

# The Characteristic Properties of Poly(methyl methacrylate)/Polystyrene Core-Shell Composite Polymer Latex

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**ABSTRACT:** In this study, the poly(methyl methacrylate)/polystyrene (PMMA/PS) core-shell composite latex was synthesized by the method of soapless seeded emulsion polymerization. The morphology of the PMMA/PS composite latex was core-shell structure, with PMMA as the core and PS as the shell. The core-shell morphology of the composite polymer latex was found to be thermally unstable. Under the effect of thermal annealing, the PS shell region first dispersed into the PMMA core region, and later separated out to the outside of the PMMA core region. This was explained on the basis of lowering interfacial tension between the PMMA and PS phases owing to the interpenetration layer. The interpenetration layer, which was located at the interface of the core and shell region, contained graft copolymer and entangled polymer chains. Both the graft copolymer and entangled polymer chains had the ability to lower the interfacial tension between the PMMA and PS phases. Also, the effect of thermal annealing on the morphology of commercial polymer/composite latex polymer blends was examined. The result showed that the core-shell composite

latex had the ability to enhance the compatibility of the components of polymer blends. The compatibilizing ability of the core-shell composite latex was better than that of a random copolymer. Moreover, the effect of the amount of core-shell composite latex on the morphology of the polymer blend was investigated. The polymer blends, which contained composite latex above 50% wt, showed the morphology of a double sea-island structure. In addition, the composite latex was completely dissolved in solvent to destroy the core-shell structure and release the entangled polymer chains, and then dried to form the entangled free composite polymer. The entangled free composite polymer had the ability to enhance the compatibility of the components of the polymer blend as usual. The weight ratio 3/7 commercial polymer/entangled free composite polymer blend showed the morphology of the phase inversion structure. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 312–321, 2003

**Key words:** core-shell polymers; compatibility; morphology; thermal properties; blends

## INTRODUCTION

Polymer blend systems play an important role in the plastic industry because they could be tuned to have a better combination of physical properties than the homopolymers. But the major problem of the polymer blends was the poor stability of the quality. This was due to the fact that the interfacial tension between the components of the polymer blends was large. After thermal annealing, the phase domains of the polymer blends would increase to decrease the interfacial area. The process temperature and process time would influence the morphology and mechanical properties of the polymer blends. Adding the compatibilizing agent into the polymer blends has mitigated the problems. Chen et al.<sup>1</sup> pointed out that the compatibilizing agents would lower the interfacial tension of the polymer blends and prevent phase growth or coalescence. Also, they pointed out that the ability of the compatibilizing agents to locate themselves at the polymer-polymer interface seems to be the important factor in determining how well they perform. Shay et al.<sup>2</sup> con-

sidered that the mechanical properties of the polymer blends would be influenced by the polymeric composition and the processing history employed during formation of those components. They reported a nonlinear, thermoviscoelastic constitutive equation for amorphous polymers to predict the mechanical properties of poly(vinyl acetate). The model predicted that the samples that were cooled below  $T_g$  and then isothermally annealed for specified times would exhibit yield stresses, and the yield stresses would increase with increasing the annealing time.

Much literature<sup>3–9</sup> reported that using the extruders or kneaders could make the polymer blends. The morphology of the polymer blends coarsens as soon as the blends leave the extruder. This was due to the fact that the fine phase structures produced by extrusion have large interfacial areas, and the interfacial tension was so large that it would make the morphology of the polymer blend unstable. When the polymer blend was annealed, the morphology structure would become coarse to lower the interfacial tension, and this made the structure stable. In 1995, Andradi et al.<sup>6</sup> investigated the morphology of the PMMA and PS polymer blends produced by extrusion. They pointed out that annealing after extrusion led to structure coarsening

and the morphology structure was changed until the structure was stable. Also, there were scholars who investigated the methods to strengthen the interfaces of the polymer blends. They added a random copolymer<sup>10–12</sup> or chemically grafted copolymer,<sup>13</sup> or a block copolymer<sup>14–18</sup> to the interface of the polymer blends. The results showed that the fracture toughness of the strengthened interface was larger than that of the original interface. Moreover, Creton et al.<sup>19</sup> pointed out that the small domains of the polymer blend could remain in higher stress than those of larger domains in the same polymer blend, so that the polymer blends with the small domains had a higher fracture toughness than the polymer blends with the large domains size. To decrease the domain size of the polymer blends, the block copolymers could be added to the polymer–polymer interface of the polymer blends.

In recent years, seeded emulsion polymerization was often used to synthesize core-shell composite polymer latex.<sup>20–22</sup> The core-shell composite polymer latex may include reinforced elastomers, high-impact plastics, toughened plastics, etc. Many studies had focused on the kinetics of polymerization and the morphology of composite polymer latex.<sup>20–24</sup> To extend the applicability of composite polymer latex, many articles<sup>25–30</sup> studied the synthesis of composite polymer latex or latex IPN to improve the degree of compatibility between the two polymer phases of the composite polymer latex. Our previous works studied the properties of the core-shell PBA/PS composite particles<sup>31</sup> and core-shell PMMA/PS composite particles.<sup>32</sup> Under the influence of thermal annealing, the morphology of the composite particle showed the interpenetration structure. The PMMA/PS composite particles blend with the commercial PMMA and commercial PS to form the commercial polymer/composite latex polymer blends. The morphology of the polymer blend, which consisted of 30% wt PMMA/PS composite particles, was stable under the influence of thermal annealing.<sup>32</sup> In this present work, the effect of the amount of PMMA/PS composite particles on the stability of the morphology of commercial polymer/composite latex polymer blend was studied. We also compared the compatibilizing ability of the core-shell composite latex with that of the random copolymer. Moreover, the effect of PMMA–PS grafted copolymer, which consists of the PMMA/PS composite particle, on the morphology of the polymer blend, was also investigated.

