

Morphology of Composite Polymer Emulsion Particles Consisting of Two Kinds of Polymers Between Which Ionic Bonding Intermolecular Interaction Operates*

MASAYOSHI OKUBO, SEITARO YAMAGUCHI, and TSUNETAKA MATSUMOTO, *Department of Industrial Chemistry, Faculty of Engineering, Kobe University, Rokko, Nada-ku, Kobe 657, Japan*

Synopsis

The morphology of particles (I) produced by seeded emulsion copolymerization of styrene (S) and sodium *p*-styrene sulfonate (NaSS) with butyl acrylate (BA)-methacryloyloxyethyltrimethylammonium chloride (QDM) copolymer particles as seed was examined in comparison with poly(butyl acrylate) (PBA)-polystyrene (PS) composite polymer emulsion particles (II). In an electron microscopic observation, it was observed that II particles had an anomalous shape and the electron densities at different points in the particle were heterogeneous, whereas I particles had an almost spherical shape and the electron densities were homogeneous. The maximum tensile strength and toughness were much larger in II than I. The dynamic mechanical studies indicate that II film had a macroheterogeneous structure consisting of PS-rich and PBA-rich phases, whereas I film had a microheterogeneous structure. These results suggest that there is an effect of intermolecular interaction between polymers of different kinds on the formation of heterogeneous structure in particles consisting of two kinds of polymers.

INTRODUCTION

We have studied so-called polymer blends in polymer emulsion particles, 0.1–0.7 μm in diameter, prepared by utilizing seeded emulsion polymerization technique. This technique is effective for producing composite polymer emulsion particles consisting of more than two kinds of polymers. In general, most polymer pairs are not compatible.¹ In practice, we clarified the formation of some heterogeneous structures, such as core-shell,^{2,3} POO (polymeric oil in oil),^{4,5} and PL (partial localized)⁶ in various blend systems. In this connection, we found some anomalous polymer emulsion particles: raspberrylike,⁶ confettilike,⁷ void-containing particles,⁸ and so on. The polymer blend proceeds in the process of seeded emulsion polymerization in particles that contact the water phase. These are the characteristics of this polymer blend.

The heterogeneous structures of the particles should be maintained in the process of film formation. Utilizing this point, for example, we succeeded in preparing composite polymer emulsion film with so-called temperature-sensitive properties, which means that the properties are changes by heat treatment.⁹

* This article is Part LXXXV of the series Studies on Suspension and Emulsion.

On the other hand, it has been reported that the formation of macroheterogeneous structures can be controlled by depressing the phase separation properly. This is well known as the IPN (interpenetrating polymer networks) technique.¹⁰ They are synthesized by copolymerizing a second monomer (II) with crosslinking agents in a crosslinked polymer (I). Crosslinked polymers I and II interpenetrate each other; therefore the phase separation of polymer I and II can be depressed. Consequently, the microheterogeneous structure is formed. This technique has already been applied to emulsion polymerization.¹¹ A number of applications are suggested, such as impact resistant plastics,¹² ion-exchange resins,¹³ noise-damping materials,¹⁴ and so on.

In this article, we introduce the ionic bonding between two kinds of polymer molecules in polymerizing particles in the process of seeded emulsion particles for the purpose of controlling its heterogeneous structure by depressing the phase separation properly.

EXPERIMENTAL

Materials

Butyl acrylate (BA) and styrene (S) were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Sodium *p*-styrene sulfonate (NaSS, Toyosoda Corp.) and methacryloyloxyethyltrimethylammonium chloride (QDM, Nittokagaku Kogyo Corp.) were used without further purification. Potassium persulfate (KPS) and 2,2'-azobis-(2-amidinopropane) hydrochloride (AIBA) were reagent grade. Nonionic polyoxyethylene-Sorbitan monooleate (Tween 80, Kao-Atlas Corp.) emulsifier was commercial grade.

Seeded Emulsion Polymerization

Seeded emulsions were prepared in 500-ml reaction flasks under conditions 1 and 2 listed in Table I. The seeded emulsion polymerizations of S and S-NaSS were carried out at 70°C in a 300-ml flask under conditions 3–

TABLE I
Recipes of Emulsion Polymerization^a

Sample	1	2	3	4	5	6
Emulsion (ml)	—	—	No. 1 100	No. 2 100	No. 2 100	No. 2 100
BA (ml)	89.9	85.7	—	—	—	—
S (ml)	—	—	22.2	21.1	21.1	21.1
QDM (g)	—	7.63	—	—	—	—
NaSS (mg)	—	—	—	316	630	949
Water (ml)	320	320	102	102	102	102
KPS (mg)	400	—	100	—	—	—
AIBA (mg)	—	400	—	2	2	2
Tween 80 (mg)	—	1600	400	1100	1100	1100
Time (h)	24	22	5	5	5	3

^a Polymerization temperature, 70°C. Atmosphere, N₂O

6. All monomers were preliminarily absorbed in the seed particles at 2°C for 24 h before the seeded emulsion polymerizations were started.

