

# Studies on Suspension and Emulsion. LX. Composite Polymer Emulsion Film with Temperature-Sensitive Properties

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## Synopsis

The mechanical and optical properties of film cast from poly(ethyl acrylate)/polystyrene composite emulsion prepared by seeded emulsion polymerization were changed drastically by heat treatment. Such temperature-sensitive properties can be controlled by regulating the contents and the glass transition temperature of polymer. It was concluded that such a specific phenomenon is due to phase inversion in the heterogeneous structure of the film derived from the particle morphology determined by the polymerization recipe.

## INTRODUCTION

Composite polymer emulsion particles consisting of two kinds of polymers are prepared by seeded emulsion polymerization. In general, there are few situations in which the two polymers are completely mixed. Therefore, during polymerization, phase separation of polymers occurs in the particles, and polymer particles having different heterogeneous structures are formed at the end of the process.<sup>1-7</sup> Occasionally, some anomalous composite polymer emulsion particles are produced corresponding to peculiar heterogeneous structures.<sup>2,3,5,7</sup> The properties of polymer blends depend on their morphologies. This also applies in the case of film prepared from the above composite polymer emulsion. For example, the mechanical and optical properties of film prepared from poly(butyl acrylate)/polystyrene composite emulsion evidently differed by monomer addition methods in seeded emulsion polymerization which resulted in different polymer morphologies in particles. Moreover, the properties of film cast from poly(ethyl acrylate)/polystyrene composite emulsion prepared by monomer absorption in the seeded emulsion polymerization are changed by heat treatment. There are no other reports dealing with such a phenomenon. Therefore, this work was undertaken to clarify it.

## EXPERIMENTAL

### Materials

Styrene (St), ethyl acrylate (EA), and butyl acrylate (BA) were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Analytical-grade potassium persulfate and benzene were used without further purification. Deionized water was distilled.

TABLE I  
Polymerization Recipes of PEA Seed Emulsion and PEA/PSt and PEA/P(St-BA) Composite Emulsions<sup>a</sup>

	Condition no.						
	1	2	3	4	5	6	7
Emulsion (No. 1) <sup>b</sup> (mL)	—	47.6	47.6	47.6	47.6	47.6	47.6
EA (mL)	108.2	—	—	—	—	—	—
St (mL)	—	11.0	7.4	5.5	3.7	9.2	7.4
BA (mL)	—	—	—	—	—	1.9	3.7
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (mg)	500	50	33	17	25	50	50
Water (mL)	400	41	45	47	49	41	41
Polymn. time (h)	10	5	5	5	5	7	7

<sup>a</sup> Atmosphere nitrogen; polymn. temperature, 70°C.

<sup>b</sup> Polymer content, 0.21 g/mL.

### Seeded Emulsion Polymerization

Poly(ethyl acrylate) (PEA) seed emulsion was prepared in a 500-mL reaction flask under condition 1 listed in Table I. The seeded emulsion polymerization for St or St-BA was carried out at 70°C in a 300-mL flask under conditions 2–7. All monomers were preliminarily absorbed in the seed particles at 0°C for three days before the seeded emulsion polymerizations were started. The polymer combinations of various composite particles in this article are designated A/B, where A is the polymer used as seed and B is the polymer polymerized by the seeded emulsion polymerization.

### Film Formation

Films having a dry thickness of ca. 0.2 mm were prepared by casting emulsions or solution on glass plates at room temperature and were designated emulsion film and solution film, respectively. The solution was the benzene solution in which the emulsion film was dissolved.

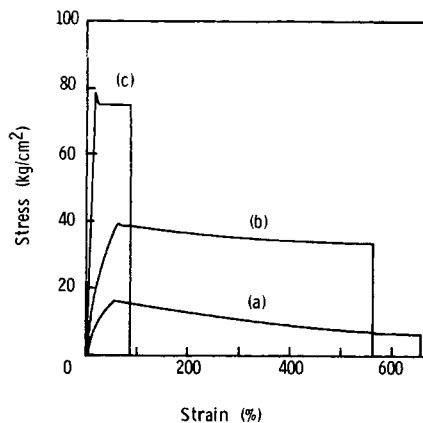


Fig. 1. Variation in stress-strain curves of PEA/PSt (1/1, w/w) composite emulsion film with heat treatment: (a) untreated; (b) 100°C, 10 min; (c) 150°C, 10 min.

