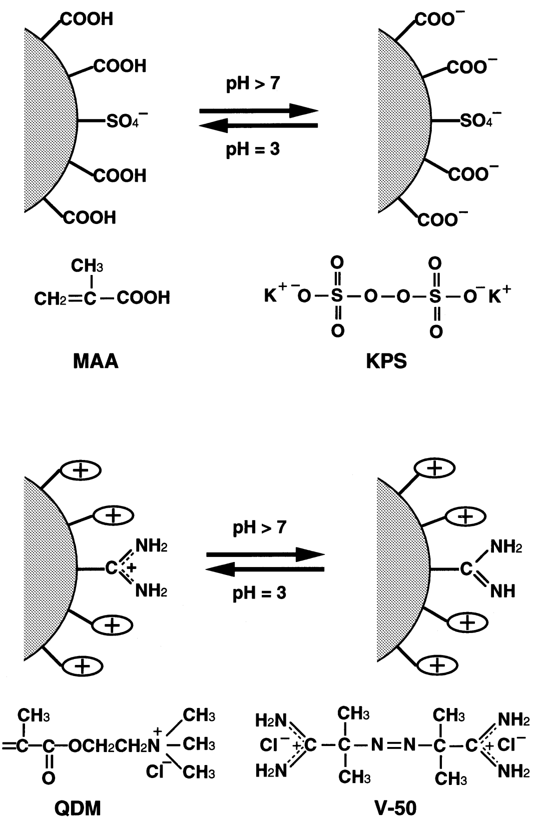

Fig. 1 Surface of anionic large particle (LP) P(MMA-EA-MAA) and cationic small particle (SP) P(S-BA-QDM) at different pH values. See Tables 1 and 2 for abbreviations

[5, 6] also reported the preparation of core-shell particles and particles in which some small particles were engulfed by heterocoagulation.

Recently, core-shell composite polymer particles with soft rubber cores covered by hard plastic shells have been more and more widely used to study the toughening mechanism of brittle resins [7–10].

In a previous article [11], the individual stable soft core/hard shell composite polymer emulsion was prepared from a LP with a T_g of −7 °C and a SP with a T_g of 90 °C by the stepwise heterocoagulation method with heat treatment, and the powder state of the composite particles was obtained after drying at 0 °C.

In this article, the experimental results of the above-mentioned four steps of the stepwise heterocoagulation for the preparation of soft core/hard shell composite particles are described.

Experimental

Materials

All reagents were the same as those in Ref. [11].

Preparation of polymer particles

The LP emulsion was produced by emulsifier-free emulsion terpolymerization of ethyl acrylate, ethylene glycol dimethacrylate, and methacrylic acid under the conditions listed in Table 1. The SP emulsion was produced by emulsion copolymerization of styrene and QDM under the conditions listed in Table 2. The T_g values of LP and SP measured with a differential scanning calorimeter (Seiko Instruments SSC-5200) at a heating rate of 10 °C/min were −7 and 90 °C, respectively.

Stepwise heterocoagulation

Heterocoagulation of LP and SP was carried out as follows. LP and SP emulsions were separately diluted with water to 5 wt% solid and the pH values were adjusted to 3 with 0.1 N HCl. The LP and SP emulsions

Fig. 2 Schematic process of the “stepwise heterocoagulation method”

