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SHORT COMMUNICATION

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Production of soft core/hard shell composite polymer particles by the stepwise heterocoagulation method with heat treatment

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Abstract Soft core/hard shell composite polymer particle was prepared by the stepwise heterocoagulation, which was proposed by authors in 1990, of many cationic hard small polymer particles (SPs) onto an anionic soft large polymer particle (LP). The powder was obtained by freeze-drying at 0 °C which was higher than glass transition temperature of LP (−7 °C) and lower than that of SP (90 °C).

Key words Soft core/hard shell – composite polymer particle – emulsion polymerization – stepwise heterocoagulation – heat treatment

Introduction

In previous articles, the internal stress of cured epoxy resin was reduced by dispersing therein submicron-sized poly(butyl acrylate)/poly(methyl methacrylate) core–shell composite particles produced by seeded emulsion polymerization [1, 2]. Recently, soft core/hard shell composite polymer particles have been also widely applied to toughen some amorphous thermoplastics such as polystyrene and poly(methyl methacrylate) [3, 4].

On the other hand, in previous articles [5–7] we suggested a novel technique to produce composite polymer particles by depositing stepwise many cationic small particles (SPs) with glass transition temperature (T_g) of 100 °C onto an anionic large particle (LP) with T_g of 70 °C. It was named "stepwise heterocoagulation method". Furthermore, the method was applied to produce hard core/soft shell composite polymer particles in which core and shell should be, respectively, derived from LP and SP, regardless of the difference in hydrophilicities of the two kinds of polymers [8, 9]. Furthermore, the changes of the surface morphology of the composite polymer particles produced by the stepwise heterocoagulation method, with heat treatment were estimated utilizing ζ-potential measurement [10].

In this article, soft core/hard shell composite particles for the above mentioned applications will be tried to prepare from LP with T_g of −7 °C and SP with T_g of 90 °C by the stepwise heterocoagulation method with heat treatment.

Experimental

Materials

Ethyl acrylate (EA), methacrylic acid (MAA), 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. Reagent grade ethylene glycol dimethacrylate

(EGDM) was used as received. Analytical grade potassium persulfate (KPS) and 2,2′-azobis (2-amidinopropane) hydrochloride (V-50, Wako Pure Chem. Ind. Ltd.), as initiators were recrystallized. Commercial grade nonionic polyoxyethylene sorbitan monooleate (Tween 80, Kao Atlas Corp.) was used as received. Analytical grade hydrochloric acid (HCl) and potassium hydroxide (KOH) were used directly. Deionized water was distilled before used.

Preparation of polymer particles

As LP, anionic soft EA-MAA-EGDM terpolymer [P(EA-MAA-EGDM)](90/5/5, molar ratio) particles were produced by emulsifier-free emulsion terpolymerization under the conditions listed in Table 1. As SP, cationic hard S-QDM copolymer [P(S-QDM)] (97/3, molar ratio) particles were produced by emulsion copolymerization under the conditions listed in Table 2. The T_g values of the LP and SP were, respectively, $-7\,^\circ$ and 90 °C measured by using a differential scanning calorimeter (Seiko Instruments Inc. SSC-5200) at a heating rate of 10 °C/min.

Blend and stepwise heterocoagulation

Heterocoagulation of LP and SP was carried out according to the previous articles [5–7] as follows. (1) 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 were blended at the LP/SP ratio of 1/1 (w/w) and kept at room temperature for 1 h. Nonionic emulsifier Tween 80 (cloud point = 70 °C) was added to the LP emulsion with 8 wt% per LP before blend in order to obtain the stable emulsion [6]. (2) The pH of the blend emulsion was adjusted to 7 with 0.1 N KOH slowly and kept at 7 for 2 h. Unheterocoagulated free SPs were removed by centrifugation at 3000 rpm for 20 min at 0 °C. The weight percent of the unheterocoagulated free SPs was determined from the depletion of SP concentration before and after the heterocoagulation. The concentration was measured with a spectrophotometer (Hitachi Seisakusho Corp. Model 100-50) using the calibration curve between the SP concentration and the absorbance at 460 nm. The heterocoagulated particles (HPs) were removed from the blend emulsion by centrifugation, following the filtration with a cellulose nitrate membrane having pore size of 300 nm. The degree of coverage of LP surface by SPs was designated to Eq. (1) 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. (2) [11]:

$$P_c = (N/N_{max}) \times 100 , \quad (1)$$

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

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 (g)	41.5
EGDM (g)	4.6
MAA (g)	1.98
KPS (g)	0.190
H_2O (g)	192
T_g[b] (°C)	−7

[a] N_2; 70 °C; 24 h.
[b] Glass transition temperature measured by differential scanning calorimeter. *Abbreviations*: EA, ethyl acrylate; EGDM, ethylene glycol dimethacrylate; MAA, methacrylic acid; KPS, potassium persulfate.

Table 2 Recipe of emulsion polymerization[a] for preparing cationic small P(S-QDM) (97.0/3.0, molar ratio) particles

S (g)	94.2
QDM (g)	5.80
Tween80 (g)	8.00
V-50 (g)	0.500
H_2O (g)	500
T_g[b] (°C)	90

[a] N_2; 70 °C; 24 h.
[b] Confirmed by dynamic light scattering spectroscopy. Glass transition temperature measured by differential scanning calorimeter.
Abbreviations: S, styrene; QDM, methacryloyoxyethyl trimethyl ammonium chloride; V-50, 2,2′-azobis (2-amidinopropane) hydrochloride; Tween 80, polyoxyethylene sorbitan monooleate.

Particle sizes

The gamma-average diameter (D_g), weight-average diameter (D_w), number-average diameter (D_n) and the particle size distribution of LP and SP were determined by dynamic light scattering spectroscopy with a particle analyzer (Otsuka Electronics Inc., Model DLS-700), separately, at room temperature.

Morphology of particles

The morphology of the heterocoagulated particles prepared at different conditions were observed with a scanning electron microscope (SEM, Hitachi Seisakusho

S-2500) and a transmission electron microscope (TEM, Nippon Electron Inc. JEM 2010). The samples were dried at 0 °C and then stored below −5 °C before observation.

Results and discussion

Figure 1 shows size distributions of LP and SP emulsions, separately. D_g of LP was 714 nm and D_w/D_n was 1.01. D_g of SP was 103 nm and D_w/D_n was 1.02.

Figure 2 shows gamma particle-size distributions of blend emultion of LP/SP under different conditions. In Fig. 2(a), the LP emulsion, in which Tween 80 nonionic emulsifier was pre-added with 8 wt%, and SP emulsion were blended at pH 3. Two peaks of D_g at 99 and 701 nm were, respectively, nearly equal to those of the original SP (D_g = 103 nm) and LP (D_g = 714 nm) emulsions. This indicates that the heterocoagulation did not occur at pH 3, although the blend was carried out at room temperature which was higher than T_g of LP. At pH 7 (←3) shown in Fig. 2(b), two peaks of D_g appeared at 91 and 950 nm. As compared with the Fig. 2(a), the position of the peak due to SP did not shift, but that (D_g = 714 nm) due to LP disappeared and a new peak appeared at 950 nm. This indicates that in the blend emulsion at pH 7(←3) there existed unheterocoagulated free SPs and HPs which were formed by heterocoagulation of SPs onto LP with a monoparticle layer. In the size distribution of HP shown in Fig. 2(c) after the heat treatment at 70 °C for 2 h, following centrifugation at 0 °C to remove the unheterocoagulated free SPs, the peak around 100 nm due to the unheterocoagulated free SP disappeared and that due to HPs did not shift before and after the treatment. This indicates that stable HP emulsion was obtained.