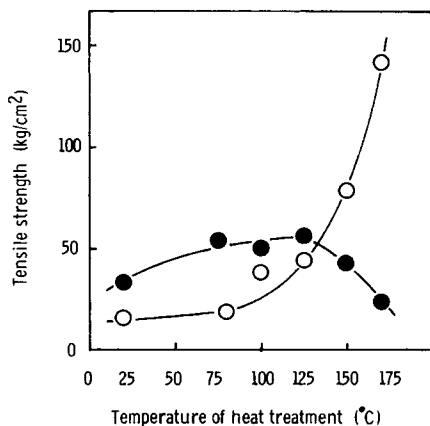


Fig. 2. Variation in tensile strength of PEA/PSt (1/1, w/w) composite polymer films: (O) cast from emulsion; (●) recast from benzene solution.

### 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.

Peel strength between the film and the glass substrate was measured under the same conditions as the above measurement. The film was reinforced by bonding poly(ethylene terephthalate) film, 80  $\mu$ m in diameter, with a double-coated tape.

### Optical Property

Visible light transmittance of emulsion films was measured by a spectrometer (Shimazu Seisakusho Corp., MPS-50) at room temperature.

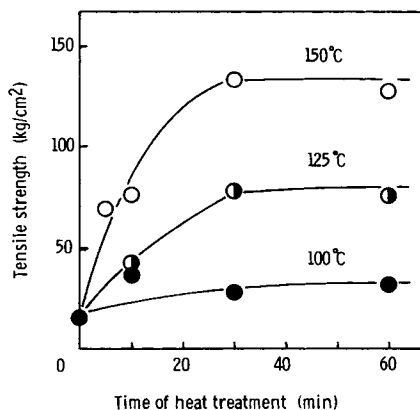


Fig. 3. Variation in tensile strength of PEA/PSt (1/1, w/w) composite emulsion film with heating time at 100, 125, and 150°C.

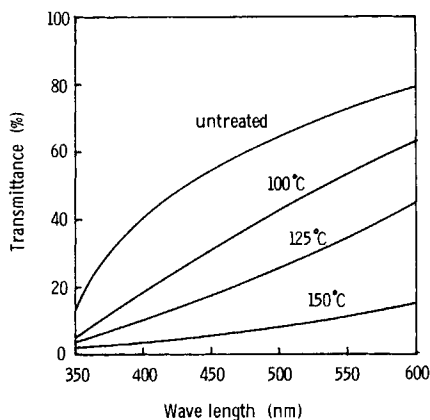


Fig. 4. Variation in optical transmittance in the visible region of PEA/PSt (1/1, w/w) composite emulsion film with heat treatment at various temperatures for 10 min.

### 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  $-50$  to  $150^{\circ}\text{C}$ , with a heating rate of approximately  $0.7^{\circ}\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

Figure 1 shows the variation of stress-strain diagrams of PEA/PSt (1/1, w/w) composite emulsion film with heat treatment. The film before heat treatment resembled a PEA emulsion film, which is soft and weak. However, the film after heat treatment became stiff and brittle, like PSt film.

Figure 2 shows the variation in tensile strength of the emulsion and the solution films of PEA/PSt (1/1, w/w) with heat treatment at different temperatures for

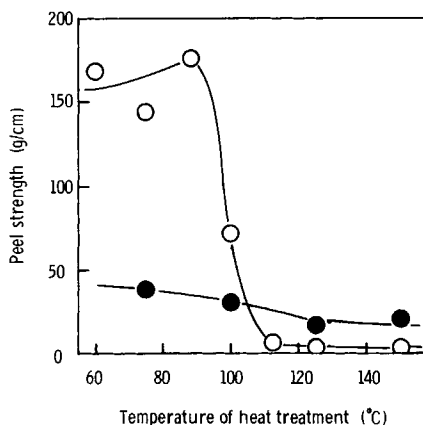


Fig. 5. Variation in peel strength of PEA/PSt (1/1, w/w) composite polymer films from the glass substrate with heat treatment at various temperatures for 10 min: (O) cast from emulsion; (●) recast from benzene solution.

