

# Influence of Microstructure on Dynamic Mechanical Property of Emulsion Blend Containing Heterocoagulated Composite Particles

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**ABSTRACT:** In this article, the dynamic mechanical properties of a multiphase system containing a dispersed phase with complex morphology is discussed with respect to the microstructure of the dispersed phase. The samples are prepared by emulsion blending of matrix particles (MP) and particles for a dispersed phase that are obtained with heterocoagulation techniques. The heterocoagulated particles were prepared using two kinds of particles of different sizes: small negative particles (SP) and large amphoteric particles (LP), taking advantage of their opposite surface charge in the colloidal state. To vary compatibility between SP and LP, two kinds of small particles were used: poly(methyl methacrylate-butyl acrylate-acrylic acid) and poly(styrene-butyl acrylate-acrylic acid) (SP-M and SP-S). Dynamic mechanical behavior of simple blends composed of MP and SP were also measured to examine the effect of microstructure. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1899-1909, 1997

**Key words:** dynamic mechanical behavior; heterocoagulation; morphology; core-shell morphology; emulsion blends

## INTRODUCTION

In general, emulsion polymerization produces spherical polymer particles. However, in the series of investigations on composite polymer particles consisting of two kinds of polymers, the seeded emulsion polymerization technique has been employed to produce some anomalous polymer particles (e.g., "confetti-like," "raspberry-like," "void-containing," "snowman-like"),<sup>1-4</sup> which are often called structured latex. Because there

are many parameters that determine the structures of latex particles, such as the nature of the monomers, compatibility among polymers, polymerization sequences, and crosslinking agent, etc., it is difficult to prepare core-shell particles of absolute specifications, and the limited number of monomer pairs are known to form the definite core-shell structures.<sup>5</sup>

In this article, core-shell particles were prepared by the heterocoagulation method using small polymer particles (SP) and large particles (LP), which have opposite surface charges in the colloidal state. Compared with conventional techniques of core-shell polymerization, this technique has an advantage of being applicable to many different types of monomer pairs that cannot be used in the conventional core-shell poly-

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merization. On the other hand, the structure or morphology of the heterocoagulated particles is not as stable as that of core-shell structure stabilized by grafting, because there is no chemical bonding between SP and LP in the heterocoagulated particle. The possibility of morphological variation in heterocoagulated particles may depend on a number of factors such as the glass-transition temperature of SP and LP components and the compatibility between LP and SP.<sup>6</sup>

In terms of structural investigation of the core-shell particle or general multiphase polymeric system, the electron microscopy might be most effective. However, the direct observation of particle structure with electron microscopy is often unsuccessful, especially if the size of the particle and the shell are too small. As an alternative, a number of attempts have been made for the analysis of dynamic mechanical properties of multiphase materials. Caville et al.<sup>7,8</sup> have compared the dynamic mechanical behavior of polymer films made from lattices by different emulsion processes: (1) conventional batch, (2) two-step polymerization, (3) corrected batch, and (4) mixture of two homopolymers, and discussed them in relation to particles morphologies. The major differences in spectra were attributed to morphological differences. Guest et al.<sup>9</sup> have examined PC/SAN blends prepared from two different procedures—compression molding and injection molding—and discuss the morphological difference based on dynamic mechanical measurements. One of the most interesting features in terms of morphology would be

the case with complex inclusion such as HIPS and ABS. Cigna et al.<sup>10</sup> have studied a series of impact styrene. The following factors have been investigated: morphology and content of the dispersed phase and continuous phase, composition of dispersed phase, and molecular weight of the continuous phase. Moreover, theoretical attempts have been made for analysis of dynamic mechanical properties of multiphase materials. Dickie<sup>11</sup> has calculated the dynamic mechanical response of a particulate composite with complex inclusion based on the Kerner equation. As predicted in Dickie's model calculation, the modulus and  $\tan \delta$  of HIPS were experimentally found to be dependent on the effective volume fraction of dispersed phase rather than the content of rubber.<sup>12</sup>

The purpose of this article is to investigate the effect of the morphology-dispersed phase on the dynamic mechanical response of the multiphase system that contains the dispersed phase with a well-defined structure. The dispersed phase is prepared by a heterocoagulation technique, and the variation of the microstructure has been attempted by varying compatibility between LP and SP, and annealing temperature in the dispersion state.

## EXPERIMENTAL

### Materials

Monomers—styrene (ST), methyl methacrylate (MMA), butyl acrylate (BA), 2-ethyl aminoethyl

**Table I** The Recipe for the Preparation of Large Particle (LP), Small Particle (SP), and PMMA Matrix Particle (MP)

Component	Reaction Makeup (g)				
	LP	SP-S	SP-M	X-SP-M	MP
MMA	180	—	197.1	197.1	500
ST	—	197.1	—	—	—
BA	—	72.9	72.9	72.9	—
AA	0.9	1.35	1.35	1.35	—
DEAEM	1.8	—	—	—	—
SDS	—	52	52	3.9	7.2
KPS	—	—	—	2.7	3.4
AIBH	1.8	—	—	—	—
AIBN	—	5.5	5.5	—	—
1,4-Butandiol dimethacrylate	—	—	—	1.35	—
Acetone	—	17.5	17.5	—	—
Distilled water	1800	1530	1530	1522	1272