Table 3 shows the effects of heterocoagulation conditions on N, P_c and dried state of the heterocoagulated particles prepared in three systems of A, B, and C. The dry process was carried out at 0 °C which was higher than T_g of LP, but lower than that of SP, after the unheterocoagulated free SPs were centrifuged at 0 °C. At pH 3 (system A), only a few of SP were adsorbed onto LP surface in the blend emulsion and P_c was 3%. This indicates that the heterocoagulation did not occur. A continuous film was obtained from the emulsion in which the unheterocoagulated free SPs had been removed at 0 °C. At pH 7 (←3) (system B), N increased to 51 and P_c increased to 22%. This indicates that the heterocoagulation occurred at pH 7 between LP and SPs. No continuous film, but small discontinuous films (or pieces) were obtained from the heterocoagulated emulsion at 0 °C, suggesting that SPs adsorbed onto LP partially

Fig. 1 Gamma particle-size distributions of P(EA-MAA-EGDM) emulsion (a) and P(S-QDM) emulsion (b)

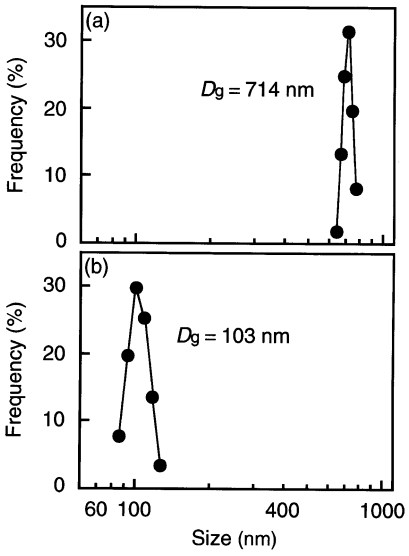
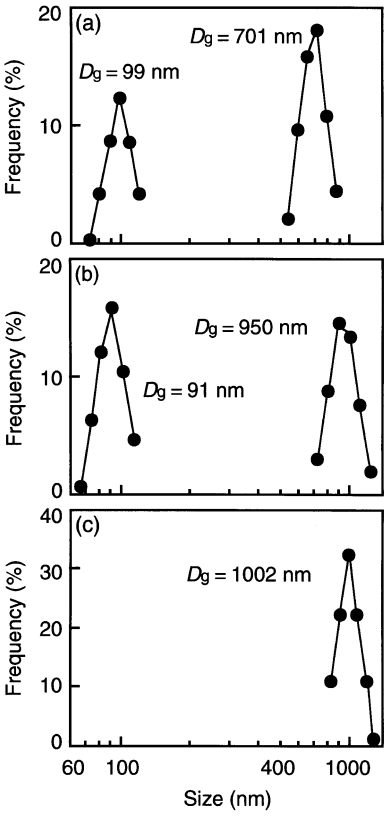


Fig. 2 Gamma particle-size distributions of blend emulsion of LP/SP at pH 3 (a), at pH 7(←3) (b), and at pH 7(←3) after the heat treatment at 70 °C for 2 h, following centrifugation at 0 °C to remove the free-SPs (c)



prevented the direct coalescence between LP cores. When the heterocoagulated emulsion obtained at pH 7(←3) was treated at 70 °C for 1 h (system C), N increased to 121 and P_c increased to 52%. After drying at 0 °C the powder was obtained. This suggests that SPs adsorbed onto LP prevented completely the direct coalescence between LP cores at 0 °C.

Table 3 The effects of heterocoagulation conditions on N, P_c, and dried state

Sample	A[1)]	B[2)]	C[3)]
N[4)]	7	51	121
P_c (%)[5)]	3	22	52
Dried state[6)]	Continuous film	Cracked	Powder

[1)] Blended at pH 3 and centrifuged to move free SPs.
[2)] Heterocoagulated at pH 7 and centrifuged to move SPs.
[3)] Heterocoagulated at pH 7 and treated at 70 °C for 1 h, following centrifuged to move free SP.
[4)] Number of SPs adsorbed onto one LP.
[5)] Calculated according to Eqs. (1) and (2).
[6)] Dried at 0 °C.