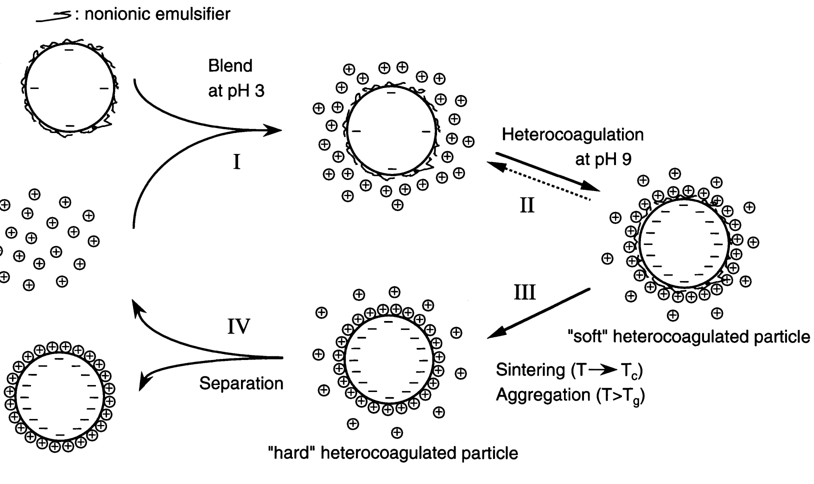

Table 1 Recipe of emulsifier-free emulsion polymerization[a] for preparing anionic large P(EA-EGDM-MAA) (90.0/5.0/5.0, molar ratio) particles (*EA* ethyl acrylate; *EGDM* ethylene glycol dimethacrylate; *MAA* methacrylic acid; *KPS* potassium persulfate)

EA	(g)	41.5
EGDM	(g)	4.6
MAA	(g)	1.98
KPS	(g)	0.19
H_2O	(g)	192
T_g^b	(°C)	−7

[a] N_2; 70 °C; 24 h
[b] glass transition temperature measured by differential scanning calorimetry

Table 2 Recipe of emulsion polymerization[a] for preparing cationic small P(S-QDM) (97.0/3.0, molar ratio) particles (*S* styrene; *QDM* methacryloyoxyethyl trimethyl ammonium chloride; *V-50* 2, 2′-azobis (2-amidinopropane) hydrochloride; *Tween 80* polyoxyethylene sorbitan monooleate)

S	(g)	94.2
QDM	(g)	5.80
Tween 80	(g)	8.00
V-50	(g)	0.50
H_2O	(g)	500
T_g^b	(°C)	90

[a] N_2; 70 °C; 24 h
[b] glass transition temperature measured by differential scanning calorimetry

were blended at the LP/SP ratio of 1/1 (w/w). Different amounts of nonionic emulsifier Tween 80 (cloud point = 70 °C) were added to the LP emulsion before the blend. The LP and SP emulsions were blended at pH 3 and kept at this value for 1 h. Then the pH value of the blend emulsion was slowly adjusted to that desired with 0.1 N KOH at a rate of 1 pH unit/h and finally kept at this value for 2 h. All the processes were carried out at room temperature.

The free SPs were removed as a supernatant by centrifugation at 3000 rpm for 20 min at 0 °C. The weight percent of the free SPs was obtained from the depletion of SP concentration before and after heterocoagulation. The concentration was determined with a spectrophotometer (Hitachi Seisakusho model 100-50) using the calibration curve between the SP concentration and the absorbance at 460 nm. Before the absorbance measurement of the supernatant, the supernatant was filtered through membranes having pore sizes of 300 nm to remove residual HPs after centrifugation. The degree of coverage of the LP surface by SPs was given by Eq. (1) as the percentage (Pc) of the experimental number (N) of SPs adsorbed by one LP against the theoretical maximum number ($N_{\max}$) which is calculated according to Eq. (2) [12].

$$\mathrm{Pc} = (N/N_{\max}) \times 100 \qquad (1)$$

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

Particle size and distribution

The gamma-average (D_g), weight-average (D_w), and number-average diameters (D_n) of LP, SP and HP were determined by dynamic light-scattering spectroscopy with a particle analyzer (Otsuka Electronics, model DLS-700) at room temperature.

Results and discussion

The size distributions of the original LP and SP emulsions are shown in Fig. 3. The D_g of LP was 714 nm and D_w/D_n was 1.01. The D_g of SP was 103 nm and D_w/D_n was 1.02.

The size distributions of the blend emulsions of LP/SP at pH 3, pH 7 (← 3), and pH 3 (← 7 ← 3) are shown in Fig. 4. Nonionic emulsifier, Tween 80 was added to the LP emulsion with 8 wt% based on the polymer solid before the blend. At pH 3 two peaks of D_g appeared at 99 and 701 nm which were nearly equal to those of the original SP and LP emulsions, respectively. This indicates that LPs and SPs were dispersed independently and stably in the blend emulsion although the blend was carried out at room temperature, which was higher than the T_g of LP. That is, heterocoagulation did not occur at pH 3, because at pH 3 the electrostatic attraction between LP and SP is very weak, and the hydrated protective layer at the surface of LP derived from the nonionic emulsifier prevents the contact of LP and SPs.