## EXPERIMENTAL

### Material

Methyl methacrylate (MMA) and styrene (st) were distilled under a nitrogen atmosphere and reduced pressure prior to polymerization. Water was redi-

**TABLE I**  
Ingredients and Conditions for the Synthesis of PMMA Seed Latex and the PMMA/PS Composite Polymeric Particles

	PMMA seed latex (first-stage reaction)	PMMA/PS composite particle (second-stage reaction)
Methyl methacrylate (g)	120	
Styrene (g)		98.36
Seed latex emulsion (g)		500
Initiator (K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ) (g)	0.866	0.5
Deionized water (g)	1100	310
Reaction time (hour)	1	2
Conversion (%)	99.6	99.5

(N<sub>2</sub>; 80°C; stirring rate, 300 rpm)

tilled and deionized. Other chemicals were analytical grade and used without further purification. The commercial grades of PS and PMMA were used directly. The weight average molecular weight of commercial PMMA and commercial PS was 429,000 and 425,000, respectively. The weight average molecular weight of the polymer was measured by gel permeation chromatography (GPC) (Shodex RI-71).

### Polymerization

Synthesis of PMMA/PS core-shell composite polymer latex

The core(PMMA)-shell(PS) composite polymer particles were synthesized by the method of soapless seeded emulsion polymerization. The ingredients and reaction conditions were shown as Table I. In the first stage of reaction, methyl methacrylate was used to synthesize PMMA seed latex. In the second stage of reaction, styrene monomer was poured into the PMMA seed latex emulsion and stirred to proceed the swelling process. After PMMA seed latex swelled the styrene for 24 h at room temperature, the aqueous solution of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was poured into the reaction mass to begin the second-stage reaction. The detail process of the soapless seeded emulsion polymerization was mentioned in our previous work.<sup>20,22</sup> After the second stage reaction, the PMMA/PS core-shell composite polymer latex was obtained; the weight ratio of PMMA/PS was 1/2. The weight-average molecular weight of PMMA seeds and PMMA/PS composite polymer latex were 423,500 and 426,900, respectively. The molecular weight of the polymer was measured by GPC (Shodex RI-71)

Synthesis of the PMMA–PS random copolymer

The PMMA–PS random copolymer (weight ratio of PMMA/PS is 1/2) was synthesized by the method of

**TABLE II**  
**Ingredients and Conditions for the Synthesis**  
**of PMMA-PS Copolymer**

Methyl methacrylate (g)	60
Styrene (g)	120
Deionized water (g)	1500
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (g)	1.3
Temperature (°C)	80
Stirring rate (rpm)	300

soapless emulsion copolymerization; the ingredients and reaction conditions are shown in Table II.

#### Differential scanning calorimetry (DSC) analysis

The PMMA/PS core-shell composite polymer latex was dissolved in tetrahydrofuran (THF) for various periods of time to form the polymer solution. Then the composite polymer solution was dried completely by vacuum oven at 50°C for 1 week to form the dry composite polymer. The glass transition temperature ( $T_g$ ) of the dry composite polymers was measured by differential scanning calorimetry (Du Pont 2200 series) with the heating rate of 10°C/min.

#### Preparation of the polymer blends

Commercial polymer/core-shell composite latex polymer blend

The PMMA/PS core-shell composite polymer latex and the commercial PMMA and commercial PS were blended in a twin-screw extruder. The blending was performed at 210–245°C, employing a twin-screw speed of 40 rpm. The composition and symbols of the polymer blends were shown as Table III.

#### Commercial polymer/entangled free composite polymer blend

The core-shell composite polymer latex (1 g) was dissolved in tetrahydrofuran (THF) (50 g) by the method of stirring. After stirring for 72 h, the composite latex was dissolved in THF completely, and the core-shell structure was destroyed by THF; then the entangled PMMA, PS polymer chains contained in the composite polymer latex was released. Afterwards, the solvent

was removed completely under vacuum to give a dry entangled free composite polymer. The dry entangled free composite polymer was thus blended with the commercial PS and commercial PMMA to form the commercial polymer/entangled free composite polymer blend. The blending was performed at 210–245°C, employing a twin-screw speed of 40 rpm.

#### Commercial polymer/random copolymer blend

The PMMA-PS random copolymer (weight ratio of PMMA/PS = 1/2) and commercial PMMA, commercial PS (weight ratio of commercial PMMA/commercial PS = 1/2) were blended in a twin-screw extruder, employing a blending temperature of 210–245°C, and twin-screw speed of 40 rpm.

#### Observation of ultrathin cross-sections of composite polymer particles

The samples were microtomed to form the sections about 900 Å thick. The ultrathin cross-sections were stained with RuO<sub>4</sub> vapor at room temperature for 2 min in the presence of 1% RuO<sub>4</sub> solution. The RuO<sub>4</sub> can stain the PS phase, but cannot stain the PMMA phase. The stained ultrathin cross-sections were observed using the transmission electron microscope (TEM) (JEOL-JEM1200EX). Under the observation of TEM, the PS phase shows the dark image, and the PMMA phase shows the bright image.

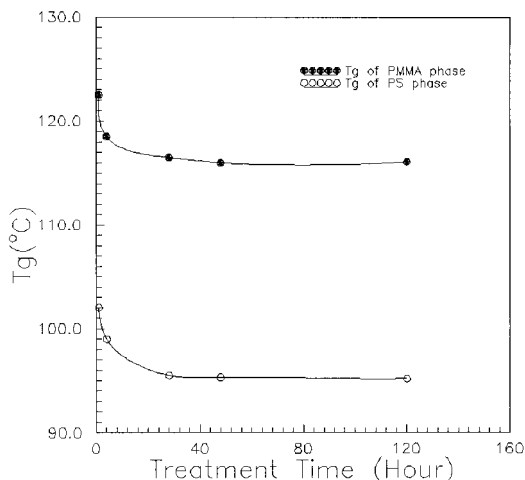
## RESULTS AND DISCUSSION

#### Effect of solvent on the $T_g$ of core-shell composite latex

The morphology of the PMMA/PS composite polymer latex synthesized by the method of soapless seeded emulsion polymerization was a core-shell structure, as shown in Figure 3(a). The inner bright region was a PMMA core and the outer dark region was a PS shell. The core-shell morphology had been pointed out and explained in our previous studies.<sup>21–33</sup> The PMMA/PS core-shell composite polymer latexes were dissolved in THF to destroy the core-shell structure, and formed the PMMA/PS polymer solution, and then the polymer solution was dried to form