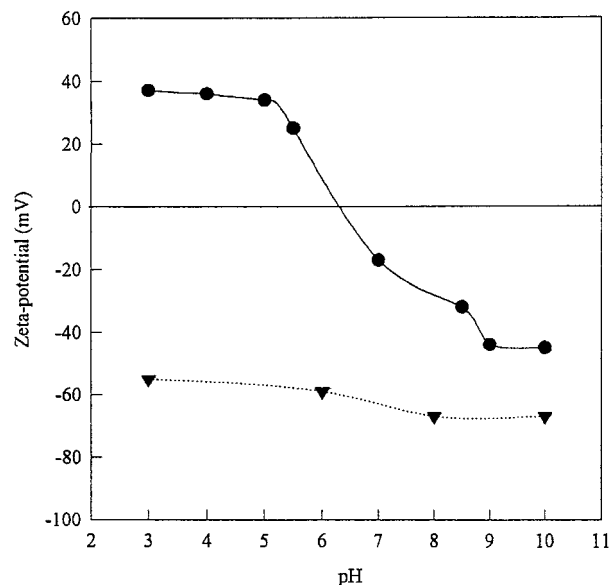
**Table II Particle Sizes and Particle Size Distributions for LP, SP, and MP**

	Number Average Diameter ( $D_n$ )	Weight Average Diameter ( $D_w$ )	$D_w/D_n$
LP	295 nm	301 nm	1.02
SP-M	48 nm	51 nm	1.05
SP-S	41 nm	46 nm	1.12
X-SP-M	74 nm	78 nm	1.05
MP	103 nm	110 nm	1.07

methacrylate (DEAEM), and acrylic acid (AA)—were purchased from Junsei Chemical Co. (Japan). They were purified by vacuum distillation and stored in the refrigerator. Initiators, potassium persulfate (KPS: Samchun Pure Chemical Ind., Ltd., Korea), 2,2'-azobis (2-amidino propane) hydrochloride (AIBH: Waco Chem., USA), and azobisisobutyronitrile (AIBN: Junsei Chemical Co., Japan) were used as received. Sodium dodecyl sulfate (SDS: Ducksan Chemical Ind., Ltd., Korea) and reagent grade chemicals were also used without further purification. Distilled and deionized water was used throughout.

### Polymerization

Three different latexes are prepared as follows. Table I shows the recipes for the synthesis of large particle (LP), small particle (SP), and PMMA