Electron Microscopy

The emulsion was properly diluted and dropped onto Formvar films supported by mesh copper screens. Then it was dried at room temperature in a desiccator. Electron microphotographs were taken by means of a HU-12 (Hitachi Seisakusho Corp.) transmission electron microscope.

Film Formation

Films with a dry thickness of about 0.3 mm were prepared by casting the emulsions on poly(ethylene terephthalate) (PET) films supported by a glass plate (10 × 10 cm) at 40°C.

Tensile Properties

Stress-strain diagrams of films were measured on a tensile tester (Shimazu Seisakusho Corp., Autograph IM-100) at room temperature with a crosshead speed of 50 mm/min.

Heat Distortion Temperature

The strain of films (breadth, 2.0 mm; thickness, 0.3 mm; primary length, about 1.0 cm), at the bottom of which a 2.3-g weight was hung, was measured as the temperature was raised from room temperature at a heating rate of about 0.6°C/min. For convenience, we defined the temperature at which the strain increased remarkably as the heat distortion temperature.

Optical Property

Visible light transmittance of emulsion films was measured by a spectrophotometer (Hitachi Seisakusho Corp., 100-50) at room temperature.

Viscoelastic Property

Dynamic mechanical spectroscopy studies were carried out under shear conditions with a Rheovibron (Toyo Measuring Instrument Corp., DDV-II) at 110 Hz. The temperature range was -60 to 200°C, at a heating rate of approximately 0.7°C/min.

RESULTS AND DISCUSSION

Configurations of Composite Polymer Emulsion Particles

In earlier articles,^{5,15} we found the formation of obvious heterogeneous structure in PBA-PS composite emulsion particles. In order to clarify the effect of ionic bonding interaction between the two polymers on the formation of the heterogeneous structure, a small quantity of amino group and sulfonic group was introduced into PBA and PS main components, respectively. That is, S-NaSS copolymer [P(S-NaSS)] was produced in BA-

QDM copolymer [P(BA-QDM)] seed particles by seeded emulsion polymerization.

Figure 1 shows electron micrographs of PBA-PS and P(BA-QDM)-P(S-NaSS) composite emulsion particles. It was observed that PBA-PS particles had a "POO" type of heterogeneous structure and an anomalous shape, whereas P(BA-QDM)-P(S-NaSS) particles had an almost spherical shape and the electron density in the particles was homogeneous. This result suggests that the phase separation of PBA and PS is depressed by the ionic bonding interaction.

Properties of the Emulsion Films

Figure 2 shows stress-strain diagrams of PBA-PS (functional group: 0 mol%) film and P(BA-QDM)-P(S-NaSS) composite emulsion films. The BA-QDM composition in the latter films was 97:3 (mol ratio), and QDM-NaSS mol ratios were changed to 75:25, 60:40, and 50:50. Thus, the amounts of a pair of functional groups to form the ionic bonding were 1, 2, and 3 mol%, respectively. As the amount of functional groups was increased, the maximum tensile strength increased and the ultimate elongation decreased, except in the case of 0 mol% functional group.

Figure 3 shows heat distortion curves of various composite emulsion films. PS film was formed by heat pressing (200°C, 100 kg/cm²) PS powder, which was obtained by drying PS emulsion at room temperature. The heat distortion temperatures of P(BA-QDM)-P(S-NaSS) films were much higher than PBA-PS and PS films. It increased with the increase in functional groups.

Figure 4 shows optical transmittance in the visible region of various composite emulsion films. The transmittance of emulsion film increased by the introduction of functional groups. As shown, the physical properties of film were enhanced by the introduction of the ionic bonding interaction between two polymers. Those results suggest that the introduction of the ionic bonding into composite polymer emulsion particles apparently enhances the compatibility of different polymers.