**TABLE III**  
**Symbols and Compositions of the Commercial Polymer/Core-Shell Composite Latex Polymer Blends**

Symbol	Weight of commercial polymer (g)	Weight of core-shell composite latex (g)	Weight ratio of commercial polymer/core-shell composite latex
CL91	270	30	9/1
CL64	180	120	6/4
CL55	150	150	5/5
CL37	90	210	3/7



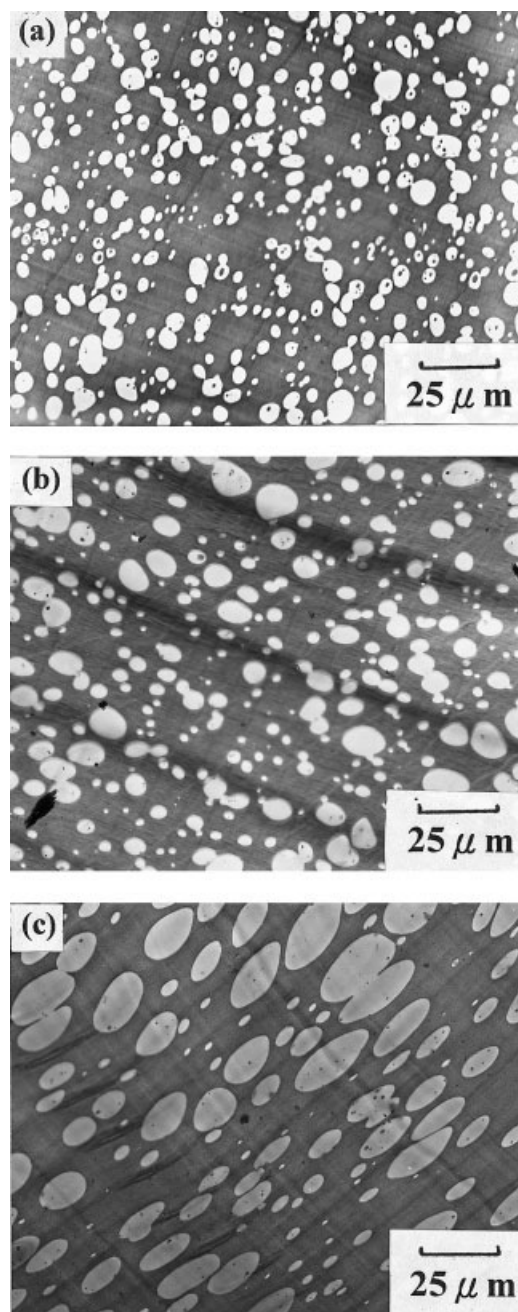
**Figure 1** Glass transition temperature of the PMMA/PS composite polymer as a function of treatment time for the PMMA/PS composite polymer latex dissolved in THF.

the PMMA/PS composite polymer. DSC measured the  $T_g$  of the PMMA/PS composite polymers; the results are shown as Figure 1. Increasing the treatment time for the PMMA/PS composite latexes dissolved in THF might decrease the  $T_g$  of the PMMA/PS composite polymer. This indicated that the solvent destroyed the interfacial interaction such as physical entanglements, which were located at the interface of the PMMA core and the PS shell of the composite polymer latex, to increase the free volume of the polymer chains and lower the  $T_g$  of the composite polymer. The morphology of the PMMA/PS composite polymer did not show the core-shell structure, but showed the PMMA phase dispersed in the PS continuous phase. The composite polymer latex dissolved in THF for a longer time might produce the larger domain size of the PMMA dispersed phase, as shown in Figure 2. This showed that THF destroyed the entangled PMMA, PS polymer chains so as to lower the compatibility between the PMMA phase and the PS phase, and increased the domain size of the PMMA dispersed phase. Moreover, in our previous work,<sup>34</sup> the PMMA/PS composite latex was analyzed by using thin-layer chromatographic (TLC) analysis. The result showed that there was PMMA-*graft*-PS copolymer in the composite latex. From the results of this work and the previous work, we suggested that both PMMA-*graft*-PS copolymer and entangled PMMA, PS polymer chains, which were in the composite latexes, had the ability to improve the compatibility of the PMMA phase and the PS phase.

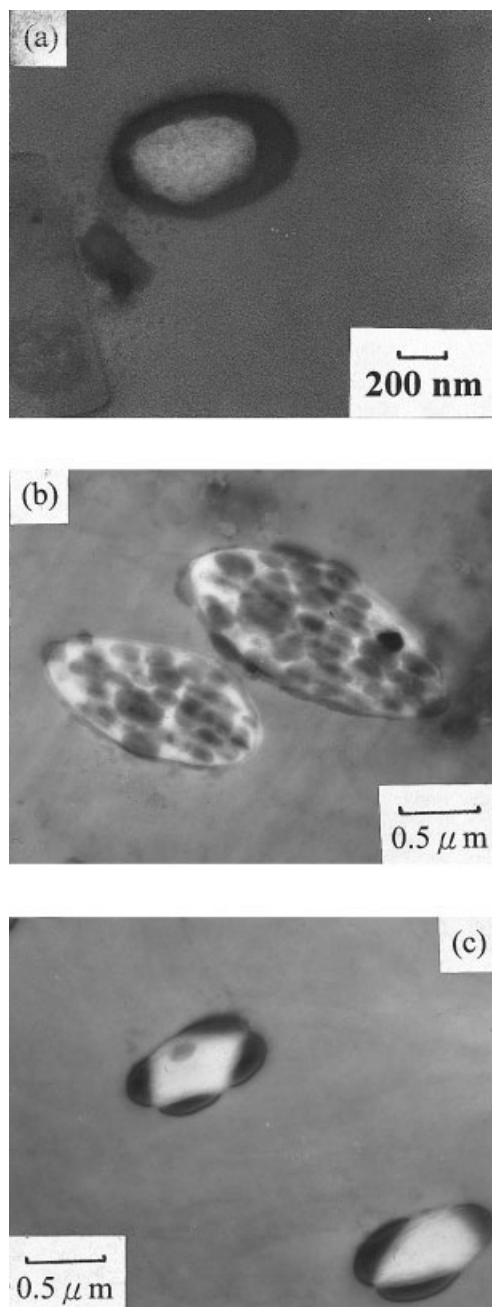
#### Effect of thermal annealing on the morphology of core-shell composite polymer latex