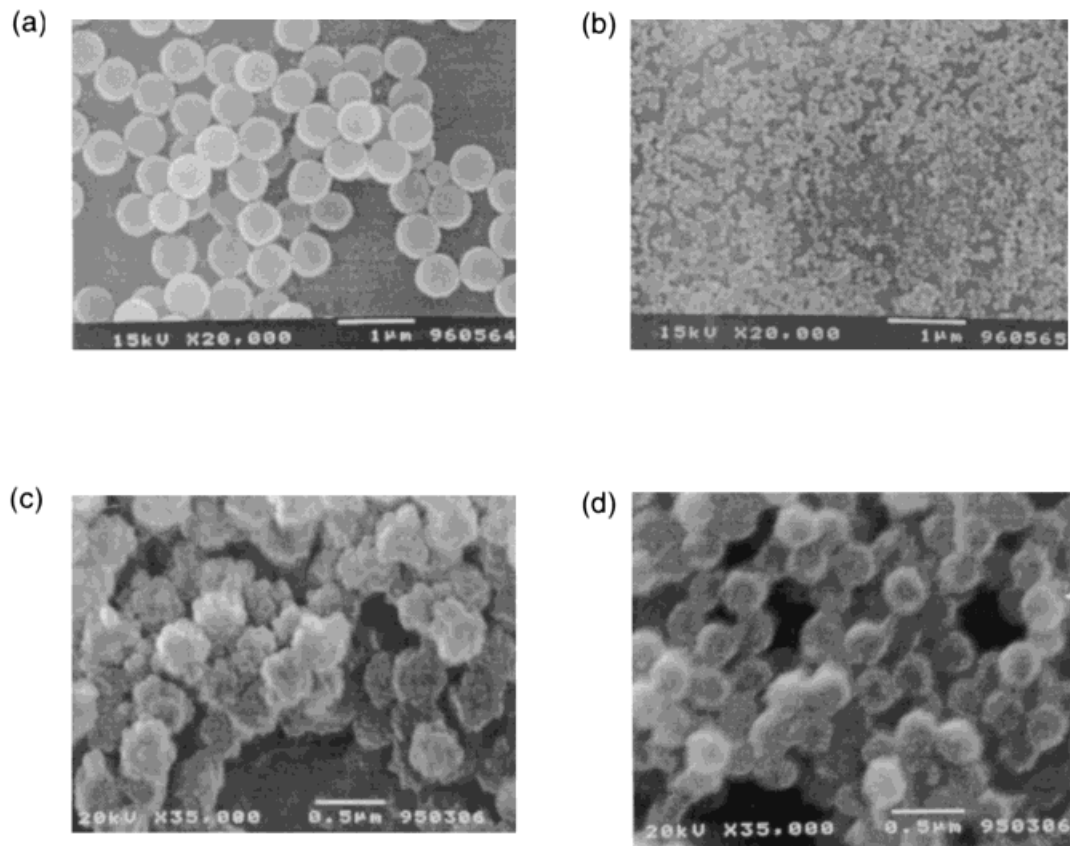


**Figure 1** pH dependence of zeta potential (●): large amphoteric particle (LP), (▼): small anionic particle (SP).

particles for matrix (MP). Polymerizations were performed in a 2-L stirred glass reactor under nitrogen atmosphere. Large poly(MMA-DEAEM-AA) amphoteric particles (LP) were prepared by emulsifier-free emulsion polymerization at 70°C for 24 h.<sup>13</sup> In the synthesis of LP, the isoelectric point was controlled by adjusting the relative amounts of amine and carboxyl functional comonomers in the medium of the optimized pH range. Two kinds of small poly(MMA-BA-AA) and poly(ST-BA-AA) anionic particles (SP-M and SP-S) were prepared by the microemulsion polymerization method at 80°C for 24 h. In the synthesis of SP-M and SP-S, surfactant, and monomer mixtures were stirred. Subsequently, distilled water was added to prepare the microemulsion. The microemulsion mixture was heated in a reactor and initiated by adding the concentrated solution of AIBN in acetone. Upon adding the initiator solution, the reaction mixture became turbid and transparent again after a few seconds. Another kind of SP, crosslinked poly(MMA-BA-AA) (X-SP-M), was prepared by using 1,4-butandiol dimethacrylate as a crosslinking agent. PMMA particles for matrix (MP) and X-SP-M were prepared by the same procedure for LP and SP-M, respectively, at 70°C for 4 h, except that there was a slight change in the recipe, as summarized in Table I. The measured particle sizes and particle size distributions for the above latexes are shown in Table II. The particle sizes and particle size distributions were characterized by using the capillary hydrodynamic fractionation (CHDF-1100, Matec Applied Sciences).

### Zeta Potential

Zeta potentials of synthesized latexes were measured by the zeta potential analyzer (Dynamic Laser Light Scattering, ZetaPlus, Brookhaven Instruments Co., USA), while its ionic strength was



**Figure 2** Electron micrograph of latex particles. (a) Large particle (LP); (b) small particle (SP); (c) heterocoagulated particle; (d) after annealing.

adjusted to 0.01 using sodium chloride (NaCl), and its pH was controlled by adding 0.1N HCl or NaOH solutions. Figure 1 shows the typical zeta potential curves of LP and SP as a function of medium pH.

### Heterocoagulation

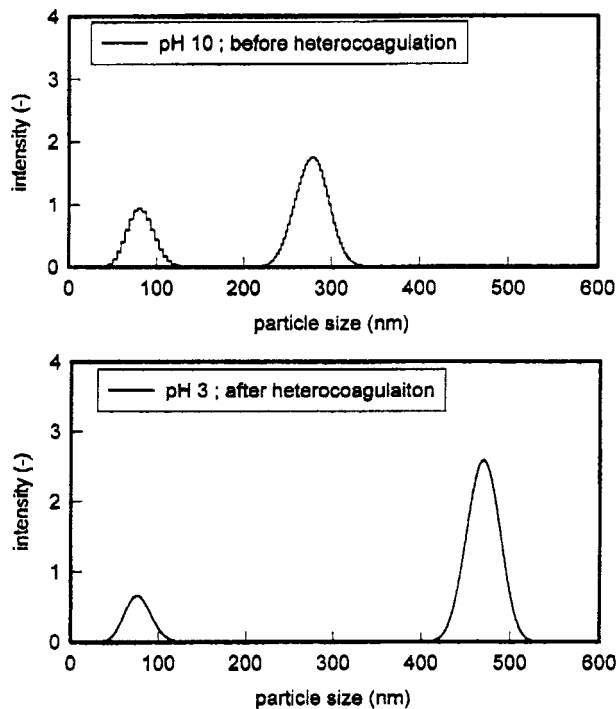
Heterocoagulation was carried out as follows: (1) LP and SP (SP-M, SP-S, or X-SP-M) were separately diluted with water to 10 wt % solid, and pH values were adjusted to 10 with 0.5 N NaOH solution for both LP and SP having the same charge. (2) Then the LP latex and SP latex are blended and kept at room temperature for 10 min. (3) The pH of blended latex was changed from 10 to 3 with 0.5N HCl solution to provide the zeta-potential difference between LP and SP. (4) The temperature was maintained at 25 or 70°C for 24 h<sup>1</sup> for the film formation of SP on the surface of LP. Figure 2 shows the typical variation of particle size and shape at each step. Figure 2(a) and

(b) are the microphotographs of LP and SP, respectively; Figure 2(c) shows that the the surface of LPs are covered by SPs just after adjusting the pH. After annealing for 24 h, the spherical shapes of SPs are disappeared and thin films are formed on the surface of LPs, as shown in Figure 2(d).