Effects of Composition (BA-S) on Physical Properties of Films

Figure 5 shows stress-strain diagrams of PBA-PS and P(BA-QDM)-P(S-NaSS) composite emulsion films with various BA-S compositions. In the latter, the BA-QDM mol ratio was 97:3 and the amount of NaSS in P(S-

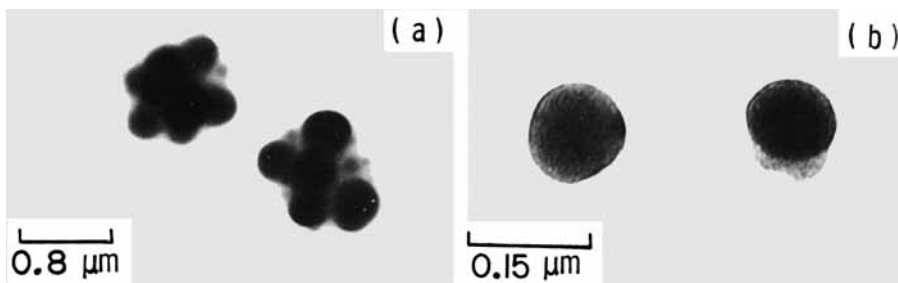


Fig. 1. Electron micrographs of PBA-PS (a) and P(BA-QDM)-P(S-NaSS) (b) composite emulsion particles: BA-S (w/w) = 50:50; BA-QDM (mol/mol) = 97:3; QDM-NaSS (mol/mol) = 50:50.

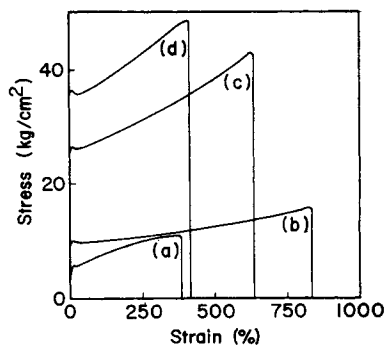


Fig. 2. Stress-strain curves of PBA-PS (a) and P(BA-QDM)-P(S-NaSS) (b, c, d) composite emulsion films: BA-S (w/w) = 50:50, BA-QDM (mol/mol) = 97:3. QDM-NaSS (mol/mol): (b) 75:25; (c) 60:40; (d) 50:50.

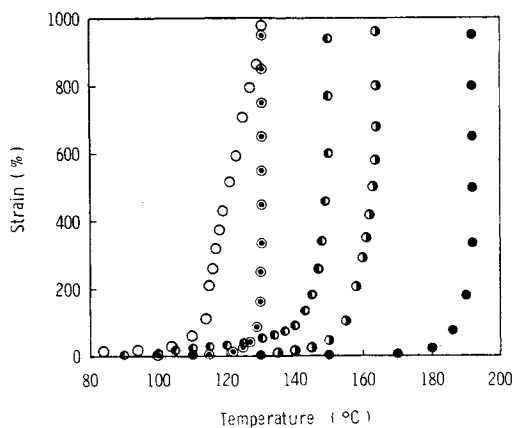


Fig. 3. Heat distortion curves of PS (○) film, PBA-PS (○), and P(BA-QDM)-P(S-NaSS) (◐, ◑, ●) composite emulsion films: BA-S (w/w) = 50:50; BA-QDM (mol/mol) = 97:3. QDM-NaSS (mol/mol): (◐), 75:25; (◑), 60:40; (●), 50:50. PS film was prepared by heat pressing.

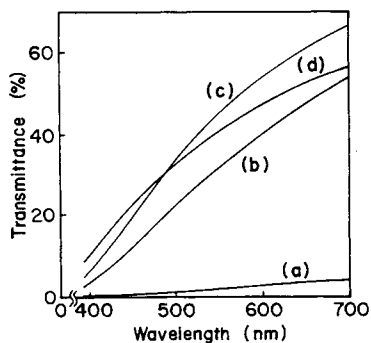


Fig. 4. Optical properties of PBA-PS (a) and P(BA-QDM)-P(S-NaSS) (b, c, d) composite emulsion films: BA-S (w/w) = 50:50; BA-QDM (mol/mol) = 97:3. QDM-NaSS (mol/mol): (b) 75:25; (c) 60:40; (d) 50:50.