The morphology of the core-shell composite polymer latex was found to be unstable toward thermal anneal-

ing. With the increase of thermal annealing time, the PS shell region was destroyed and dispersed into the PMMA core region in the beginning, as shown in Figure 3(b), and subsequently separated out to the outside of the PMMA core region as shown as Figure 3(c). The core-shell morphology was finally destroyed. The above results seem to show that the compatibility between the PMMA phase and PS phase of the composite polymer latex was so good as to show the morphology of PS dispersed into the PMMA phase, as shown in Figure 3(b). With the increase of thermal



**Figure 2** The morphology of PMMA/PS composite polymer obtained from dissolving PMMA/PS composite latex in THF for (a) 30 min, (b) 60 min, (c) 90 min.



**Figure 3** The morphology of individual PMMA/PS core-shell composite latex under the influence of thermal annealing for (a) 0 min, (b) 30 min, (c) 150 min (bright zone is PMMA, dark zone is PS).

annealing time, the entangled PMMA, PS polymer chains relaxed gradually, and resulted in the PMMA, PS phase-separated structure, as shown in Figure 3(c).

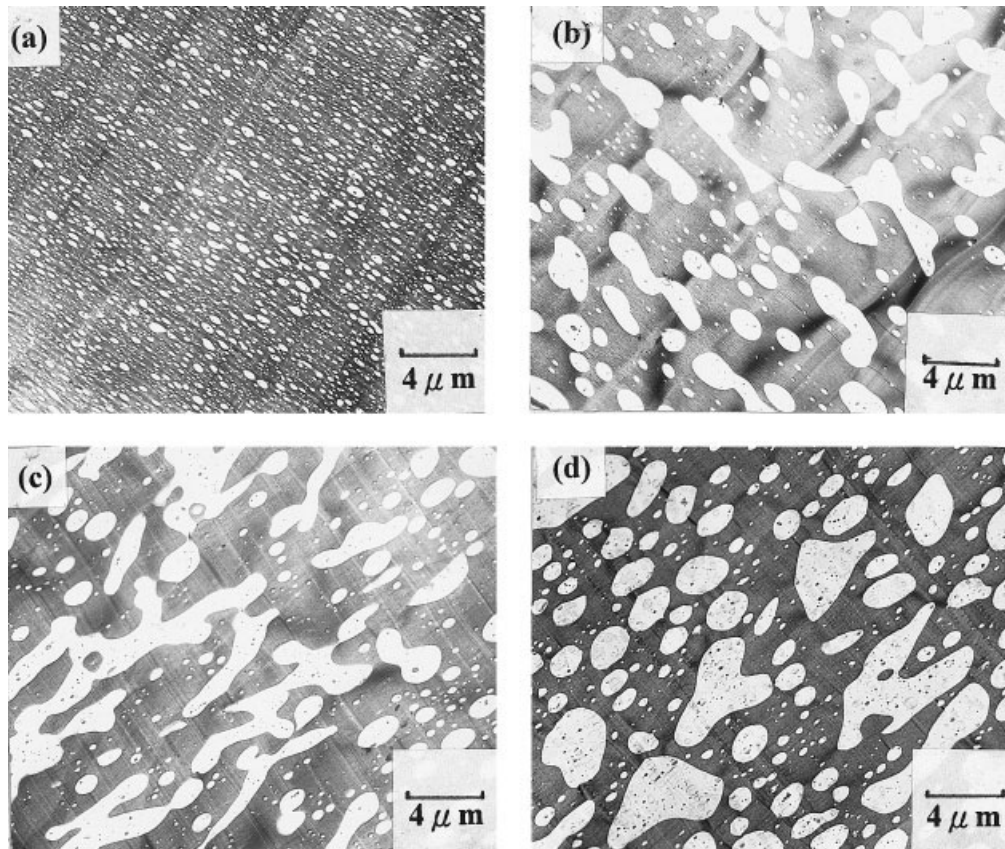
#### **Effect of thermal annealing on the morphology of commercial polymer/core-shell composite latex polymer blends**

Figures 4–7 show the TEM photographs of the polymer blends CL91, CL64, CL55, and CL37, respectively,

