

Formation of Microheterogeneous Film from Composite Polymer Emulsion Prepared by the Stepwise Heterocoagulation Method

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Received 12 August 1997; accepted 4 February 1998

ABSTRACT: Blend emulsion of 2 kinds of particles, in which composite polymer particles were prepared by utilizing the stepwise heterocoagulation method proposed by the authors in 1990, was cast to prepare a microheterogeneous film. In the film, a discontinuous phase consisted of large anionic hard polymer particles and a continuous one consisted of small cationic soft polymer particles with the content of 30 wt % as film-forming additives. The storage stabilities of the blend emulsions after the stepwise heterocoagulation were examined under various conditions. The morphology of the film prepared was estimated from attenuated total reflectance Fourier transform infrared spectroscopic and dynamic mechanical spectroscopic measurements. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2221–2228, 1998

Key words: heterocoagulation; composite particle; film formation; morphology; emulsion polymerization

INTRODUCTION

One of the major applications of polymer emulsions is for casting various waterborne coating.¹ In these applications, polymer particles dispersed in water are deformed and coalescence and then transform into continuous film,^{2–4} and many newly developed, powerful techniques such as small-angle neutron scattering,⁵ freeze-fracture transmission electron microscopy,⁶ atomic force microscopy,⁷ ellipsometry, and environmental scattering electron microscopy,⁸ have been used to study the mechanism of the film formation. The studies show that the film formation and mechanical properties of film are affected by many factors, such as the kinds of emulsion, polymer particle morphology, cast conditions, and so on. A blend

technique of hard and soft polymer particles is used to modify the mechanical properties of film in which the hard particles act as filler to provide mechanical reinforcement and resistance, and the soft ones act as deform to fill space and provide a continuous phase.^{9,10} However, in order to prepare micro-heterogeneous film from the blend emulsion consisting of hard and soft particles at the temperature, which is below the glass transition temperature (T_g) of hard particle, 2 kinds of polymer particles should have similar size. For example, a continuous film was prepared by casting the blend emulsion consisting of polystyrene and poly(ethyl acrylate) polymer particles at room temperature at the poly(ethyl acrylate) content above 40 wt %.¹¹ Feng and Winnik also obtained a similar result in which a continuous film could be prepared until the soft polymer particles comprised at least 50 vol % of the total polymer solids.¹² On the other hand, by utilizing 2 kinds of polymer particles with different sizes the asymmetric, 2 layered films were obtained.^{13–15}

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Journal of Applied Polymer Science, Vol. 69, 2221–2228 (1998)
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In previous articles,^{16–18} we suggested the stepwise heterocoagulation method in which small cationic particles (SP) were adsorbed onto a large anionic particle (LP) to form an anomalous composite particle having uneven surface. Moreover, by treating it at a higher temperature than the T_g of SP, a core-shell particle in which the core consisted of hydrophilic polymer and the shell consisted of hydrophobic one was prepared.^{19,20}

In this article, a continuous film will be tried to prepare directly from a composite polymer emulsion obtained by mixing LP and SP at SP content of 30 wt % at temperature, which is lower than the T_g of LP and higher than that of SP, where almost all SP should be tried to be adsorbed onto LP in the blend process of 2 kinds of emulsions.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), ethyl acrylate (EA), methacrylic acid (MAA), butyl acrylate (BA), and styrene (S) were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Methacryloyloxyethyl trimethyl ammonium chloride (QDM, Nitto Chem. Ind. Co., Japan) was used without further purification. Analytical grade potassium persulfate (KPS) and 2,2'-azobis (2-amidinopropane) hydrochloride (V-50, Wako Pure Chem. Ind. Ltd., Japan), as initiators, were recrystallized. Commercial-grade nonionic polyoxyethylene sorbitan monooleate (Tween 80, Kao Atlas Corp., Japan), analytical-grade hydrochloric acid (HCl) and potassium hydroxide (KOH) were used as received. Deionized water was distilled before use.