Figures 3 and 4 show TEM and SEM photographs of particles in the three systems from which the unheterocoagulated free SPs were removed by centrifugation. In the system A shown in Figs. 3(a) and 4(a), only few SPs were adsorbed on LP and LPs coagulated directly, and the continuous film was obtained at 0 °C. In the system B shown in Figs. 3(b) and 4(b), the heterocoagulated particles in which many SPs were adsorbed onto LP were observed, but interfacial boundary between HPs was not clear. In the system C shown in Figs. 3(c) and 4(c), in which the system B was treated at 70 °C for 1 h, more SPs were adsorbed onto LP and interfacial boundary between HPs was clear, that is, the SPs depressed the direct coagulation among LP cores.

From these results, it is concluded that soft core/hard shell composite polymer particles which can be obtained as powder by drying at 0 °C were produced from anionic LP with T_g of −7 °C and cationic SP with that of 90 °C by the stepwise heterocoagulation method with heat treatment. The analysis of the process of the stepwise heterocoagulation with heat treatment to produce the soft core/hard shell composite particles will be discussed more in detail in the following article.

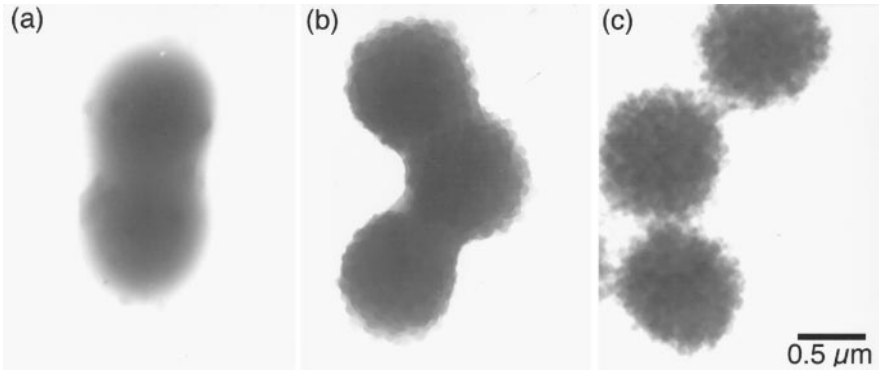


Fig. 3 TEM photographs of particles at pH 3 (a), at pH 7(←3) (b), and at pH 7(←3) after heat treatment at 70 °C for 1 h (c). All free SPs were removed from their blend emulsions by centrifugation

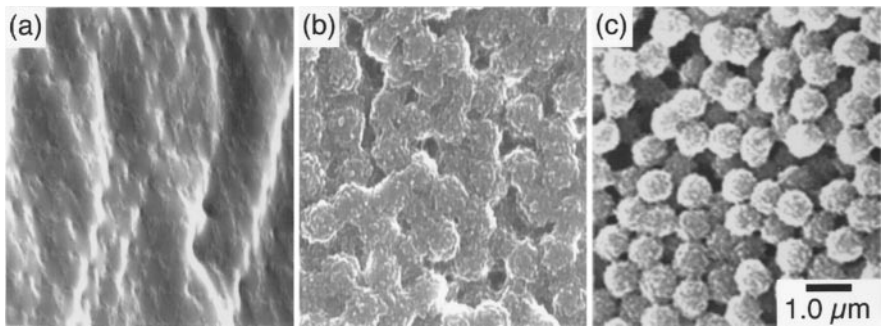


Fig. 4 SEM photographs of particles at pH 3 (a), at pH 7(←3) (b), and at pH 7(←3) after heat treatment at 70 °C for 1 h (c). All free SPs were removed from their blend emulsions by centrifugation

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