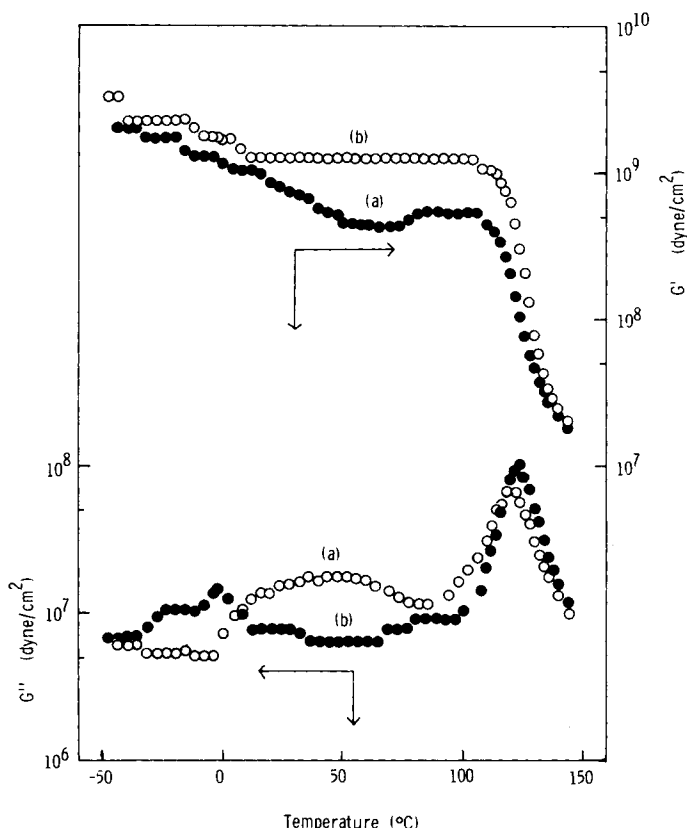


Fig. 6. Variation in storage and loss modulus as a function of temperature for PEA/PSt (1/1, w/w) composite emulsion film before (a) and after (b) heat treatment at 100°C for 10 min.

10 min. In the emulsion film, the tensile strength increased from 20 kg/cm<sup>2</sup> to 140 kg/cm<sup>2</sup> with increasing temperature, especially above 100°C. With the solution film, such a behavior was not observed; the tensile strength varied only between 20 and 60 kg/cm<sup>2</sup> in a range of 30 to 170°C.

Figure 3 shows the variation in tensile strength with treatment time at 100, 125, and 150°C. The tensile strength increased with treatment time and leveled off after about 30 min at each temperature.

Figure 4 shows the variation in optical transmittance in the visible region of emulsion film with heat treatment. The transparent emulsion film, which appeared yellow-red or blue under transmitted or reflected light, respectively, changed to a white, turbid one with heat treatment.

Figure 5 shows the variation in peel strength of the emulsion and solution films with heat treatment. In the case of the emulsion film, the peel strength decreased drastically from about 160 kg/cm<sup>2</sup> to almost zero upon heat treatment at 100°C. With the solution film, such a drastic variation did not occur; the peel strength was low, constant at 20–40 kg/cm<sup>2</sup>, regardless of heat treatment.

Figure 6 shows the storage and loss modulus as a function of temperature for PEA/PSt (1/1, w/w) emulsion film before and after heat treatment.  $G'$  peaks for PEA and PSt homopolymers occurred at -4 and 125°C, respectively, under

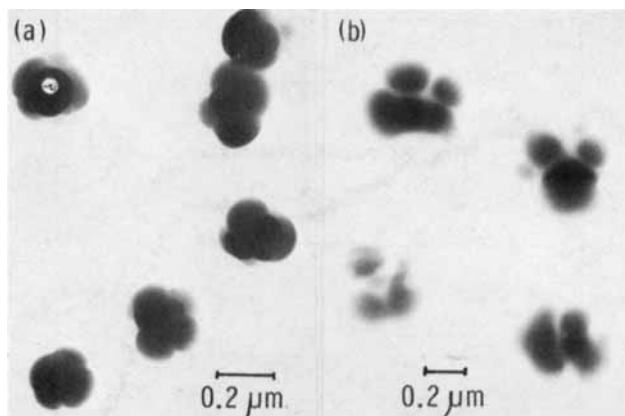


Fig. 7. Electron micrographs of PEA/PSt (1/1, w/w) composite emulsion particles before (a) and after (b) heat treatment at 150°C for 10 min.

the same experimental conditions. Before heat treatment, a very broad  $G''$  peak was observed around 50°C, which indicates the mixing of PSt molecules to the whole PEA phase, and a narrow phase due to PSt domains was observed at 120°C.  $G'$  decreased gradually up to 60°C, and then surprisingly increased over the range of 60 to 105°C. On the other hand, after heat treatment, the broad  $G''$  peak around 50°C observed before heat treatment disappeared and reappeared at -3°C. The PSt transition was shifted to a higher temperature compared to that before treatment, though lower than that for PSt homopolymer.  $G'$  decreased slightly up to 10°C and then was constant over the range of 10 to 105°C in which  $G'$  values were higher than those before treatment.

The distribution of molecular weight of both polymers measured by GPC, using a Waters liquid chromatograph with  $10^2$ ,  $10^3$ ,  $10^4$ , and  $10^5$  Å Styragel columns, was not changed by heat treatment. This suggests that chemical reaction between polymers, e.g., crosslinking, did not occur during heat treatment.