The theoretical maximum number of SP to cover one LP completely, assuming singular layer composed of SP, was calculated by eq. (1).<sup>1</sup>

$$N_{\max} = (2\pi/3^{0.5})[(R_L + R_S)/R_S]^2 \quad (1)$$

However, the surface of LP is usually not completely covered with SP. Figure 3 compares the difference in particle size distribution before and after adjusting the pH at the heterocoagulation step. After adjusting the pH, the average size of the LP is increased from 290 to 470 nm, confirming that SPs are adsorbed on the surface of LPs. However, the peak for SPs does not completely disappear even after adjusting the pH, suggesting



**Figure 3** Comparison of particle size distribution before and after pH adjustment.

that there exists some free SPs even after adjusting pH.

The percentage of coverage ( $P_C$ ) was determined from eq. (2).  $N$ , which is the experimental number of SP heterocoagulated by one LP, was determined by following depletion of SP concentration determined by the particle size analysis and observing the absorbance at 60 nm with spectrophotometer (UV-160A, Shimadzu, Japan) using a calibration curve of SP concentration before and after heterocoagulation.

$$P_C(\%) = (N/N_{\max}) \times 100 \quad (2)$$

Regardless of type of SP used, the value of  $P_C$  was about 80%.

### Solid Specimen Preparation

The solid specimen preparation scheme and notations for the final samples are summarized in Figure 4. At first, the heterocoagulated particles were prepared as described above. Then, by annealing the heterocoagulated particles at two different temperature, the core-shell structure of heterocoagulated particles were allowed to develop. To

prepare the solid specimen for dynamic mechanical characterization, heterocoagulated particles and matrix particles (MP) were mixed in the emulsion state. These emulsion blends were dried in a vacuum oven at 25°C. From the blends prepared, sheets of 2.5-mm thickness were obtained by compression molding in a heated press. The samples were heated to 130°C and kept 2 min between the plates without any applied pressure. After this period, a pressure of 7000 psi was applied at the same temperature for 4 min. The sample then was slowly cooled at room temperature. From the sheets so prepared, the rectangular specimens were cut to perform the dynamic mechanical tests. The specimen dimensions were of the order of 5121.8 mm<sup>3</sup>. In Table III,  $N_{\max}$  calculated based on eq. (1), SP content in heterocoagulated particle, and SP content in the final molded sample are summarized. Because the fraction of SP in the heterocoagulated particle is around 0.38, the content of SP phase in the final molded specimen is around 12%. As a comparison, the simple blend composed of SP and MP were prepared with the same procedure except that MP were directly blended with SP-M or SP-S instead of mixing with heterocoagulated particles. The content of SP in this specimen were adjusted to 10 and 30% to compare with the solid specimen containing heterocoagulated particles.

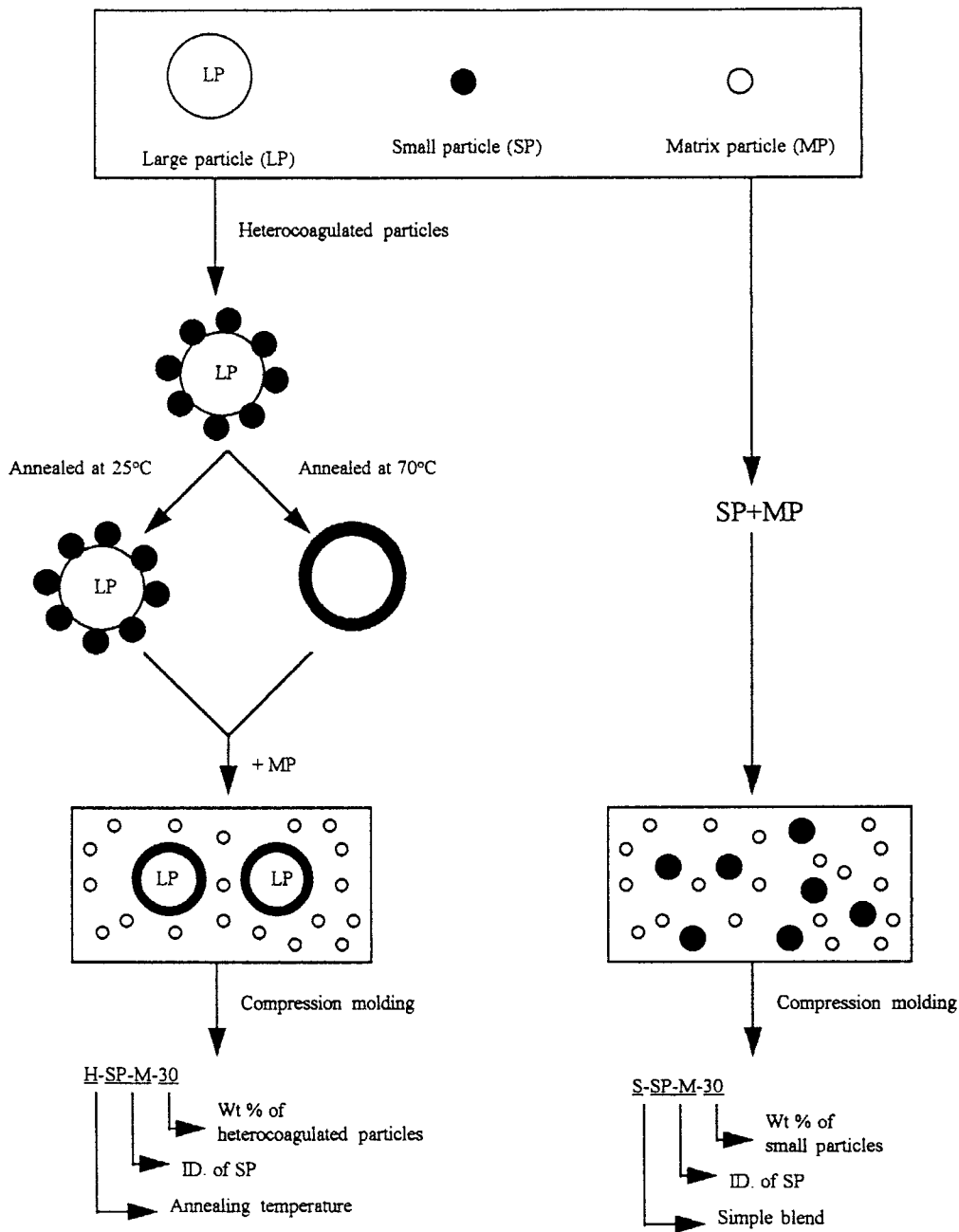
### Dynamic Mechanical Measurements and DSC

