

# The properties of core–shell composite polymer latex. Effect of heating on the morphology and physical properties of PMMA/PS core–shell composite latex and the polymer blends

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## Abstract

In this study, the poly(methyl methacrylate)/polystyrene (PMMA/PS) composite polymer latex were synthesized by the method of soapless seeded emulsion polymerization. The morphology of the PMMA/PS composite polymer latex was core–shell structure with PMMA core and PS shell. There was an interpenetration layer between the PMMA core and PS shell. The interpenetration layer contained the PMMA/PS graft copolymer and physical interpenetration of PMMA and PS polymer chains.

We found that the behavior of the interpenetration layer was the same as compatibilizer that would increase the degree of compatibility of polymer blend. In this investigation, three kinds of PMMA/PS polymer blends were prepared. The one was commercial PMMA and commercial PS polymer blend, weight fraction of PMMA/PS = 1/2 (polymer blend (A)). Another one was PMMA/PS core–shell composite polymer latex with PMMA core and PS shell, weight fraction of PMMA/PS = 1/2 (polymer blend (B)). The other one was commercial PMMA, PS and PMMA/PS core–shell composite latex blending (polymer blend (C)), i.e. polymer blend (B) blending with commercial PMMA and PS. The weight fraction of PMMA/PS of polymer blend (C) was 1/2, the weight percent of the commercial PMMA and PS was 70% and the core–shell composite latex was 30%.

The morphology of polymer blend (A) was unstable. The effect of thermal annealing on the morphology of polymer blend (A) showed the phase separation structure. The thermal annealing would influence the tensile strength, Young's Modulus and viscosity properties of the polymer blend (A).

The compatibility of the components of polymer blend (B) was very well. With increasing the thermal annealing time, the morphology of the polymer blend (B) appeared the interpenetration structure first, and then appeared the co-continuous structure.

The morphology of polymer blend (C) was very stable. The effect of thermal annealing on the tensile strength, Young's Modulus and viscosity properties of the polymer blend (C) were insignificant. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Core–shell composite latex; Polymer blend; Thermal annealing

## 1. 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 homo-polymers. Nevertheless, the major problem of the polymer blends was the poor stability of the quality. It 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 in order 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. [1] pointed out that the compatibilizing agents

would lower the interfacial tension of the polymer blends and prevent phase growth or coalescence. Besides, they also 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. [2] considered 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 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.

Table 1  
Ingredients and conditions for the synthesis of seed latex (first stage)

Methyl methacrylate (g)	120
Initiator ( $K_2S_2O_8$ ) (g)	0.866
Deionized water (g)	1100
Temperature ( $^{\circ}C$ )	70
Stirring rate (rpm)	300
Reaction method	Batch

Many literatures [3–9] 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. It was due to the fact that the fine phase structures produced by extrusion have large interfacial areas, and the interfacial tension was large that would make the morphology of the polymer blend unstable. When the polymer blends was annealed, the morphology structure would become coarse, in order to lower the interfacial tension and made the structure stable. In 1995, Andradi et al. investigated the morphology of the PMMA and PS polymer blends produced by extrusion. They pointed out that annealing after extrusion led to structure coarsening, the morphology structure was changed until the structure was stable. Sometimes, matrix inversion was observed.

Besides, there were scholars who investigated methods to strengthen the interfaces of the polymer blends. They added a random copolymer [10–12] or chemically grafting copolymer [13], or a block copolymer [14–18] 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. [19] pointed out that the small domains of the polymer blend could remain in high stress than those of larger domains in the same polymer blend. Thus the polymer blends with the small domains had the higher fracture toughness than the polymer blends with the large domains size. In order to decrease the domain size of the polymer blends, the block copolymers could be added to the polymer–polymer interface of the polymer blends. Xu et al. [20] studied the segregation of a block copolymer of poly( $d_8$ -styrene-*b*-2-vinylpyridine)(dPS-PVP) at the interface between polystyrene and a random copolymer of poly(styrene-*ran*-4-hydroxystyrene) (PS-*r*-PPHS). They showed that the hydrogen bonding between PVP and PPHS polymer chains

Table 2  
Ingredients and conditions for the synthesis of composite latex in seeded polymerization (second stage)

Seed latex emulsion (g)	500
Styrene (g)	98.36
Initiator ( $K_2S_2O_8$ ) (g)	0.5
Deionized water (g)	310
Temperature ( $^{\circ}C$ )	70
Stirring rate (rpm)	300
Reaction method	Batch

could increase the segregation of a dPS-PVP diblock copolymer to the interface between PS and PS-*r*-PPHS.