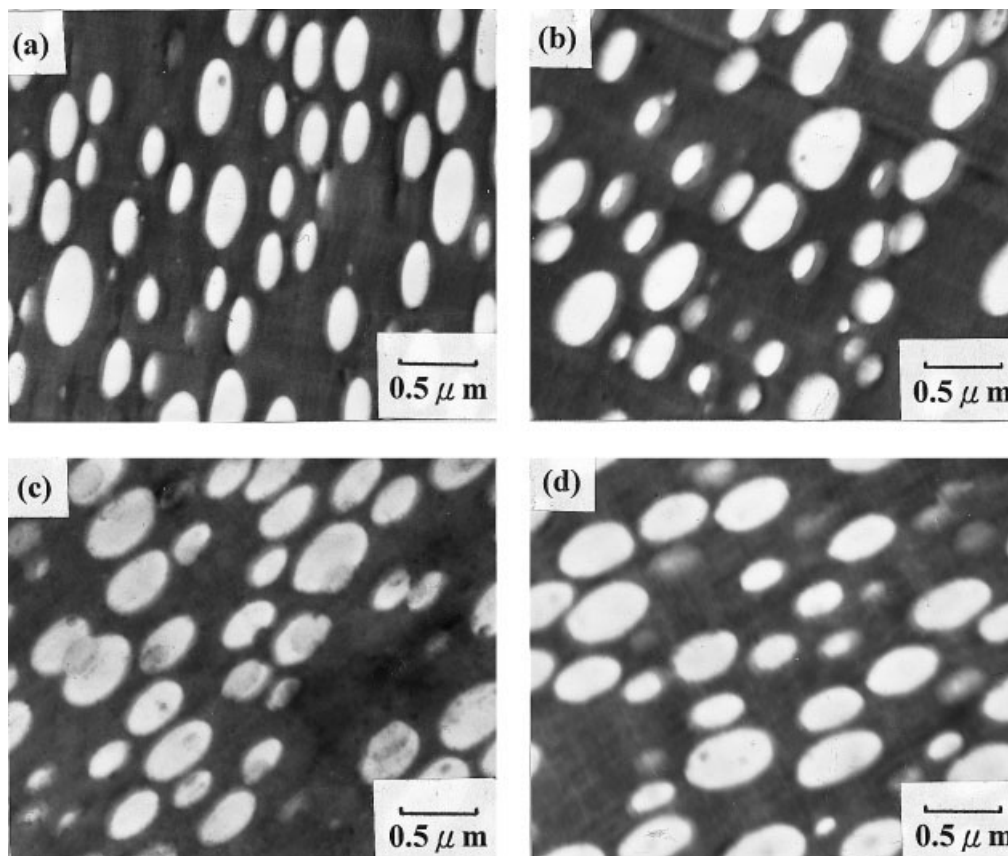
subjected to thermal annealing. The morphology of CL91, which consisted of 10% wt of the core-shell composite latex, showed that the PMMA phase dispersed in the PS continuous phase, with the increase of annealing time, might increase the domain size of PMMA phase. Although the PMMA-*graft*-PS copolymer and entangled polymer chains, which consisted of composite latexes, had the ability to improve the compatibility of the PMMA and PS phases, but the C91 polymer blend consisted of only 10% wt of the composite latex, which was not enough to lower the interfacial tension between the PMMA and the PS phases. The influence of thermal annealing increased the domain size of the PMMA phase, to reduce the interfacial area and reduce the interfacial tension between the PMMA and the PS phases. However, the CL64 polymer blend, which consisted of 40% wt of core-shell composite latex, had stable morphology; the diameter of the PMMA domains of CL64 was stable under the effect of thermal annealing, as shown in Figure 5. The reason for this was due to the fact that the sufficient core-shell composite latex, which were in CL64 polymer blend, lowered the interfacial tension between the PMMA and the PS phases effectively. Moreover, the compatibility of the components of CL55 was so good as to form the morphology of a double sea-island structure, as shown in Figure 6. The double sea-island structure of CL37 was more pronounced than that of CL55, as shown in Figure 7. With the increase of the amount of composite polymer latex it might decrease the domain size of the PMMA dispersed phase of the polymer blend, as shown in Table IV. This result was due to the fact that both the PMMA-*graft*-PS copolymer and the entangled PMMA, PS polymer chains, which were in the core-shell composite latex, were able to lower the interfacial tension of PMMA and PS phases, and lower the domain size of the dispersed phase of the polymer blend.

#### **Effect of thermal annealing on the morphology of commercial polymer/entangled free composite polymer blends**

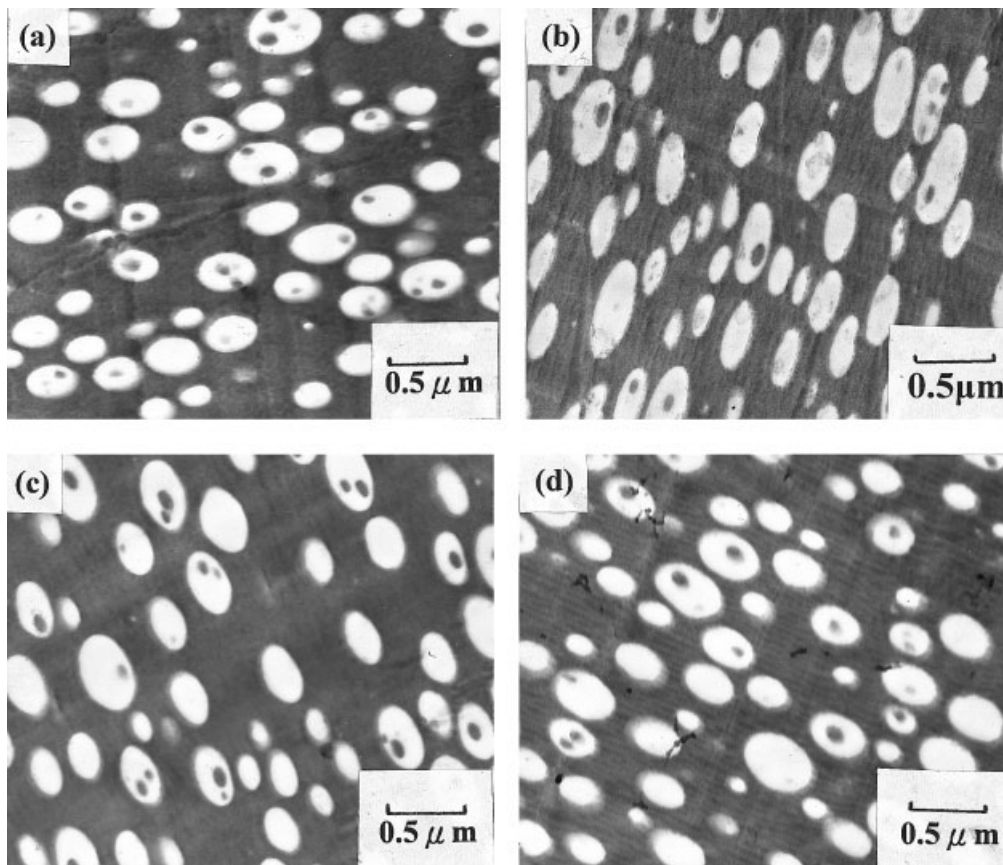
To investigate the effect of entangled free composite polymers on the compatibility of the components of polymer blends, the PMMA/PS core-shell composite latex was dissolved by THF to destroy the core-shell structure and release the entangled PMMA, PS polymer chains, and then the polymer solution was dried to form the entangled free composite polymer. The effect of thermal annealing on the commercial polymer/entangled free composite polymer blends was examined. Figure 8 shows the TEM photographs of weight ratio 6/4 commercial polymer/entangled free composite polymer blends (weight ratio of PMMA/PS is 1/2) subjected to thermal annealing. The polymer blends showed the morphology of the PMMA phase