Measurement of dynamic mechanical properties as a function of temperature were made by using DMTA (Polymer Laboratories, Model MK-, UK). The frequency and the temperature range employed were 1 Hz and 20–200, respectively. The magnitude of the storage tensile modulus ( $E'$ ) and the tangent of the phase angle ( $\tan \delta$ ) were recorded with a heating rate of 3°C/min.

The glass transition temperature of some samples were analyzed using differential scanning calorimetry (DSC) (Polymer Laboratories, UK) with a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

In Figure 5, the storage tensile modulus ( $E'$ ) and  $\tan \delta$  variations of LP, SP-S, SP-M, and MP are shown. Each specimen exhibits a single relaxation, which corresponds to its own glass transition of 154, 75, 65, and 147°C, respectively.<sup>7</sup> Be-



**Figure 4** Schematic description of the sample preparation.

cause the LP and MP are mainly composed of MMA except a few minor components, the glass transition temperatures of two samples are rather similar.

$E'$  and  $\tan \delta$  of H-SP-M-30 and H-SP-S-30 are compared in Figure 6. Both contain the heterocoagulated particle annealed at 70°C at the dispersion state. For H-SP-S-30, two relaxation peaks around 150 and 70 °C are observed, which corre-

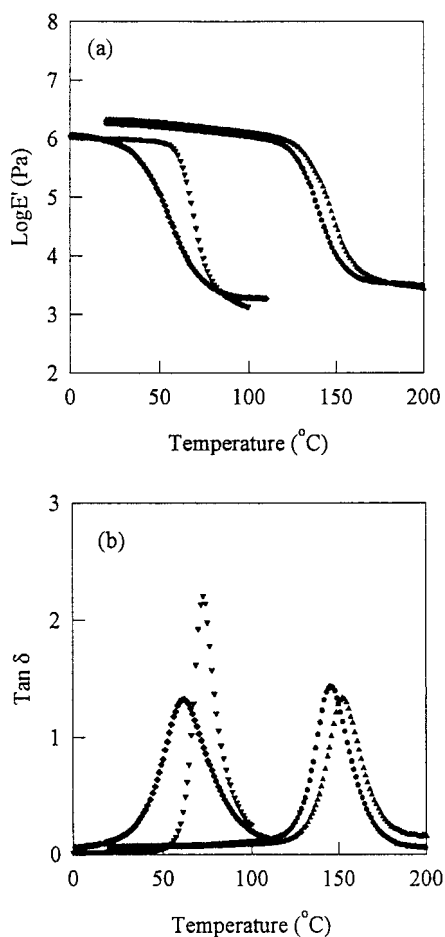
spond to that of SP-S and LP (and/or MP), respectively. On the other hand, H-SP-M-30 shows only one relaxation around 140°C, which corresponds to LP and/or MP. When the annealing temperature is changed from 70 to 25°C, it does not noticeably influence the result, as shown in Figure 7. In this figure, L-SP-M-30 again shows only one relaxation representing the LP or MP phase, while L-SP-S-30 shows two relaxation as the H-

**Table III** Calculated  $N_{\max}$ , Content of SP in Heterocoagulated Particles, and in the Final Molded Sample

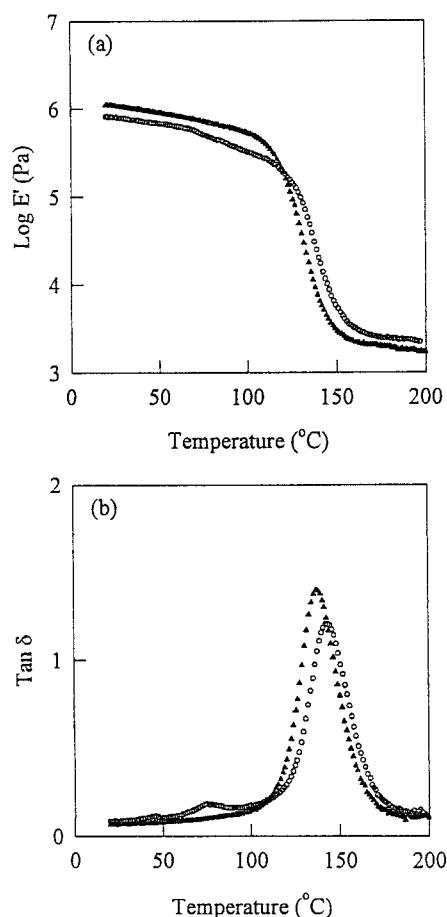
Kinds of SP	SP-M	SP-S	X-SP-M
$N_{\max}$	185	243	90
Content of SP in heterocoagulated particle (%)	44.35	39.48	58.68
Content of SP in the final molded sample (%)	13.30	11.84	17.60