In this study, the PMMA/PS core–shell composite latex was synthesized by the method of soapless seeded emulsion polymerization. Blending the core–shell composite latex with the commercial PMMA and PS to form the commercial polymer/composite latex polymer blends. The morphology, mechanical properties and viscosity properties of the commercial polymer/composite latex polymer blends were studied, and compared with that of the individual commercial polymer blends and the individual core–shell composite latex.

## 2. Experimental

### 2.1. Material

#### 2.1.1. Commercial polymer

Commercial grade of PS and PMMA were used directly. The weight average molecular weight of PMMA and PS was 429 000 and 425 000, respectively.

#### 2.1.2. Synthesis of core–shell composite latex particles

Methyl methacrylate (MMA) and styrene (st) were distilled under a nitrogen atmosphere and reduced pressure prior to polymerization. Water was redistilled and deionized. Other chemicals were of analytical grade and used without further purification.

### 2.2. Soapless seeded emulsion polymerization

The core (PMMA)–shell (PS) composite polymer particles were synthesized by the method of soapless seeded emulsion polymerization.

Seeded emulsion polymerization reactions were carried out with the detailed procedures mentioned in our previous work [21,22].

As seen in Table 1, in the first stage of reaction, methyl methacrylate was used to synthesize PMMA seed latex. The synthesis of seed latex was carried out at  $70^{\circ}C$ . The stirring rate was controlled at 300 rpm. Nitrogen was bubbled through the reaction mixture, quantitative methyl methacrylate and potassium persulfate were added into the reactor. The reaction went on for 1 h, completing the first stage of the polymerization reaction. The seed latex was then quenched to room temperature. In the second stage of the reaction, as seen in Table 2, quantitative styrene was added into the seed latex emulsion, and the seed latex particles were swollen for 24 h at room temperature. The reaction system was heated in a water bath at the temperature of reaction. The aqueous solution of  $K_2S_2O_8$  was added into the reactor after the temperature of the system reached the temperature of reaction, and the reaction of second stage began. So that the PMMA/PS core–shell composite polymer particles would be synthesized, and the weight ratio of PMMA/PS = 1/2. The weight average molecular weight of