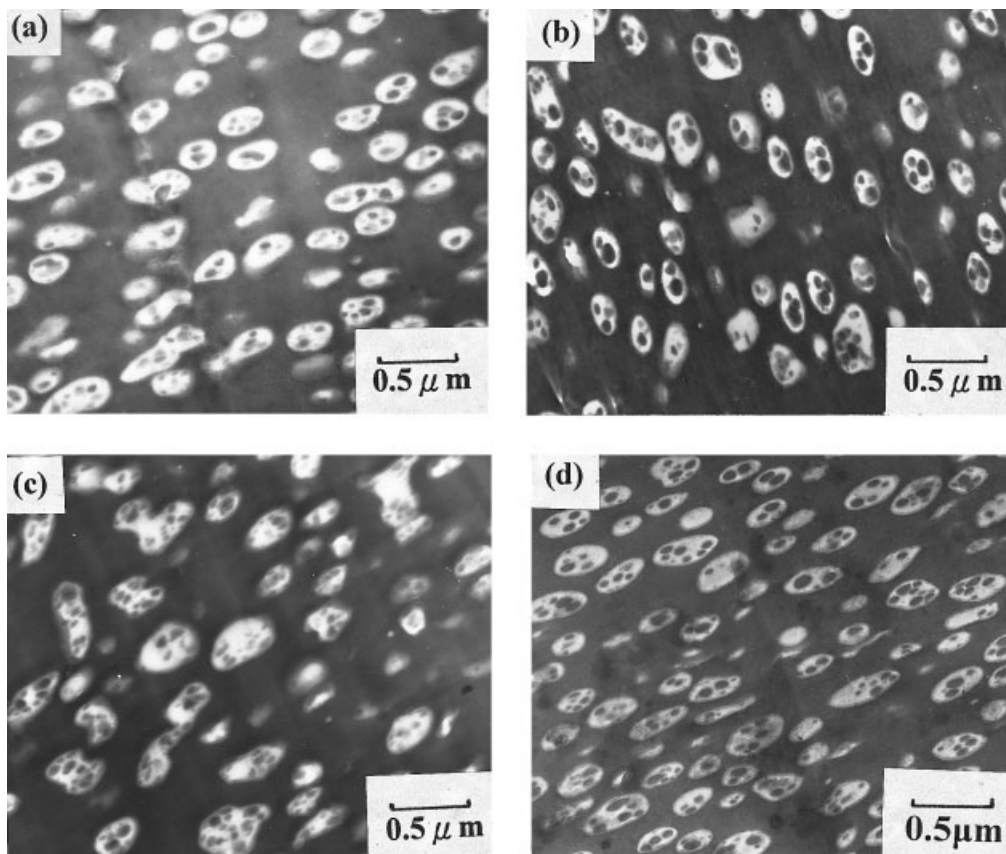
**Figure 4** The morphology of commercial polymer/core-shell composite latex blend under the influence of thermal annealing for (a) 0 min, (b) 30 min, (c) 120 min, (d) 180 min (weight ratio of commercial polymer/core-shell composite latex = 9/1).



**Figure 5** The morphology of commercial polymer/core-shell composite latex blend under the influence of thermal annealing for (a) 0 min, (b) 30 min, (c) 120 min, (d) 150 min (weight ratio of commercial polymer/core-shell composite latex = 6/4).



**Figure 6** The morphology of commercial polymer/core-shell composite latex blend under the influence of thermal annealing for (a) 0 min, (b) 60 min, (c) 90 min, (d) 150 min (weight ratio of commercial polymer/core-shell composite latex = 5/5).



**Figure 7** The morphology of commercial polymer/core-shell composite latex blend under the influence of thermal annealing for (a) 0 min, (b) 60 min, (c) 110 min, (d) 150 min (weight ratio of commercial polymer/core-shell composite latex = 3/7).

TABLE IV  
Effect of Thermal Annealing on the Domain size of PMMA Dispersed Phase of Polymer Blends

Polymer blend	Annealing time (min)	Average domain size of PMMA dispersed phase (nm <sup>2</sup> )
Commercial polymer/core-shell composite latex = 6/4	0	$6.65 \times 10^4$
	30	$6.71 \times 10^4$
	120	$6.70 \times 10^4$
	150	$6.68 \times 10^4$
Commercial polymer/core-shell composite latex = 5/5	0	$5.49 \times 10^4$
	60	$5.52 \times 10^4$
	90	$5.50 \times 10^4$
	150	$5.56 \times 10^4$
Commercial polymer/core-shell composite latex = 3/7	0	$4.48 \times 10^4$
	60	$4.51 \times 10^4$
	110	$4.50 \times 10^4$
	150	$4.52 \times 10^4$
Commercial polymer/entanglement free composite polymer = 6/4	0	$9.18 \times 10^5$
	90	$8.92 \times 10^5$
	120	$9.21 \times 10^5$
	150	$9.36 \times 10^5$
Commercial polymer/random Copolymer = 6/4	0	$2.62 \times 10^6$
	30	$2.78 \times 10^6$
	90	$2.52 \times 10^6$
	150	$2.86 \times 10^6$