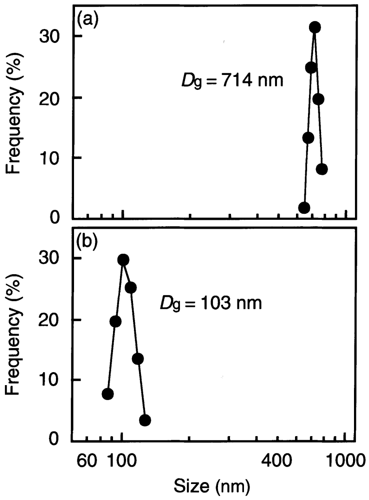

Fig. 3 Gamma particle-size distributions of **a** P(EA-EGDM-MAA) emulsion (LP) and **b** P(S-QDM) emulsion (SP). See Tables 1 and 2 for abbreviations

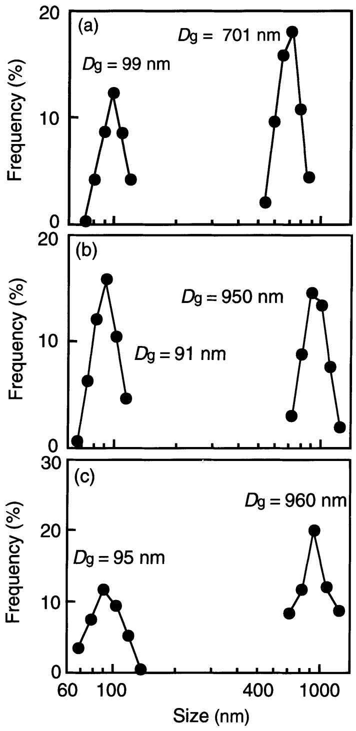

Fig. 4 Gamma particle-size distributions of blend emulsion of LP/SP, in which Tween 80 of 8 wt% per polymer solid was added to the LP emulsion before the blend, at **a** pH 3, **b** pH 7 (← 3), and **c** pH 3 (← 7 ← 3)

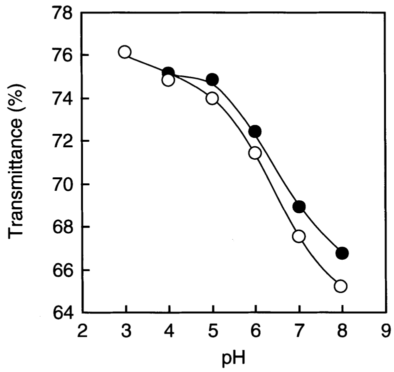

Fig. 5 Transmittances at 760 nm of the blend emulsion (polymer solid, 0.01%) of LP/SP (1/1, w/w), in which Tween 80 of 8 wt% per polymer solid was added to the LP emulsion before the blend, at different pH values adjusted from pH 3 (○) and those readjusted to pH 3 (●)

At pH 7 (← 3) two peaks of D_g appeared at 91 and 950 nm which accorded well with the diameters of SP and HP, respectively, calculated assuming that SPs are adsorbed onto LP as a single-particle layer. On the other hand, at pH 8 (← 3) (the datum is omitted) a peak appeared at 2655 nm beside the two peaks due to free SP and HP. This indicates that at pH 8 (← 3) not only were HPs formed but some macro-coagula above 2 μm were also produced. At pH 9 (← 3), macro-coagula were observed with the naked eye. At pH 3 (← 7 ← 3), the two peaks were almost the same as those at pH 7 (← 3). This indicates that SPs which had adsorbed onto LP at pH 7 could not desorb from the LP surface at pH 3. This point is quite different from the results reported in previous articles [1, 2] as shown in Fig. 2. In those systems, SPs adsorbed on LP desorbed and redispersed by readjusting the pH from 9 to 3. This difference seems to be based on the fact that room temperature was much lower and much higher than the T_g of LP for the previous and for these experiments, respectively.