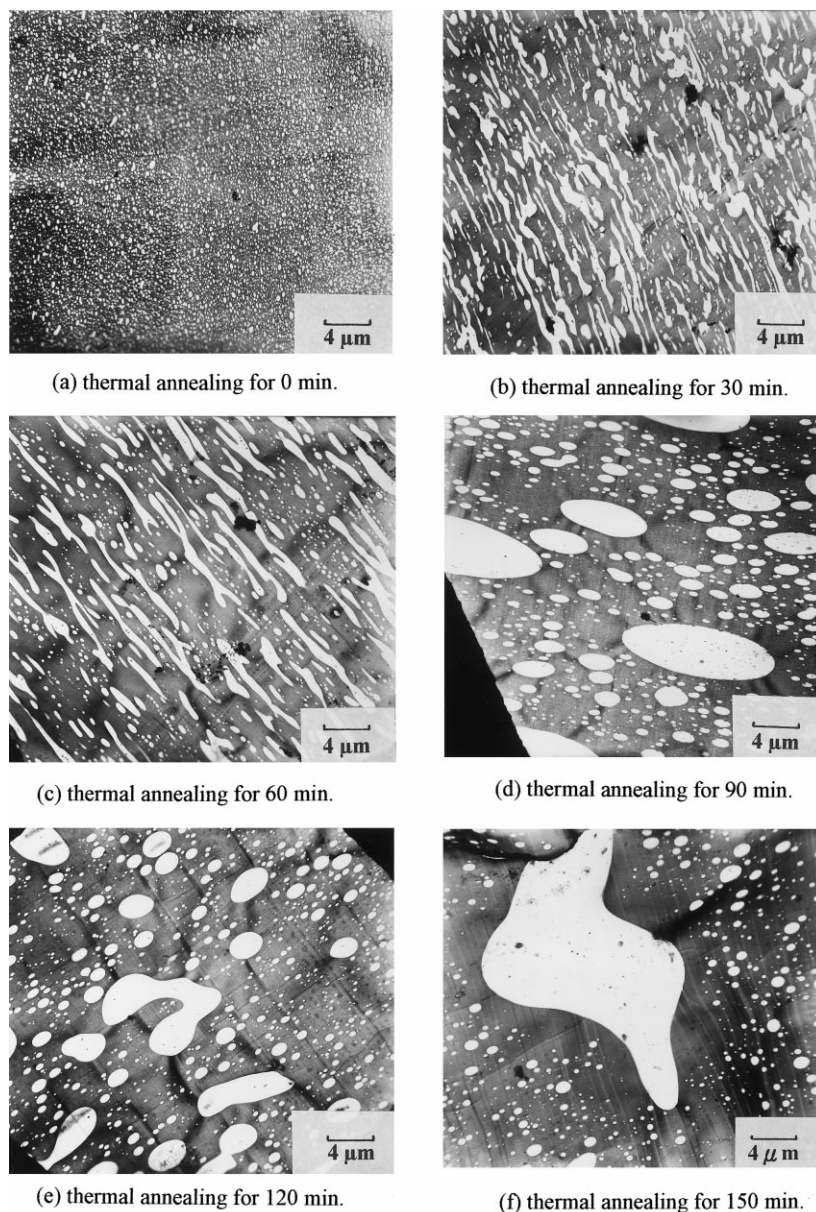


Fig. 1. TEM photographs of PS/PMMA commercial polymer blend thermal annealing at 180°C (polymer blend (A)) (dark zone is PS, bright zone is PMMA): (a) thermal annealing for 0 min; (b) thermal annealing for 30 min; (c) thermal annealing for 60 min; (d) thermal annealing for 90 min; (e) thermal annealing for 120 min; (f) thermal annealing for 150 min.

PMMA seeds was 423 500, and the molecular weight of PMMA/PS core-shell composite latex particles was 426 900.

### 2.3. Polymer blending

*Polymer blend (A):* PMMA and PS of commercial grade were blended (the weight ratio of PMMA/PS = 1/2) by twin screw extruder. The temperature for blending was 210 ~ 245°C, and the speed of twin screw was 40 rpm.

*Polymer blend (B):* the PMMA/PS core-shell composite latex particles (weight ratio of PMMA/PS = 1/2) were used directly, without the process of mechanical blending.

*Polymer blend (C):* the PMMA/PS core-shell composite latex particles (weight ratio of PMMA/PS = 1/2) and PMMA, PS commercial polymer (weight ratio of PMMA/PS = 1/2) were blended by twin screw extruder. The temperature for blending was 210 ~ 245°C, and the speed of twin screw was 40 rpm. The weight percent of core-shell composite latex particles was 30% and commercial grade polymer was 70%.