All polymerizations were carried out at 70°C for 24 h in a glass reactor equipped with a condenser, mechanical stirrer, and nitrogen inlet, and the polymerization conditions are listed in Table I. As LP, large anionic MMA-EA-MAA terpolymer [$P(\text{MMA-EA-MAA})$] (59.0/32.0/9.0, molar ratio) particles with 584 nm in number-average diameter (D_n) were produced by emulsifier-free emulsion terpolymerization. As SP, small cationic S-BA-QDM terpolymer [$P(\text{S-BA-QDM})$] (55.0/42.0/3.0, molar ratio) particles with 117 nm in D_n were produced by emulsion terpolymerization. The T_g values of the LP and SP were 70° and 18°C, respectively, measured by using a differential

Table I Recipes of Emulsion Polymerizations^a for the Preparation of Cationic Small $P(\text{S-BA-QDM})$ Particles and Anionic Large $P(\text{MMA-EA-MAA})$ Particles

Ingredient	SP	LP
	$P(\text{S-BA-QDM})$	$P(\text{MMA-EA-MAA})$
	Molar Ratio	
	55.0/42.0/3.0	59.0/32.0/9.0
BA (g)	24.4	
S (g)	22.9	
QDM (g)	2.66	
MMA (g)		44.2
EA (g)		24.3
MAA (g)		6.0
V-50 (g)	0.25	
KPS (g)		0.30
Tween 80 (g)	2.5	
H ₂ O (g)	200	500
D_n^b (nm)	117	584
D_w^b (nm)	122	587
T_g^c (°C)	18	70

^a N₂; 70°C; 24 h.

^b Number-average and weight-average diameters, separately, measured by dynamic light scattering spectroscopy.

^c T_g , glass transition temperature measured by a differential scanning calorimeter.

Abbreviations are as follows: S, styrene; BA, butyl acrylate; MMA, methyl methacrylate; EA, ethyl acrylate; QDM, methacryloyloxyethyl trimethyl ammonium chloride; MAA, methacrylic acid; V-50, 2,2'-azobis (2-amidinopropane) hydrochloride; KPS, potassium persulfate; Tween 80, polyoxyethylene sorbitan monooleate.

scanning calorimeter (Seiko Instruments Inc. SSC-5200) at a heating rate of 10°C/min.

Stepwise Heterocoagulation

Heterocoagulation of LP and SP was carried out stepwise as follows.

1. LP and SP emulsions were separately diluted with water to 10 wt % solid and the pH values were adjusted at 3 with 0.01N HCl. Nonionic emulsifier Tween 80 of 8 wt % per LP was added to the LP emulsion.
2. The LP and SP emulsions were blended at the LP/SP ratio of 70/30 (w/w). The pH of the blend emulsion was adjusted to desired value with 0.01N KOH.

The weight percents of free SPs, which were unadsorbed onto LP at various pH values, were

obtained from the depletion of SP concentration before and after the heterocoagulation. The concentration was determined with a spectrophotometer using the calibration curve between the SP concentration and the absorbance at 460 nm. The absorbance of the blend emulsion at a certain pH value was measured as follows.

1. The blend emulsion was treated at 70°C for 10 min to sinter “soft” heterocoagulated particles in which SPs had been undirectly adsorbed onto LP.
2. The heterocoagulated particles (HPs) were removed from the blend emulsion by centrifuging at 6000 rpm for 30 min, following the filtration with a cellulose nitrate filter having pore size of 300 nm.

Particle Sizes

D_n and weight-average diameter (D_w) values of LP and SP were determined by a dynamic light scattering spectroscopy with a particle analyzer (DLS, Otsuka Electronics Inc., Model DLS-700).

Storage Stabilities of Blend and Heterocoagulated Emulsions

The storage stabilities of the blend and heterocoagulated emulsions at various conditions were estimated by turbidity measurement with a spectrophotometer (Hitachi Seisakusho Corp. Model 100-50) at 760 nm. The polymer solid of each sample used for the measurement was 0.010 wt %.

Film Formation

Films with a dry thickness of about 0.5 mm were prepared from each emulsion on a glass plate (5 × 5 cm). Films from LP and SP emulsions were cast at 75 and 20°C, respectively. Films were prepared from the blend emulsion of LP/SP at pH 3 and from the heterocoagulated emulsion at pH 8 and 9 at various conditions. The polymer solid of all emulsions was about 10 wt %.

Composition of Film Surfaces

The polymer compositions at both sides of the film were compared with an attenuated total reflectance Fourier transform infrared spectrometer (ATR-FTIR) (Shimadzu Corp., FTIR-4200). Before the measurement, the films except the LP film were washed in water for 2 days at room

temperature to remove emulsifier from the surface layer.