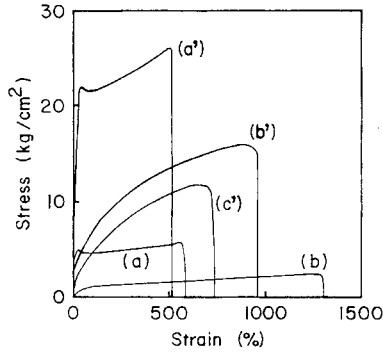


Fig. 5. Stress-strain curves of PBA-PS (a, b) and P(BA-QDM-P(S-NaSS)) (a', b', c') composite emulsion films: BA-QDM (mol/mol) = 97:3; QDM-NaSS (mol/mol) = 50:50. BA-S (w/w): (a, a') 50:50; (b, b') 66.7:33.3; (c') 83.3:16.7.

NaSS) was equivalent to that of QDM. As obvious in Figure 5, in the cases of BA-S = 50:50 and 66.7:33.3, the maximum tensile strength and toughness of P(BA-QDM)-P(S-NaSS) films were, respectively, much larger than those of PBA-PS films. In the case of BA-S = 83.3:16.7, PBA-PS film was too tacky and weak to carry out the measurement, whereas the maximum tensile strength of P(BA-QDM)-P(S-NaSS) film was relatively large. In this way, the difference between PBA-PS and P(BA-QDM)-P(S-NaSS) was most remarkable in BA-S = 83.3:16.7 composition.

Figure 6 shows heat distortion curves of the composite emulsion films. In the case of PBA-PS, the heat distortion temperature considerably decreased with a decrease in S content. Whereas in the case of P(BA-QDM)-P(S-NaSS), the difference was very small and each film was molten at about 190°C.

Figures 7 and 8 show the storage modulus (G') and the loss modulus (G'') as a function of temperature for PBA-PS and P(BA-QDM)-P(S-NaSS) (functional group: mol%), respectively. In the case of PBA-PS, the two-step descent of G' , which corresponds to the glass transitions of PBA and of PS, respectively, was observed. Here, G' increased at about 100°C in spite of an

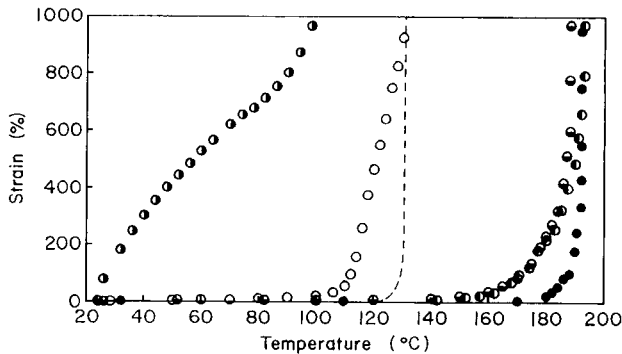


Fig. 6. Heat distortion curves of PS (—) film, PBA-PS (○, ●), and P(BA-QDM-P(S-NaSS)) (●, ○, ●) composite emulsion films: BA-QDM (mol/mol) = 97:3; QDM-NaSS (mol/mol) = 50:50. BA-S (w/w): (○, ●) 50:50; (●, ○) 66.7:33.3; (●) 83.3:16.7. PS film was prepared by heat pressing.

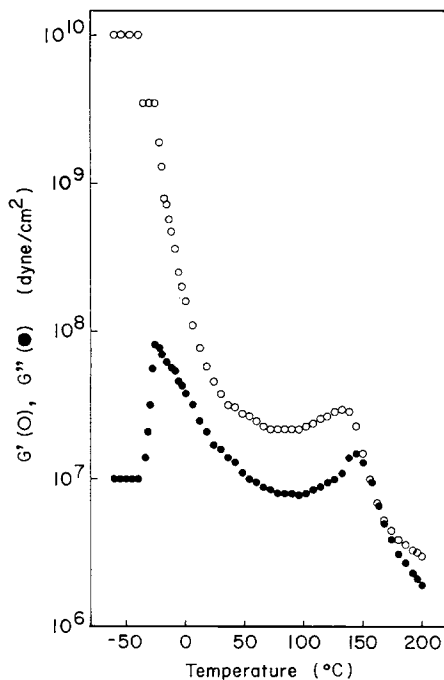


Fig. 7. The shear storage modulus (G') and the shear loss modulus (G'') of PBA-PA composite polymer emulsion film. BA-S (w/w) = 66.7:33.3.