### 2.4. Thermal annealing

After the temperature of the oven was steady, the three

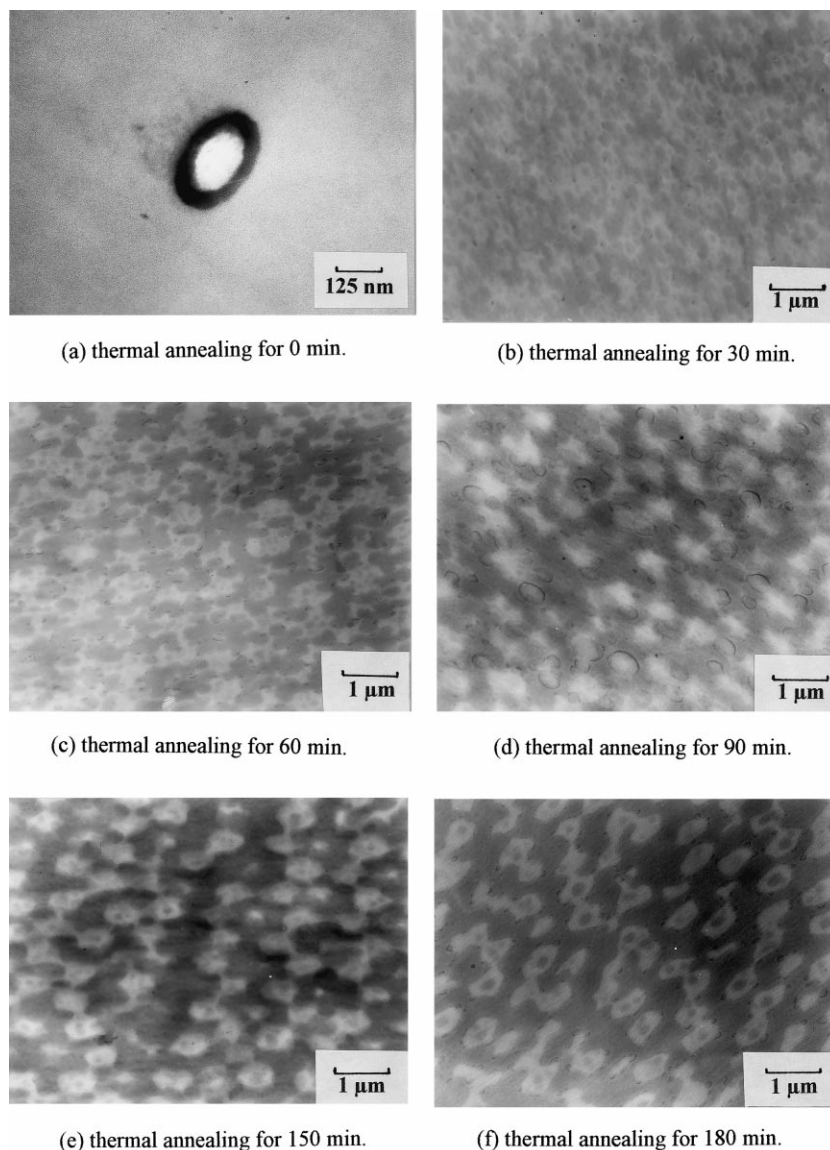


Fig. 2. TEM photographs of PS/PMMA core-shell composite latex thermal annealing at 180°C (polymer blend (B)) (dark zone is PS, bright zone is PMMA): (a) thermal annealing for 0 min; (b) thermal annealing for 30 min; (c) thermal annealing for 60 min; (d) thermal annealing for 90 min; (e) thermal annealing for 150 min; (f) thermal annealing for 180 min.

kinds of polymer blends were annealed in the oven at the temperature of 180°C.

### 2.5. Morphology

The samples were ultramicrotomed to form the sections about 900 Å thick, and stained with RuO<sub>4</sub>. The stained sections of the samples were observed under the transmission electron microscopy (TEM).

### 2.6. Mechanical property

The three kinds of polymer blends were thermal compression molded to form the samples with standard size for tensile strength test. As one aim of this work was to study the effect of thermal annealing on the mechanical properties

of the polymer blends, the samples were thermally compressed for different period of time. The Universal tensile machine was used to measure the tensile strength of the compression-molded samples. The tensile rate was 10 mm/min.

### 2.7. Viscosity property

The viscosity properties of the polymer blends were measured by the capillary rheometer. After the temperature of the rheometer reached 180°C, the polymer blends were put in the sample cell of the rheometer for annealing a period of time, then the polymer blends were extruded from the rheometer at the constant shear rate (69.44 s<sup>-1</sup>).