SP-S-30 sample does. The difference in the content of the SP phase between two samples might be one of the possible explanation for the presence of the relaxation around 70°C in H(or L)-SP-S-30. Although the content of the SP phase in the two samples are close, in fact H-SP-M-30 has a slightly higher content, as shown in Table III. Therefore, the origin of this difference should

be assigned to the morphological difference between two samples. The small particle SP-M and SP-S are composed of poly(MMA-BA-AA) and poly(PS-BA-AA), respectively. Because each polymer has a considerable amount of BA and AA in the chain, even SP-M does not have very good compatibility toward LP, which are mainly composed of MMA. However, SP-M would have much better compatibility toward LP compared with SP-S in a relative sense. Due to the better compat-



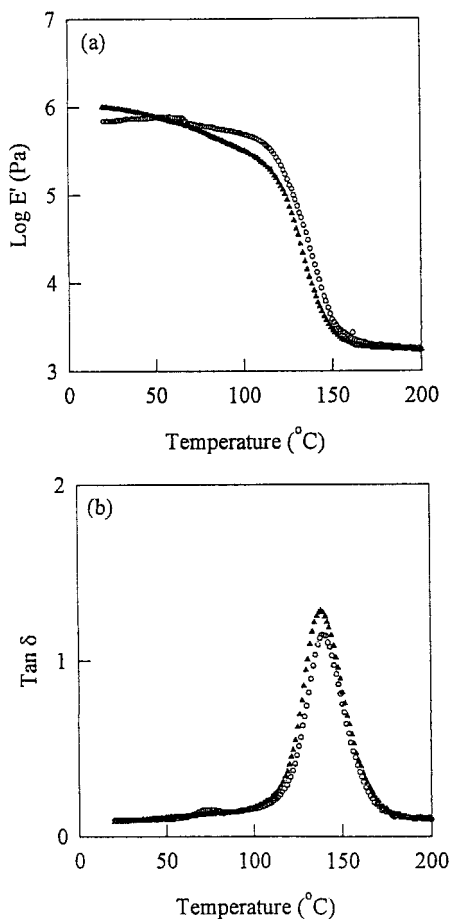
**Figure 5** Dynamic mechanical behavior of latex particles. (●): matrix particle (MP); (▲): large particle (LP); (▼): small particle, SP-S; (◆): small particle, SP-M.



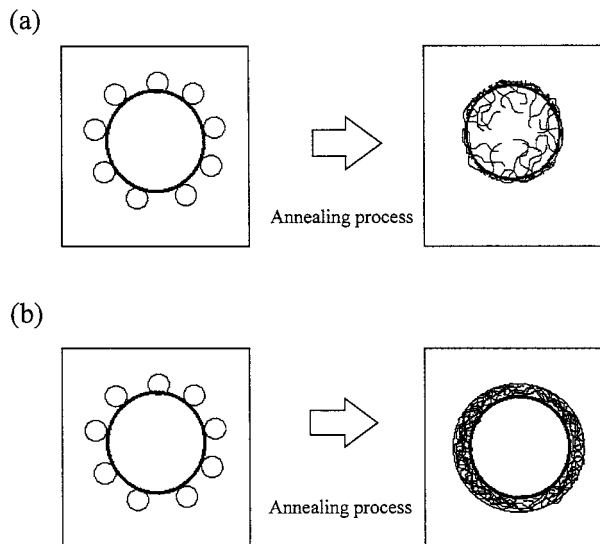
**Figure 6** Dynamic mechanical behavior of the molded specimen containing heterocoagulated particles annealed at 70°C. (○): H-SP-S-30; (▲): H-SP-M-30.

ibility between LP and SP-M, the interdiffusion may occur during the annealing process in the dispersion state performed at 70°C for 24 h.

In the recent investigation of Ottewill et al.,<sup>14</sup> it has been shown that the small particle composed of polystyrene can be engulfed into the interior of the large particle composed of poly(butyl methacrylate) by annealing for 24 h at 70°C. Even though the direct comparison might be difficult because the Ottewill's system is composed of a soft core and a hard shell, which are opposite to the current system, it might be considered that some of the chains in the shell composed of SP-M diffused into LP, resulting in a very thin shell phase after annealing. Also, the plasticization effect of water may facilitate such interdiffusion process.<sup>15</sup> On the other hand, the shell phase of the H-SP-S-30 are composed of poly(ST-BA-AA), which has a relatively higher glass transi-



**Figure 7** Dynamic mechanical behavior of the molded specimen containing heterocoagulated particles annealed at 25°C. (○): L-SP-S-30; (▲): L-SP-M-30.