Viscoelastic Property

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

RESULTS AND DISCUSSION

In the stepwise heterocoagulation carried out at the LP-to-SP ratio of about 30/70 (w/w) in the previous article,¹⁹ most of SPs remained in the medium even after the heterocoagulation because the number of SPs added was much more than the theoretical maximum number of SPs adsorbed by one LP. The blend process and pH adjustment were carried out at the temperature below T_g values of LP and SP. By heat treatment at the temperature above the T_g of SP, the spherical core-shell composite polymer particles were obtained. A film having a heterogeneous structure was prepared from the core-shell composite particles in which the soft shell content consisting of SP was 37% after removing unheterocoagulated free SPs by centrifugation.

On the other hand, in this work, since the LP/SP ratio was fixed to be 70/30 (w/w), almost all SP should be adsorbed onto LP after the stepwise heterocoagulation. First, effects of temperature and pH adjustment on the stepwise heterocoagulation were examined. When the emulsions of LP and SP whose pH values were adjusted at 3 separately were blended at 0 and 20°C, they were stable, and heterocoagulation did not occur. When the pH value of the blend emulsion was adjusted directly from 3 to 9 to ionize carboxyl groups of the LP in a short time at 20°C, which is higher than the T_g of SP, many coagula were immediately observed with the naked eye. Whereas at 0°C, which is lower than the T_g of SP, no coagulum was observed with the naked eye. However, as shown in Figure 1, the transmittance of the blend emulsion at pH 9 and 0°C decreased greatly from 72 to 30% for 2 h. This rapid decrease of the transmittance suggests that not only heterocoagulation between LP and SP occurred, but also some of the heterocoagulated particles coagulated irregularly. In the particle size distribution data, actually, the coagula over 3 μm were observed. When the tem-

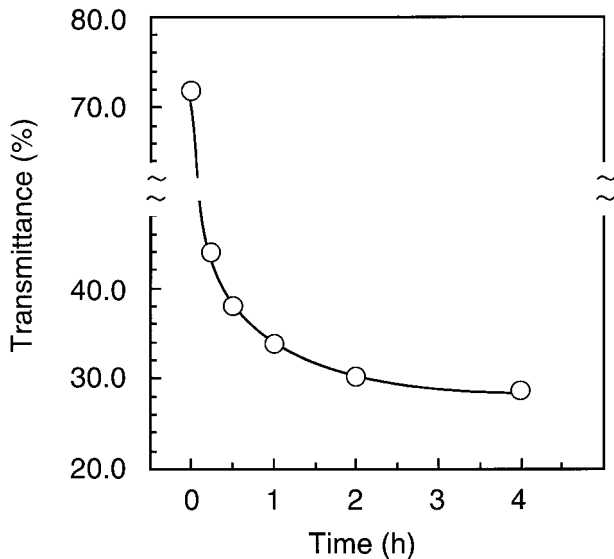


Figure 1 Storage stability of blend emulsion of LP/SP (= 70/30, w/w) with initial pH 9 at 0°C. The pH value was adjusted directly from 3 to 9.

perature of the heterocoagulated emulsion was raised to 20°C, some coagula were observed with the naked eye after gentle stirring for 1 h.

As shown in Figure 2, in which the pH adjustment from 3 to 9 was carried out stepwise at a

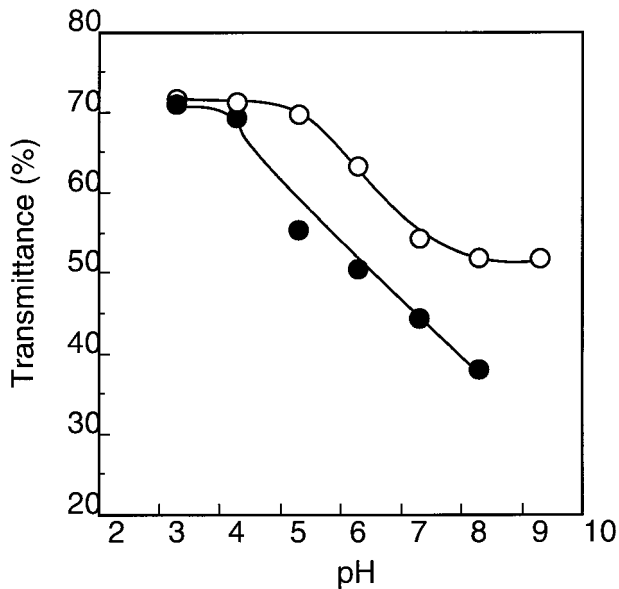


Figure 2 Relationships between pH values and transmittances of blend emulsion of LP/SP (= 70/30, w/w) at 0°C (○) and 20°C (●). The pH value was slowly adjusted with KOH aq. solution at the rate of 1 pH unit per 4 h. Measured conditions of transmittance: incident wavelength, 760 nm; polymer solid, 0.01%.