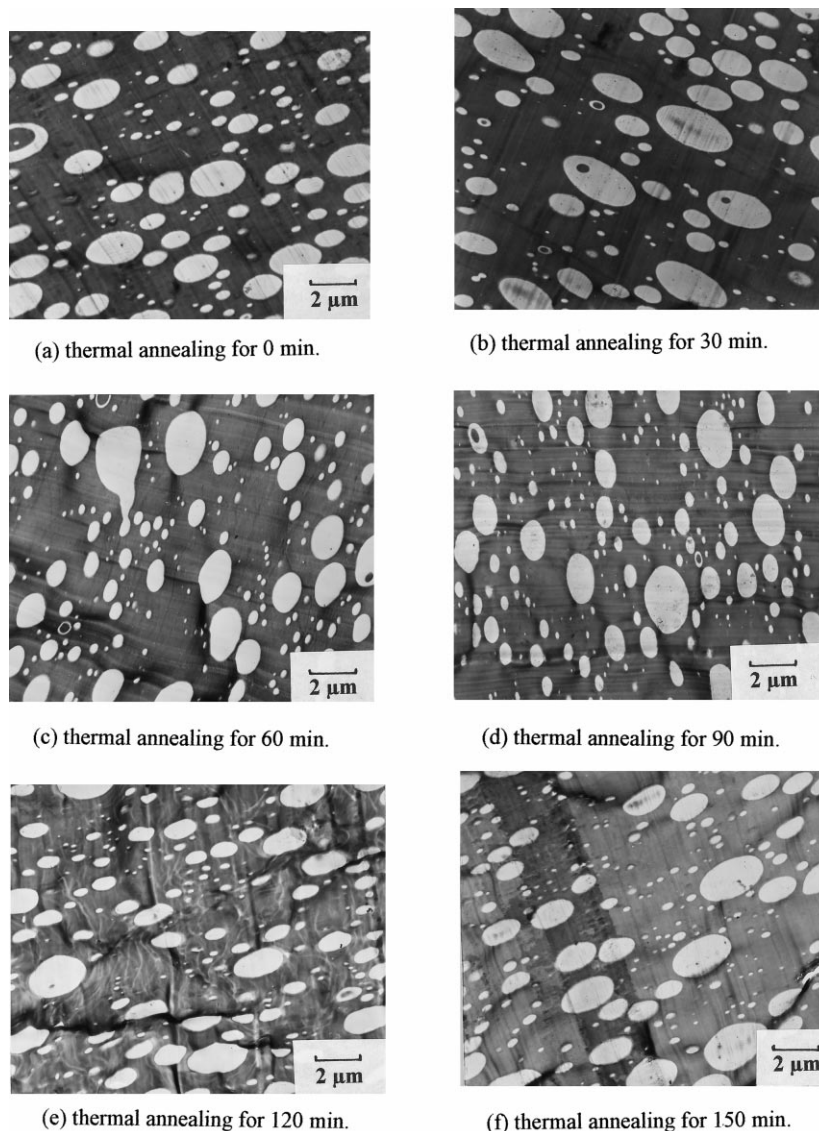


Fig. 3. TEM photographs of PS/PMMA commercial polymer and PS/PMMA core–shell composite latex blending thermal annealing at 180°C (polymer blend (C), dark zone is PS, bright zone is PMMA): (a) thermal annealing for 0 min; (b) thermal annealing for 30 min; (c) thermal annealing for 60 min; (d) thermal annealing for 90 min; (e) thermal annealing for 120 min; (f) thermal annealing for 150 min.

### 3. Results and discussion

In this study, three kinds of polymer blends were prepared. The one was commercial PMMA and PS polymer blend (polymer blend (A)), the weight average molecular weight of PMMA and PS was 429 000 and 425 000, respectively. Another one was PMMA/PS core–shell composite latex particles with PMMA core and PS shell synthesized by the method of soapless seeded emulsion polymerization (polymer blend (B)), the weight average molecular weight of PMMA seeds was 423 500 and the molecular weight of PMMA/PS core–shell composite latex was 426 900. The other one was commercial PMMA, PS and core–shell composite latex particles blending (polymer blend (C)). Because the molecular weight of commercial PMMA, PS and core–shell composite latex was approximate, the effect

of molecular weight on the properties of polymer blends would be neglected.