**Figure 8** Schematic comparison of structural development during the annealing process of heterocoagulated latexes, depending on the kinds of SP. (a) with SP-M; (b) with SP-S.

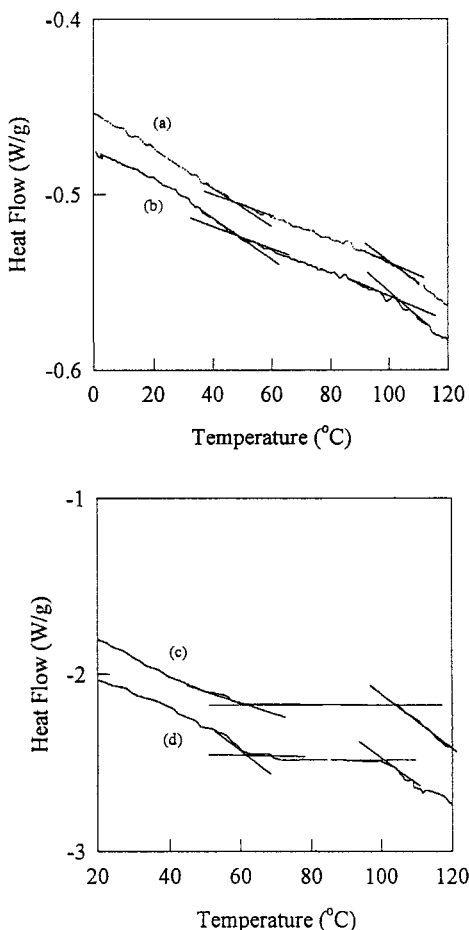
tion temperature and less compatibility with LP. Therefore, SP-S does not diffuse much into LP and rather forms a more distinct shell structure that SP-M, as represented schematically in Figure 8.

In Figure 9, DSC thermogram for H-SP-M-30, L-SP-M-30, H-SP-S-30, and L-SP-S-30 are summarized. All of the samples show two separate glass transition regions, confirming the presence of SP phase in H(or L)-SP-M-30 samples even though the characteristic  $\text{tan } \delta$  peak representing SP phase cannot be observed in dynamic mechanical spectra. Considering that a dynamic mechanical response depends not only on the nature of constituents but also on the structural arrangement such as morphology, these results support the fact that the difference between H-SP-S-30 and H-SP-M-30 in the dynamic mechanical behavior can be attributed to the structural difference of the heterocoagulated particles. This may be substantiated by another series of experiments. In this case, a crosslinked version of SP-M, X-SP-M, is used instead of SP-M at the heterocoagulation step. The dynamic mechanical behavior of this sample is shown in Figure 10, in which another relaxation peak is observed in addition to the single relaxation observed in the sample using SP-M regardless of the annealing temperature. Therefore, it can be interpreted that the presence of relaxation corresponding SP phase in H(or L)-

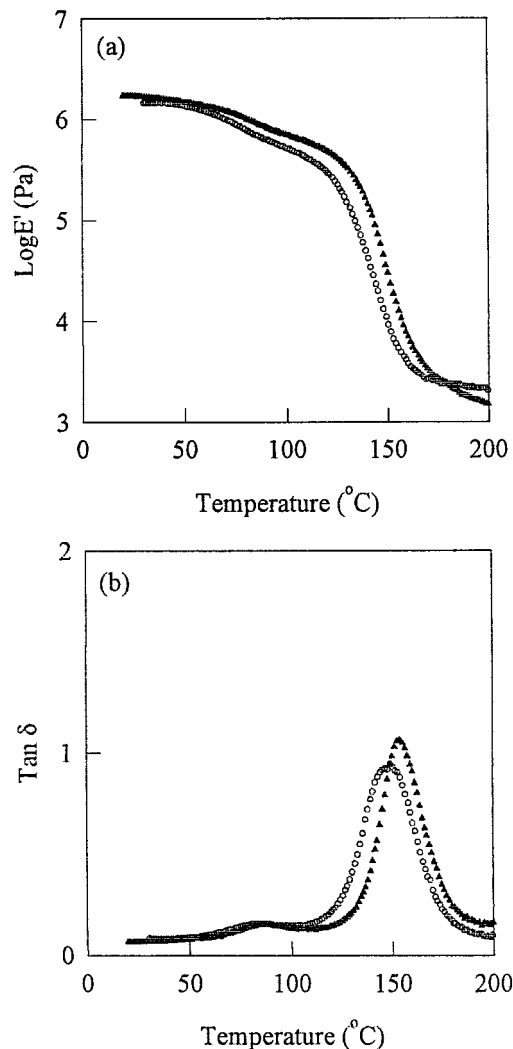


X-SP-M-30 is due to the inability of interdiffusion of X-SP-M.