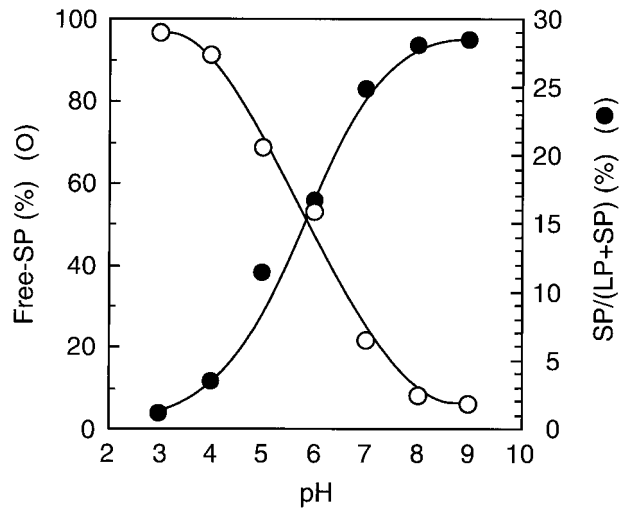


Figure 3 Effects of pH value on the weight percents of free SP (○) in medium and SP content (●) in heterocoagulated particles. Blend ratio of LP/SP is 70/30 w/w. The pH value was slowly adjusted with KOH aq. solution at the rate of 1 pH unit per 4 h at 0°C.

rate of 1 pH unit/4 h, at 20°C, the transmittance decreased continuously with an increase in the pH value to 8, and some coagula were observed with the naked eye. Whereas, at 0°C, the transmittance decreased from 70 to 52% with the increase in the pH value of 5–7, but no coagulum was observed with the naked eye, even at pH 9. These results indicate that ideal heterocoagulation was carried out by adjusting the pH value at the rate of 1 pH unit/4 h at 0°C. Therefore, in the following experiments, the heterocoagulated emulsions were prepared under the conditions.

Figure 3 shows the effects of the pH value on the percentage of unheterocoagulated SP (free SP) in the medium and SP content in the produced heterocoagulated particles. The percentage of free SP decreased continuously with an increase in the pH value and was less than 7% above pH 8. The SP content in the heterocoagulated particles increased with the pH value and was 28% at pH 8. This behavior agreed well with the change of the transmittance with the pH value shown in Figure 2. These results indicate that most of SPs were adsorbed onto LPs at pH 8 after the stepwise heterocoagulation in the blend emulsion of the LP/SP (70/30, w/w).

In order to estimate the colloid stability of the heterocoagulated emulsion in the process of film formation, the storage stabilities of the heterocoagulated emulsions with pH 8 and 9, separately,

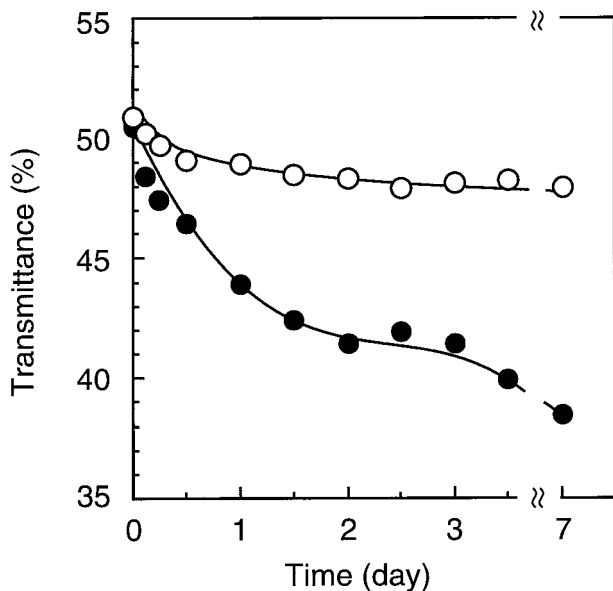


Figure 4 Storage stabilities of blend emulsion of LP/SP (= 70/30 w/w) at 20°C with different initial pH values of 8 (○) and 9 (●). The pH value was slowly adjusted with KOH aq. solution at the rate of 1 pH unit per 4 h at 0°C.

at 20°C, after the stepwise heterocoagulation at 0°C was examined for 1 week.