The effect of thermal annealing on the morphology, tensile strength, Young's Modulus and viscosity properties of the three kinds of polymer blends were investigated.

#### 3.1. Morphology of polymer blends

The transmission electron microphotographs of Fig. 1 show the effect of thermal annealing on the morphology of polymer blend (A). It appeared that the dispersive phase was PMMA and the continuous phase was PS, with increasing the annealing time, the domain size of PMMA phase would increase. The reasons were due to that the PMMA and PS phases were immiscible, the interfacial tension between PMMA and PS was large. After the

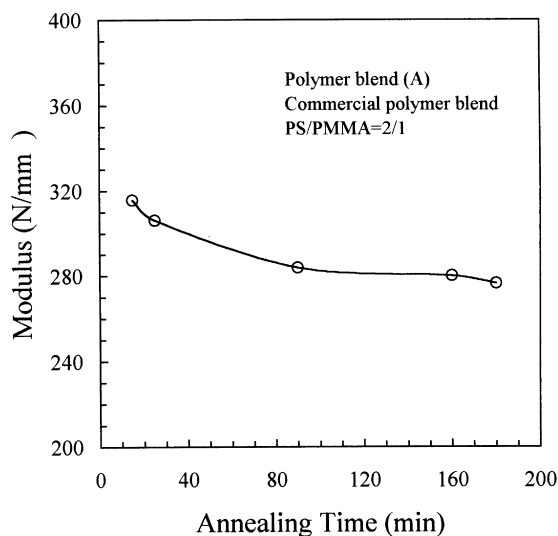


Fig. 4. Influence of thermal annealing time on the Young's Modulus of PS/PMMA commercial polymer blend (polymer blend (A)).

polymer blend (A) was annealed, the domain size of PMMA phase would increase in order to reduce the interfacial area and reduce the interfacial tension. The electron microphotographs of Fig. 2 show the effect of thermal annealing on the morphology of polymer blend (B). The polymer blend (B) was PMMA/PS composite latex particles with core-shell structure, the core was PMMA and the shell was PS. After thermal annealing, the core and shell structures were disrupted, and the PMMA and PS phases would interpenetrate with increasing the annealing time. After the polymer blend (B) was annealed for 90 min, the interpenetration structure of PMMA and PS phases was significant as seen in Fig. 2(d). Finally, the morphology of polymer blend (B) showed the co-continuous structure, i.e. PMMA domains dispersed in PS continuous phase and PS domains dispersed

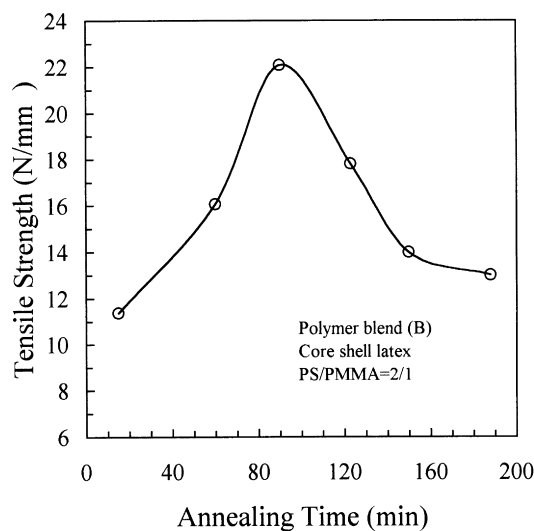


Fig. 5. Influence of thermal annealing time on the tensile strength of PS/PMMA core-shell composite latex (polymer blend (B)).