So far, the discussion is mainly concerned with the difference of dynamic mechanical response between H(orL)-SP-M-30 and H(orL)-SP-S-30. At this time, the simple blend, which is a mixture of matrix particle and small particle, is compared with the previous samples containing the heterocoagulated particle. The simple blend examined in Figure 11 contains 10% of the SP-S content, which is close to the content of the SP phase in H-SP-S-30 (11.8%). In this spectra, only one relaxation representing the MP phase is observed, suggesting that 10% of the SP is not enough to provide enough response in the dynamic mechanical characterization in the simple blend. However, the sample H(or L)-SP-S-30 has shown the relaxation peak representing the SP (Fig. 6) phase, suggesting that the morphological character, the shell structure composed of SP-S, plays an im-



**Figure 9** DSC thermogram during heating. (a) H-SP-M-30; (b) L-SP-M-30; (c) H-SP-S-30; (d) L-SP-S-30.



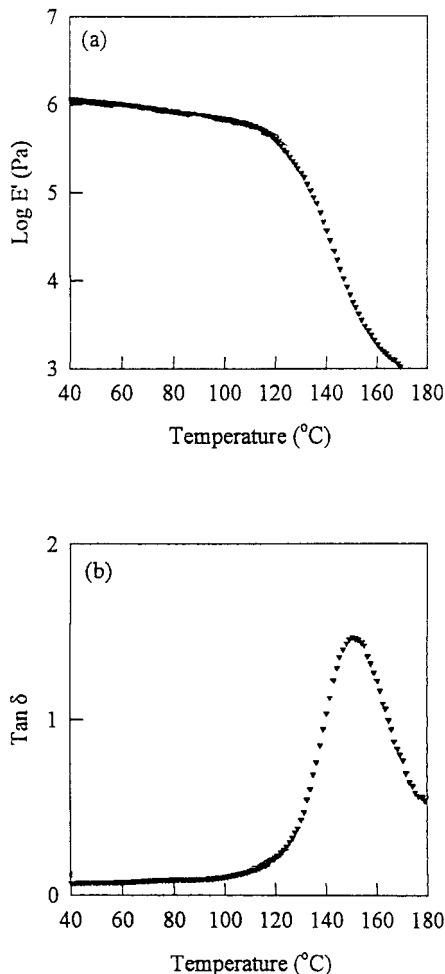
**Figure 10** Dynamic mechanical behavior of the molded specimen containing heterocoagulated particles composed of LP and X-SP-M with different annealing history at dispersion state. (○): H-X-SP-M-30; (▲): L-X-SP-M-30.

portant role in responding to dynamic mechanical stimuli. In the case of the simple blend, the relaxation peak of the SP-S phase begins to be observed at more than 30% of the SP content. At this content, the SP particles are no longer able to exist as a separate/isolated particle, and some of them may form aggregated structures. When the simple blend composed of SP-S (30%) and MP is annealed at 120°C in the mold, different dynamic mechanical spectra could be observed, depending on the annealing history, as shown in Figure 12. As the annealing time is increased, the peak representing MP phase is shifted toward a higher

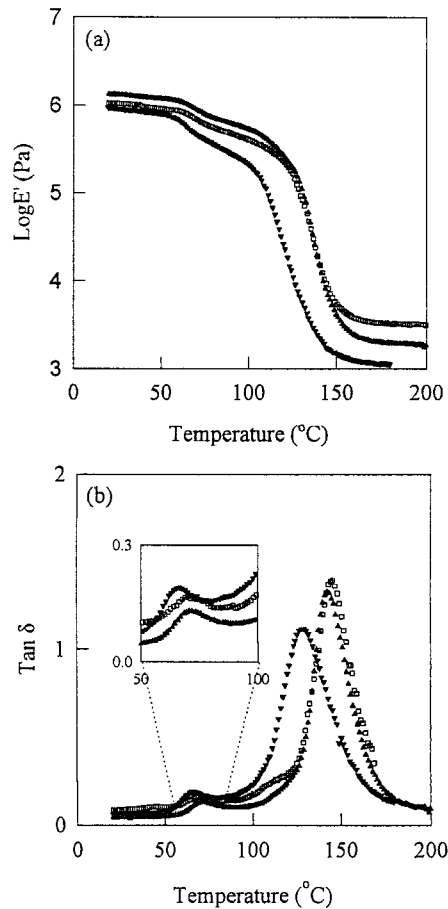
temperature and becomes more distinct. Also, the peak representing the SP-S phase becomes more apparent with annealing, suggesting that the simple blends become more phase segregated with annealing through rearrangement of aggregated particles.

**CONCLUSIONS**

The microstructure of heterocoagulated particles clearly depends on the kind of polymer forming large particles (LP) and small particles (SP). If the constituents of SP have a certain degree of compatibility with that of LP, an interdiffusion occurs during the annealing period at the dispersion state and the SP component in the heterocoag-



**Figure 11** Dynamic mechanical behavior of simple blend composed of MP and SP-S with an SP content of 10%.



**Figure 12** Dynamic mechanical behavior of a simple blend composed of MP and SP-S with an SP content of 30% under different annealing time at 120°C. ( $\blacktriangledown$ ): 0 h; ( $\square$ ): 6 h; ( $\blacktriangle$ ): 12 h.

gulated particles lose its own characteristics in the dynamic mechanical response. On the other hand, when the SP is not compatible with LP, it is found that the SP forms its own phase. As a consequence, the molded specimen made from the emulsion blend of heterocoagulated particles and matrix particles (MP) shows different dynamic mechanical behavior, depending on the kind of SP. By comparing with the simple blend, which is the molded specimen composed of MP and SP-S instead of heterocoagulated particles, it is demonstrated that the dynamic mechanical response depends not only on the amount of a certain phase but also on the detailed structure.

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