Figure 4 shows the results. At pH 9, the transmittance continuously decreased from 50 to 38% for 1 week. However, at pH 8, it decreased only a few percent for 6 h and then kept constant for 1 week. These heterocoagulated emulsions at pH 8 and 9, separately, were cast at 20°C just after the pH adjustments. The surface of the film prepared at pH 9 was a little uneven, whereas the film prepared at pH 8 had a smooth surface. On the basis of these results, in the following experiments, the final pH of the heterocoagulated emulsion adjusted at the rate of 1 pH unit/4 h at 0°C was fixed at 8.

Figure 5 shows the storage stabilities of the heterocoagulated emulsion at 20, 30, and 45°C. At 45°C, the transmittance of the heterocoagulated emulsion decreased very rapidly and after 1 h, some coagula were observed with the naked eye. The film cast at 45°C had an unevenness surface, and some cavities were observed therein with the naked eye. At 30°C, the transmittance decreased a several percent quickly and then slightly. On the other hand, at 20°C, it decreased only a few percent in the short time and then kept constant for 2 days.

The film prepared at 20°C from the heterocoagulated emulsion with pH 8 had some small

cracks, probably due to the low mobility of SP at 20°C because its T_g was about 18°C. When the heterocoagulated emulsion was cast at 20°C until the polymer solid reached about 85% and then was kept at 45°C for 1 day, a continuous film with smooth surface and without crack was obtained. On the other hand, when the blend emulsion with pH 3 in which the heterocoagulation did not occur was cast under the same conditions, no continuous film was prepared. It had an asymmetric two-layer structure: the air-side surface was continuous film, which consisted mainly of SP, and the glass-side one was powder, which consisted mainly of LP. This seems to be due to difference in the colloid stabilities of 2 kinds of polymer particles, as already reported.¹³⁻¹⁵ Therefore, in order to compare with properties of the film obtained from heterocoagulated emulsion, the film formation from the blend emulsion with pH 3 was carried out at 20°C until the polymer solid reached to 85% and then was kept for 1 day at 75°C, which was higher than T_g values of SP and LP.

Figure 6 shows the ATR-FTIR spectra of air-side surfaces of the films cast from LP [Fig. 6(a)] and SP [Fig. 6(b)] emulsions separately. It was noted that the speak at 700 cm^{-1} in the SP did not appear in the LP. For both films, similar spectra were obtained at their glass-side surfaces.

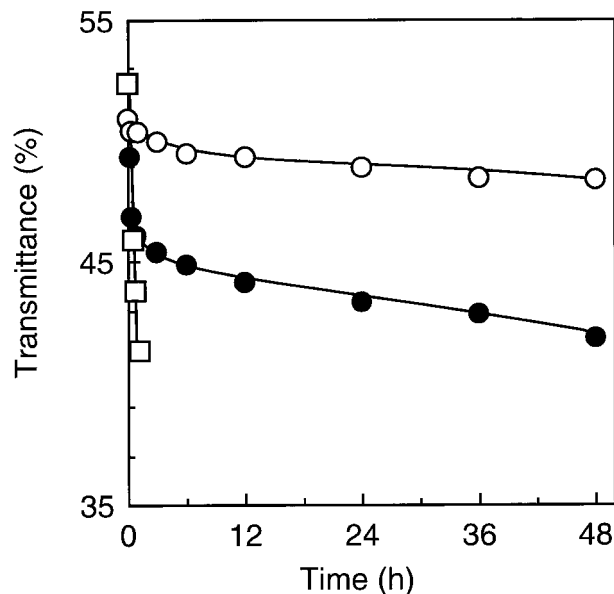


Figure 5 Storage stabilities of blend emulsion of LP/SP (= 70/30 w/w) with initial pH 8 at different temperatures (°C): (○) 20; (●) 30; (□) 45. The pH value was slowly adjusted with KOH aq. solution at the rate of 1 pH unit per 4 h at 0°C.