The transmittances of the blend emulsion adjusted from pH 3 to different pH values and of those in which the pH values were readjusted to 3 are shown in Fig. 5. The transmittance of the blend emulsion decreased with an increase in the pH value. On the other hand, when the pH value was readjusted to 3, the transmittance of the blend emulsions increased a little but did not return to that of the original blend emulsion at pH 3. These results suggest that in this experiment rather high percentage of SPs directly contact with LP and they cannot desorb even at pH 3.

The change of Pc value with pH value is shown in Fig. 6. The Pc value was only 3% at pH 3, but it increased markedly with an increase in pH value and reached 48% at pH 8.

Figure 7 shows the Pc values of the blend emulsions of SP and LP (1/1, w/w) containing various amounts of Tween 80 emulsifier at pH values of 3, 7 (← 3), and 3 (← 7 ← 3). At the three pH values, Pc values decreased similarly with an increase in the emulsifier content. At an emulsifier content of 16%, the Pc values were almost zero, 14%, and 8% at the pH values of 3, 7 (← 3), and 3 (← 7 ← 3), respectively.

The effect of heat treatment at 70 °C for 1 h on the Pc value of the blend emulsion at different pH values is

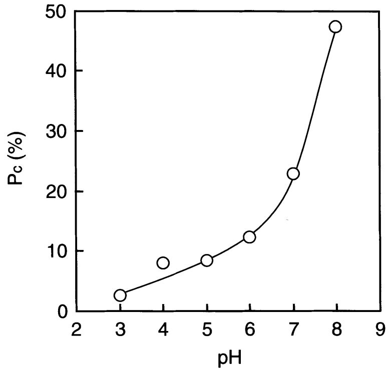

Fig. 6 Percentage of SPs adsorbed by one LP (Pc) of the blend emulsion of LP/SP (1/1, w/w), in which Tween 80 of 8 wt% per polymer solid was added to the LP emulsion before the blend, at different pH values adjusted from pH 3

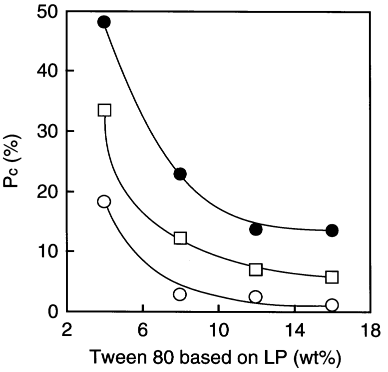

Fig. 7 Effect of the amount of Tween 80 added to the LP emulsion before the blend on the Pc of the blend emulsion of LP/SP (1/1, w/w) at pH values of 3 (○), 7 (← 3) (●), and 3 (← 7 ← 3) (□)

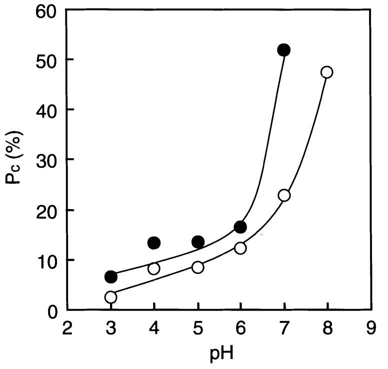

Fig. 8 Effect of pH on the Pc of the blend emulsion of LP/SP (1/1, w/w), in which Tween 80 of 8 wt% per polymer solid was added to the LP emulsion before the blend, before (○) and after (●) heat treatment at 70 °C for 1 h

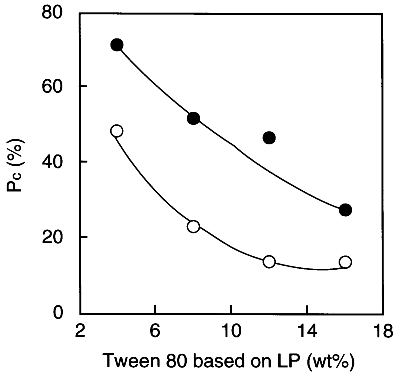

Fig. 9 Effect of the amount of Tween 80 added to the LP emulsion before the blend on the Pc of the blend emulsion of LP/SP (1/1, w/w) at pH 7, before (○) and after (●) heat treatment at 70 °C for 1 h

shown in Fig. 8. The difference between the Pc values before and after heat treatment was small at acidic pH values, but at pH 7 the Pc value increased from 23 to 53% due to heat treatment. At pH 8, an accurate Pc value was not obtained after heat treatment, because many macro-coagula, which were observable to the naked eye, were formed.