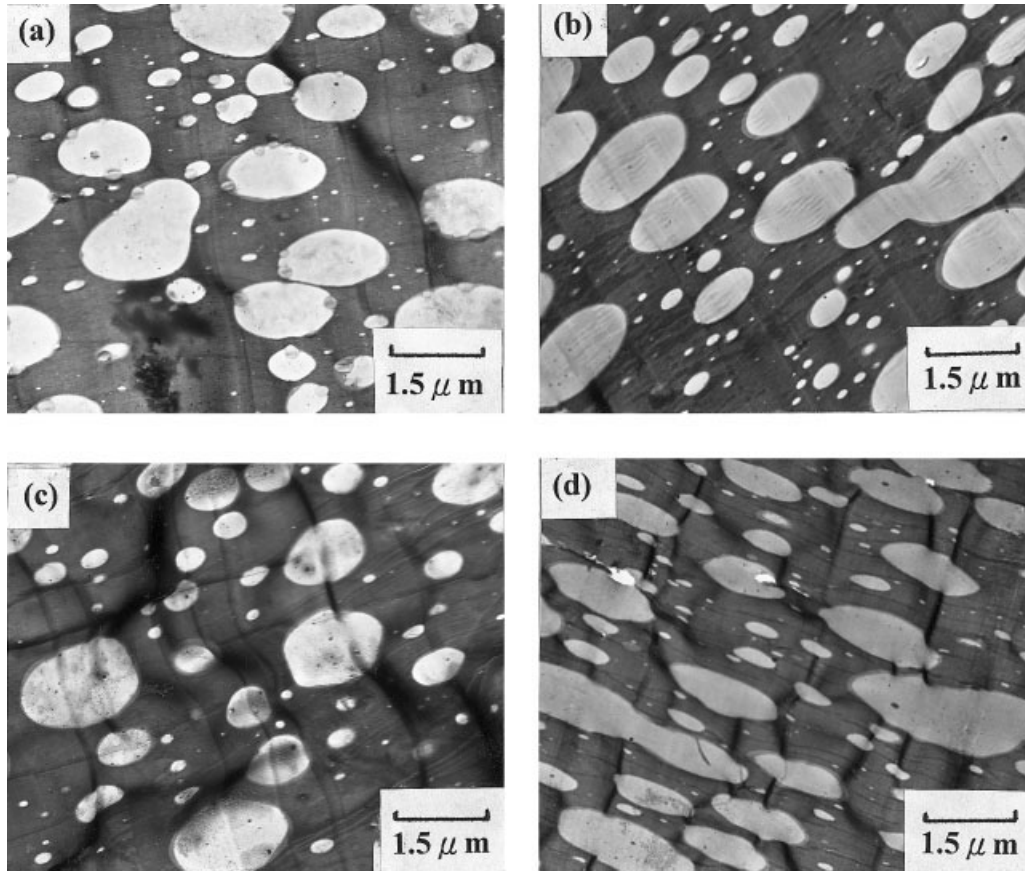
dispersed in the PS continuous phase. The domain size of the PMMA dispersed phase was stable under the influence of thermal annealing. The results showed that even if the entangled PMMA, PS polymer chains were released by THF, the PMMA-*graft*-PS copolymer were in the entangled free composite polymer to lower the interfacial tension between the PMMA phase and the PS phase of the polymer blends, and retain the domain size of the PMMA dispersed phase under the influence of thermal annealing. Although the random copolymer had the ability to stabilize the domain size of the PMMA dispersed phase, as shown in Figure 9, the compatibilizing ability of the entangled free composite polymer was better than that of the random copolymer, so the PMMA dispersed phase of the commercial polymer/entanglement free composite polymer blend was smaller than that of the commercial polymer/random copolymer blend, as shown in Table IV. On the other hand, the PMMA dispersed phase of the commercial polymer/core-shell composite latex polymer blend was smaller than that of the commercial polymer/entanglement free composite polymer blend, as shown in Table IV. The reason was due to the fact that the entangled PMMA, PS polymer chains were contained in the core-shell composite latex, but was not contained in the entangled free composite polymer, so the compatibilizing ability of the former was better than that of the latter. Increasing the amount of entangled free composite polymer to a weight ratio of 3/7 commercial polymer/entanglement free composite polymer, the polymer blend showed the phase inversion morphology, as shown in Figure 10. PS formed the disperse phase while PMMA

formed the continuous phase, even if the amount of the PS phase was larger than that of the PMMA phase. The reason may be due to the fact that the PMMA-*graft*-PS copolymer lowered the surface tension of the PMMA phase and was more significant than to lower the surface tension of PS phase. Consequently, an increase of the amount of PMMA-*graft*-PS copolymer might decrease the surface tension of the PMMA phase significantly. Once the surface tension of the PMMA phase was lower than that of the PS phase, the PMMA easily formed the continuous phase, and the PS easily formed the dispersed phase.