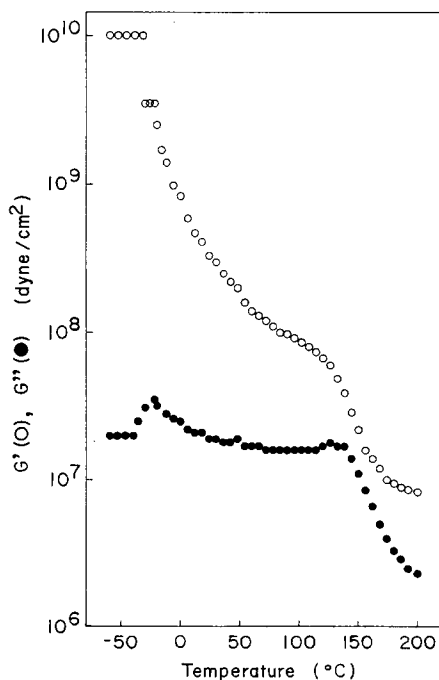


Fig. 8. The shear storage modulus (G') and the shear loss modulus (G'') of P(BA-QDM-P(S-NaSS)) composite polymer emulsion film. BA-S (w/w) = 66.7:33.3, BA-QDM (mol/mol) = 97:3, QDM-NaSS (mol/mol) = 50:50.

increase in temperature. This phenomenon is due to an alteration in the heterogeneous structure of the "POO" type accompanied by an increase in temperature, which was discussed in a previous article.¹⁵ In the P(BA-QDM)-P(S-NaSS) system the step of G' was unclear and G' decreased gradually with an increase in temperature in comparison with the PBA-PS system. In the case of PBA-PS, two peaks of G'' were observed at about -26 and 144°C , respectively. These values were nearly equal to the values for PBA and PS homopolymers under the same conditions,¹⁵ although they were higher than those observed in the literature.¹⁶ This seems to be based on differences in measuring method and conditions. In the P(BA-QDM)-P(S-NaSS) system these peaks were smaller and G'' in the intermediate temperature range (20 – 115°C) indicated higher modulus than in the PBA-PS. These results show that P(BA-QDM)-P(S-NaSS) film had microheterogeneous structure.

As mentioned above, it was clarified that it is possible to depress the macrophase separation of PBA and PS and consequently to form the microheterogeneous structure by means of the introduction of ionic intermolecular interaction into the emulsion particles in the process of the seeded emulsion polymerization. In addition, it was indicated that the maximum tensile strength and the heat distortion temperature of the emulsion films were increased by it.

References

1. S. Krause, *J. Macromol. Sci. Rev. Macromol. Chem.*, **C-7**, 251 (1972).
2. T. Matsumoto, M. Okubo, and T. Imai, *Kobunshi Ronbunshu*, **31**, 576 (1974).
3. M. Okubo, A. Yamada, and T. Matsumoto, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 3219 (1980).
4. T. Matsumoto, M. Okubo, and S. Onoe, *Kobunshi Ronbunshu*, **33**, 565 (1976).
5. M. Okubo, Y. Katsuta, A. Yamada, and T. Matsumoto, *Kobunshi Ronbunshu*, **36**, 459 (1979).
6. M. Okubo, Y. Katsuta, and T. Matsumoto, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 45 (1982).
7. T. Matsumoto, M. Okubo, and S. Shibao, *Kobunshi Ronbunshu*, **33**, 575 (1976).
8. M. Okubo, M. Ando, A. Yamada, Y. Katsuta, and T. Matsumoto, *J. Polym. Sci., Polym. Lett. Ed.*, **19**, 143 (1981).
9. M. Okubo, M. Seike, and T. Matsumoto, *J. Appl. Polym. Sci.*, **28**, 383 (1983).
10. J. R. Miller, *J. Chem. Soc.*, 1311 (1960).
11. For example, L. H. Sperling, T. W. Chiu, and D. A. Thomas, *J. Appl. Polym. Sci.*, **17**, 2443 (1973).
12. A. J. Curtius, et al., *Polym. Eng. Sci.*, **12**, 101 (1972).
13. L. H. Sperling, et al., *J. Polym. Sci., Polym. Lett. Ed.*, **13**, 713 (1975).
14. L. H. Sperling, T. W. Chiu, R. G. Gramlich, and D. A. Thomas, *J. Paint Technol.*, **16**, 47 (1974).
15. M. Okubo, Y. Katsuta, K. Inoue, K. Nakamae, and T. Matsumoto, *J. Adhesion Soc. (Japan)*, **16**, 278 (1980).
16. J. Brandrup and E. H. Immergut, *Polymer Handbook*, Interscience P, New York, 1974, Chap. III.

Received April 25, 1985

Accepted June 25, 1985