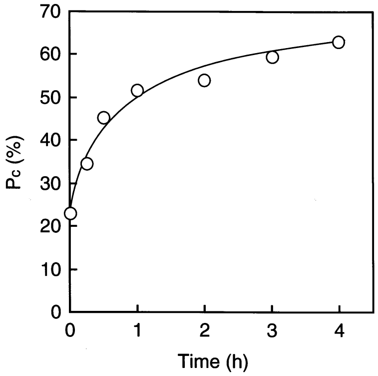

Fig. 10 Variation of the Pc of the blend emulsion of LP/SP (1/1, w/w), in which Tween 80 of 8 wt% per polymer solid was added to the LP emulsion, at pH 7 (← 3), as a function of treatment time at 70 °C

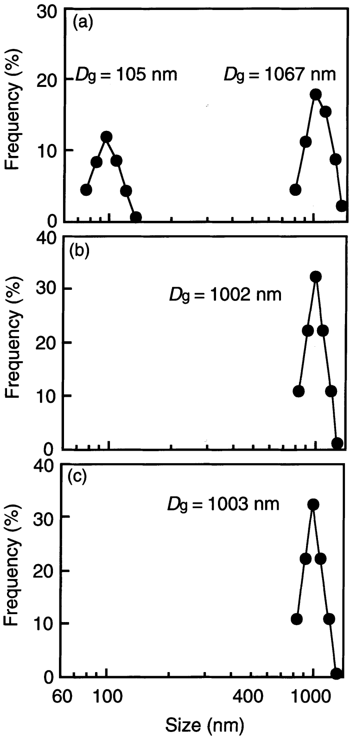

Fig. 11 Gamma particle-size distributions of blend emulsions of LP/SP, in which Tween 80 of 8 wt% per polymer solid was added to the LP emulsion before the blend, at pH values of **a,b** 7 (← 3), **c** 3 (← 7 ← 3), after heat treatment at 70° C for 2 h, **a** before and **b,c** after removal of free SPs

Figure 9 shows the effect of heat treatment at 70 °C for 1h on the Pc value of the blend emulsions of SP and LP containing different amounts of emulsifier. The Pc values after heat treatment were always higher than those before heat treatment, and continuously decreased with an increase in the emulsifier content.

The effect of heat treatment time at 70 °C on the Pc value of the blend emulsion at pH 7 (← 3) is shown in Fig. 10. The Pc value increased markedly until 1 h and then increased gradually.

In the above experiments, the reason why the Pc value did not attain a high level above 80% may be the low anionic ζ potential value of HP [11] or its inversion to a cationic one [1].

Figure 11a shows the size distribution of the blend emulsion after heat treatment at 70 °C for 2 h. Two peaks of D_g appeared at 105 nm and 1067 nm due to SP and HP, respectively. Similar results were obtained after heat treatment at 70 °C for 1, 3 and 4 h (the data were omitted). These results indicate that the colloidally stable HP emulsion was obtained. After removal of the free SPs by centrifugation at 0 °C, the peak around 100 nm due to the free SP disappeared. The peak due to the HPs was almost not shifted by centrifugation, indicating that the HPs were redispersed.

After heat treatment at 70 °C for 2 h, and the removal of free SPs, even if the pH of the HP emulsion was readjusted to 3, the peak was not shifted as shown in Fig. 11c. This indicates that after heat treatment, SPs adsorbed onto LP could not desorb.

From the above results the four steps of the stepwise heterocoagulation method for the preparation of soft core/hard shell composite polymer particles were clarified, supporting the previously proposed mechanism [2].

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