Figure 7 shows ATR-FTIR spectra of the air-side [Fig. 7(a)] and the glass-side [Fig. 7(b)] surfaces of the film cast from the blend emulsion with pH 3. The spectrum of the air-side surface [Fig. 7(a)] was similar to that of the SP. The spectrum of the glass-side surface [Fig. 7(b)] was similar to that of the LP, although a small peak at 700 cm^{-1} due to the SP appeared. These results indicate that at pH 3, the heterocoagulation did not occur, and in the film formation, the LP and SP separated, resulting in an asymmetric film as described above.

Figure 8 shows ATR-FTIR spectra of the air-

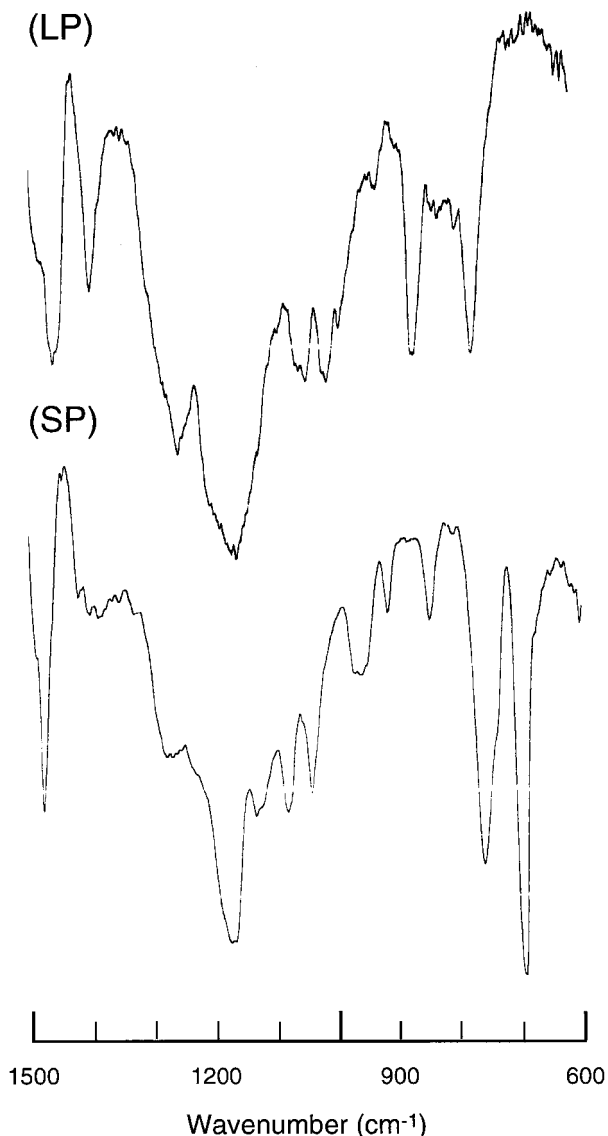


Figure 6 ATR-FTIR spectra of air-side surface of the films cast from P(MMA-EA-MAA) (LP), and P(S-BA-QDM) (SP) emulsions, separately.