Figure 7 shows the electron micrographs of PEA/PSt (1/1, w/w) composite emulsion particles before and after heat treatment at 150°C for 10 min. Before

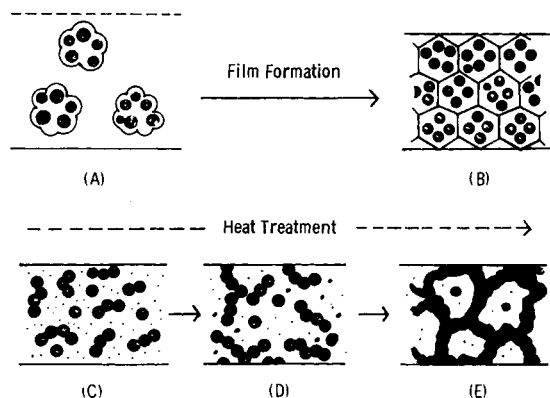


Fig. 8. Model for the phase transition in PEA/PSt composite emulsion film with heat treatment: (○) PEA-rich part; (●) PSt-rich part.

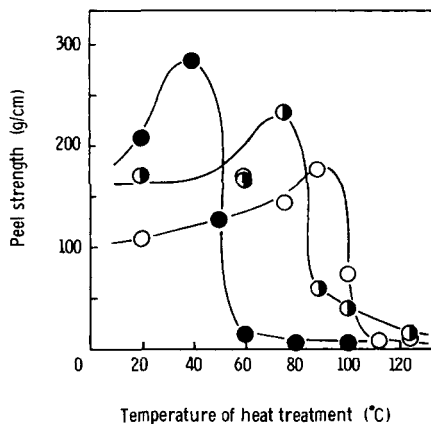


Fig. 9. Variation in peel strength of PEA/PSt and PEA/P(St-BA) composite emulsion films from glass substrate with heat treatment at various temperatures for 10 min. Polymer composition (weight ratio): (O) PEA/PSt = 1/1; (●) PEA/P(St-BA) = 1/(0.83-0.17); (●), PEA/P(St-BA) = 1/(0.67-0.33).

treatment, Figure 7(a), the particles have a "confetti" type anomalous configuration in which PSt molecules form the phase domain in the PEA matrix, as reported in an earlier article.<sup>5</sup> From Figure 7(b), it is apparent that both polymers move and the PSt domains coalesce by heat treatment.

We concluded that the variation in properties of film caused by heat treatment is due to the variation in morphologies in the film (Fig. 8). The specific morphology of PEA/PSt composite particles, Figure 8(A), should be maintained in the film, Figure 8(B). When the film is kept above the glass transition temperatures of both polymers, both polymer molecules can move. Therefore, dispersed PSt domains begin to coalesce, Figures 8(C) and 8(E). Consequently, the phase inversion finally occurs as shown in Figure 8(E). The PSt-rich part forms the continuous phase; the PEA-rich part forms the noncontinuous phase. The PSt content in PEA/PSt composite particles was changed. Figure 9 shows

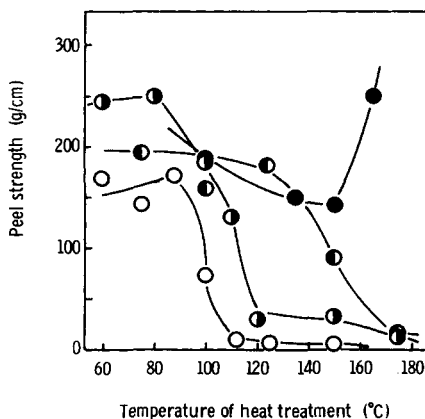


Fig. 10. Variation in peel strength of PEA/PSt composite emulsion films consisting of various polymer compositions from glass substrate with heat treatment at various temperatures for 10 min. PEA/PSt (w/w): (O) 1/1; (●) 1.5/1; (●) 2/1; (●) 3/1.

the variation in peel strength by heat treatment for 10 min. By decreasing the PSt content from 50% w/w to 25% w/w, the "transition" temperature was elevated from ca. 100° to ca. 140°C. Below 25% w/w of PSt content, the existence of the transition temperature was not further observed.

Secondly, the glass transition temperature of polymer consisting of domains in particles was changed by copolymerizing St and BA. Figure 10 shows the variation of peel strength by heat treatment for 10 min. With increasing BA content in St-BA copolymer from zero to 33% w/w, the transition temperature was dropped from ca. 100° to ca. 50°C.

These results suggest not only that the model shown in Figure 8 gives a possible explanation for the variation in properties of PEA/PSt composite emulsion film with heat treatment, but also that the "temperature-sensitive" property can be controlled.

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