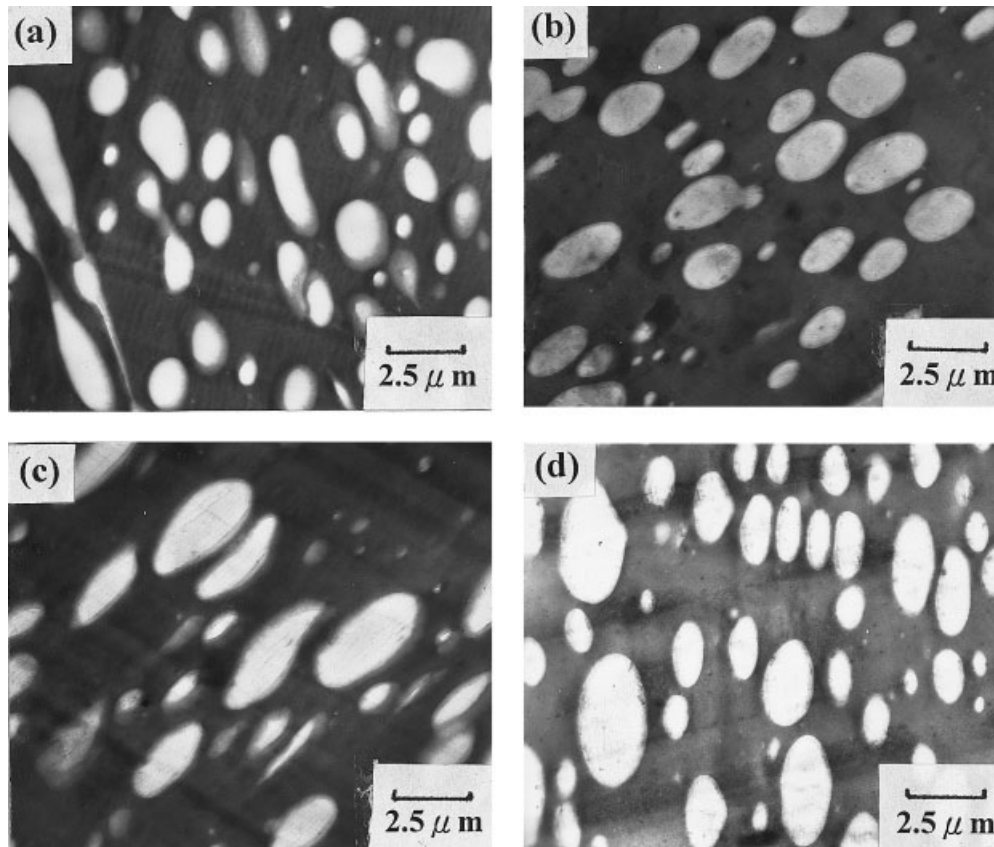
## CONCLUSION

The core-shell PMMA/PS composite latex, which was synthesized by the method of soapless seeded emulsion polymerization, was thermally unstable; the morphology of the core-shell structure was destroyed by the effect of thermal annealing. The core-shell PMMA/PS composite polymer latex had the ability to lower the interfacial tension between the PMMA phase and the PS phases of the polymer blend. Thus, under the effect of thermal annealing, the domain size of the PMMA dispersed phase of the commercial polymer/composite latex polymer blend could be retained as constant. Furthermore, the entangled free composite polymer, which only consisted of the PMMA-*graft*-PS copolymer, was capable of lowering the surface tension of the PMMA and the PS phases as usual. The compatibilizing ability of the PMMA/PS entangled free composite polymer was better than that of the PMMA-PS random copolymer. Morphology of the

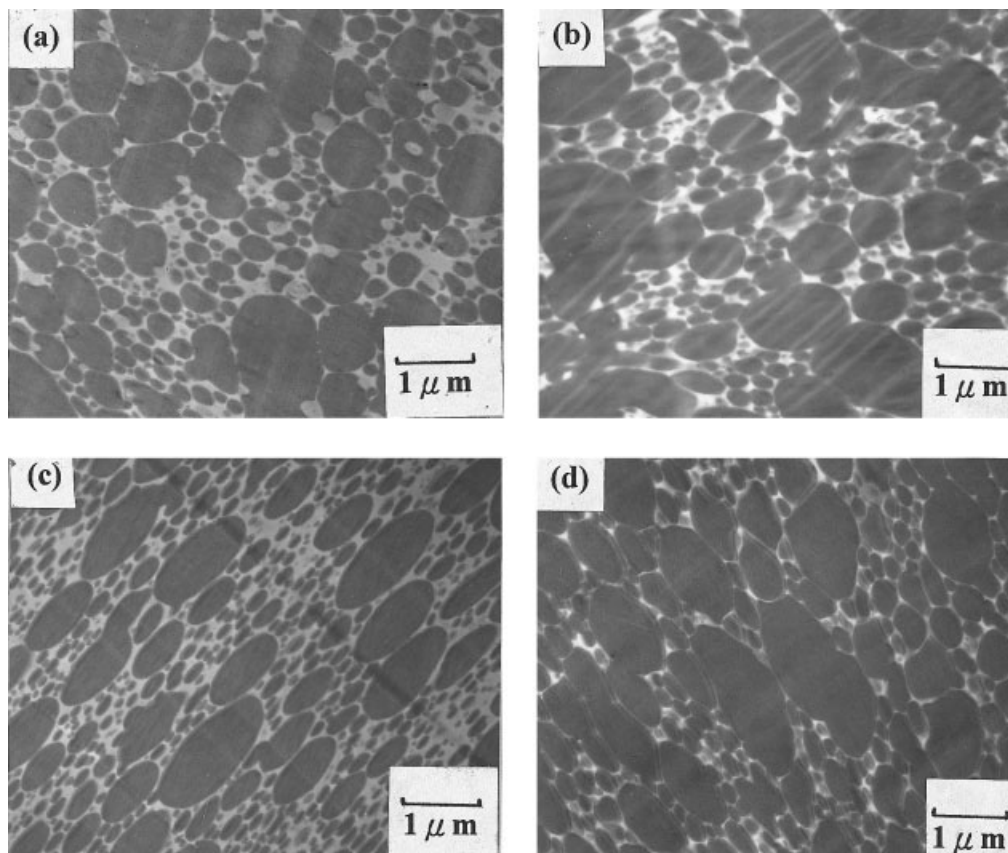




**Figure 8** The morphology of commercial polymer/entangled free composite polymer blend under the influence of thermal annealing for (a) 0 min, (b) 90 min, (c) 120 min, (d) 150 min (weight ratio of commercial polymer/entangled free composite polymer = 6/4).



**Figure 9** The morphology of commercial polymer/random copolymer blend under the influence of thermal annealing for (a) 15 min, (b) 30 min, (c) 60 min, (d) 180 min (weight ratio of commercial polymer/random copolymer blend = 7/3).



**Figure 10** The morphology of commercial polymer/entangled free composite polymer blend under the influence of thermal annealing for (a) 0 min, (b) 30 min, (c) 90 min, (d) 150 min (weight ratio of commercial polymer/entangled free composite polymer = 3/7).

polymer blend, which contained a large amount of entangled free composite polymer, showed the phases inversion structure.

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