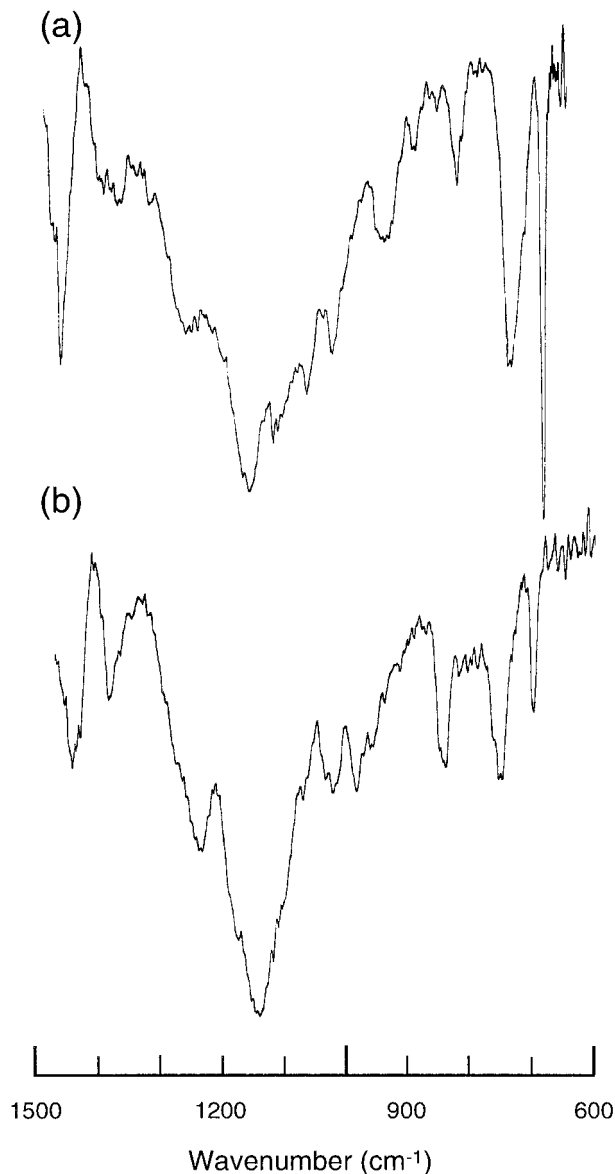


Figure 7 ATR-FTIR spectra of air-side (a) and glass-side (b) surfaces of the film cast from P(MMA-EA-MAA) and P(S-BA-QDM) blend emulsion at pH 3. The temperature of film formation was kept at 20°C until the polymer solid was attained at 85%, followed at 75°C .

side [Fig. 8(a)] and the glass-side [Fig. 8(b)] surfaces of the film cast from the heterocoagulated composite emulsion. Both spectra were similar and had a strong peak at 700 cm^{-1} due to the SP. This result indicates that almost all SPs, which were heterocoagulated onto the LP in the blend emulsion, formed a continuous phase in the film.

Figures 9 and 10 show, respectively, dynamic mechanical spectra of the films prepared from the blend emulsion with pH 3 and heterocoagulated

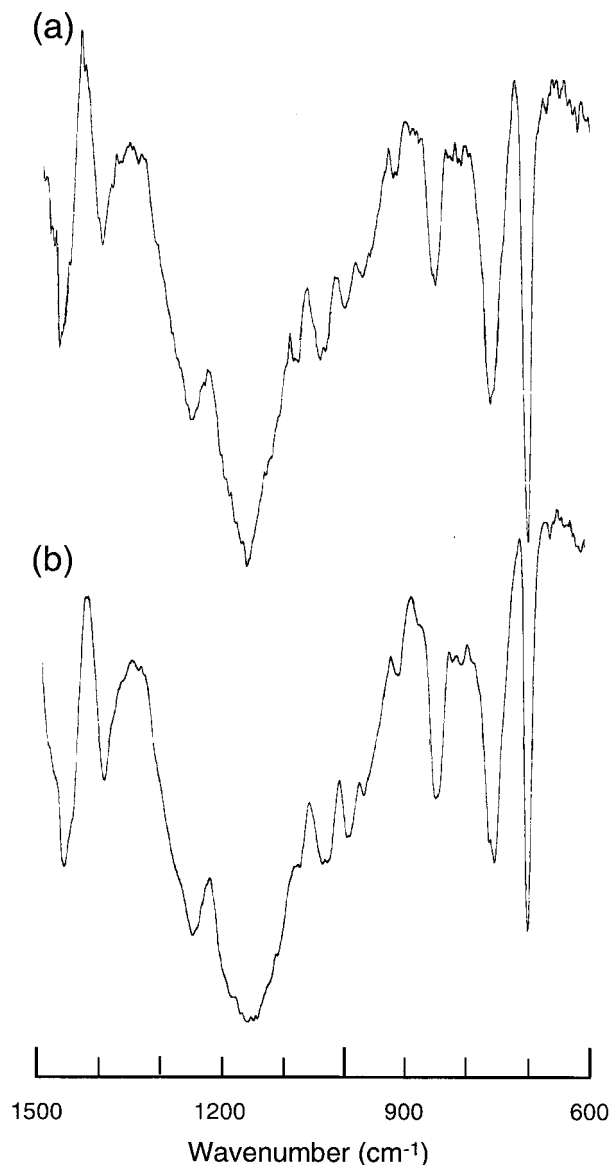


Figure 8 ATR-FTIR spectra of air-side (a) and glass-side (b) surfaces of the film cast from P(MMA-EA-MAA)-P(S-BA-QDM) heterocoagulated emulsion at pH 8. The temperature of film formation was kept at 20°C until the polymer solid attained at 85%, followed at 45°C.

emulsion with pH 8. In the film cast from the blend emulsion in Figure 9, the $\tan \delta$ curve had a small peak at about 33°C due to T_g value of SP and a strong one at about 80°C due to T_g value of LP. The $\tan \delta$ peaks of the films cast from original SP and LP emulsions appeared, respectively, at about 35 and 92°C (data were omitted). On the other hand, in the film cast from the heterocoagulated emulsion in Figure 10, the $\tan \delta$ curve had

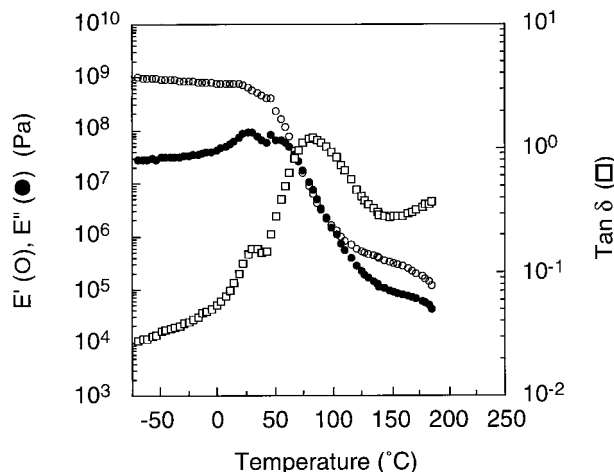


Figure 9 Mechanical spectra of the film cast from blend emulsion (70/30 w/w) of P(MMA-EA-MAA) (59.0/32.0/9.0 molar ratio) and P(S-BA-QDM) (55.0/42.0/3.0 molar ratio) with pH 3.

a very weak shoulder at 40°C and a strong peak at about 75°C. That is, the peaks due to T_g values of SP and LP, respectively, were shifted inward (the SP to a higher temperature and the LP to a lower one). The result can be explained by the fact that since the SP and LP component attached with wide interfacial area in the heterocoagulated particles, the SP molecules diffuse easily into the surface layer of the LP in the film formation at 45°C from the heterocoagulated emulsion. This is also supported by that E' values at the temperatures above 100°C was higher in the heterocoagu-

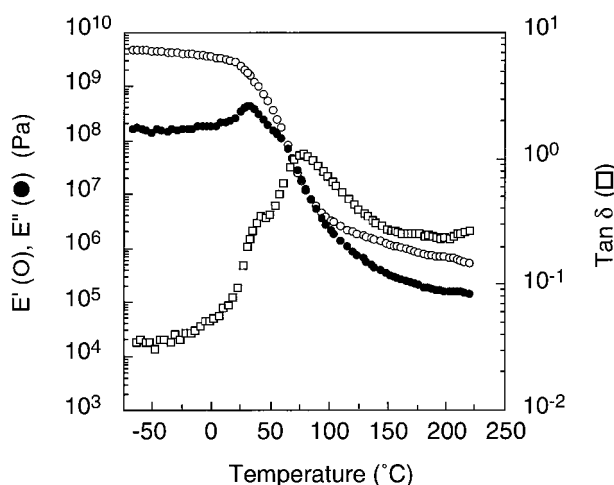


Figure 10 Mechanical spectra of the film cast from P(MMA-EA-MAA) (59.0/32.0/9.0 molar ratio)-P(S-BA-QDM) (55.0/42.0/3.0 molar ratio) (70/30 w/w) heterocoagulated emulsion with pH 8.

lated emulsion film than in the blend emulsion film. As already reported before,²¹ the high E' value seems to be based on that the ionic bonding interaction operates between the LP and SP, which consist of 2 kinds of polymer molecules having opposite charges, the ionized carboxyl groups and quaternary ammonium groups, respectively.

From these results, it is concluded that the stable heterocoagulated composite emulsion in which almost all the SPs are adsorbed onto LPs is prepared by the stepwise heterocoagulation method at the LP/SP blend ratio of 70/30 (w/w), and a continuous film having a microheterogeneous structure in which SPs having low T_g plays a continuous phase and LPs having high T_g plays a discontinuous phase is obtained directly therefrom.

This article is part CLXXIV of the series "Studies on Suspension and Emulsion."

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