in PMMA continuous phase. The reasons were because that in the PMMA/PS core-shell composite latex particles, there was an interpenetration layer between the PMMA core and PS shell. The interpenetration layer included the entanglement of PMMA and PS polymer chains, and the PMMA/PS graft copolymer. The interpenetration layer would lower the interfacial tension of PMMA and PS phases, so that after thermal annealing for a long time, the PMMA polymer chains would immigrate into the PS phases and the PS polymer chains immigrate into the PMMA phases, and formed the morphology of co-continuous structure. The influence of thermal annealing on the morphology of polymer blend (C) is shown as Fig. 3. It appeared that the diameter of the PMMA domains would not be influenced by the increase of the annealing time. It was due to that the PMMA/PS graft copolymers played the role as compatibilizing agent which would lower the interfacial tension between PMMA and PS phases in the polymer blend (C). When we compared the morphology of polymer blend (B) with polymer blend (C), we found that after thermal annealing for a long time, the co-continuous structure appeared in the polymer blend (B), but not to be found in the polymer blend (C). The reasons were due to that the polymer blend (B) was individual core-shell composite polymer latex, i.e. weight percent of core-shell composite polymer latex was 100%, but the polymer blend (C) contained 70 wt.% of commercial polymer and only 30 wt.% core-shell composite polymer latex, so that the concentration of the interpenetration layer of polymer blend (B) was higher than the polymer blend (C), and the miscibility of the components of the polymer blend (B) was higher than the polymer blend (C). On the effect of thermal annealing, the higher miscibility made the morphology of the polymer blend (B) appeared the co-continuous structure.

### 3.2. Mechanical properties of polymer blends

The influence of thermal annealing on the tensile strength of polymer blend (A) was insignificant. Although the morphology of polymer blend (A) was influenced by thermal annealing, but both of PMMA and PS were plastic, so that the properties of polymer chains were rigid, and the relationship between morphology and tensile strength were insignificant. The Young's modulus of polymer blend (A) appeared that an increase of the thermal annealing time would decrease the Young's modulus of polymer blend (A) as shown in Fig. 4. Fig. 5 shows the relationship between thermal annealing time and tensile strength of polymer blend (B). The results showed that with increasing the thermal annealing time, the tensile strength would increase first and then decrease. The reasons were due to that after the polymer blend (B) was annealed for 90 min, the interpenetration between PMMA and PS phases was significant. But thermal annealing for a longer time, the interpenetration would disappear and the morphology showed the co-continuous structure. So that, the higher degree of interpenetration the higher tensile strength

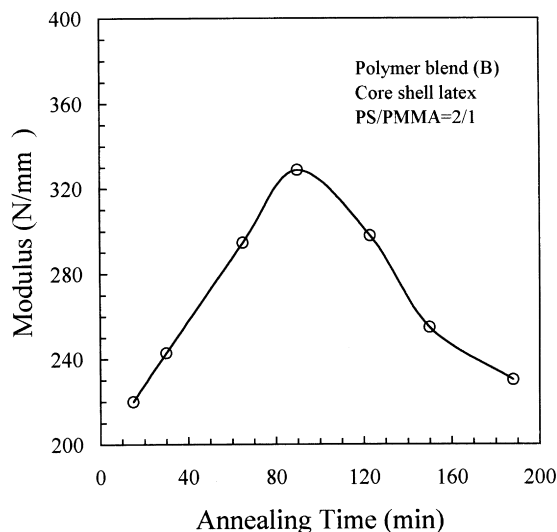


Fig. 6. Influence of thermal annealing time on the Young's Modulus of PS/PMMA core-shell composite latex (polymer blend (B)).

would be obtained. But after annealing for a longer time, the interpenetration structure disappeared and the tensile strength would decrease. The Young's Modulus of the polymer blend (B) under the effect of thermal annealing is shown in Fig. 6. The results showed that with increasing the thermal annealing time, the Young's Modulus would increase first and then decrease. Besides, the influence of thermal annealing on the tensile strength and Young's Modulus of polymer blend (C) was insignificant. The reasons were because that the morphology of polymer blend (C) was very stable, the effect of thermal annealing would not influence the morphology of polymer blend (C). So that the tensile strength and Young's Modulus of polymer blend (C) would not be influenced by the effect of thermal annealing.

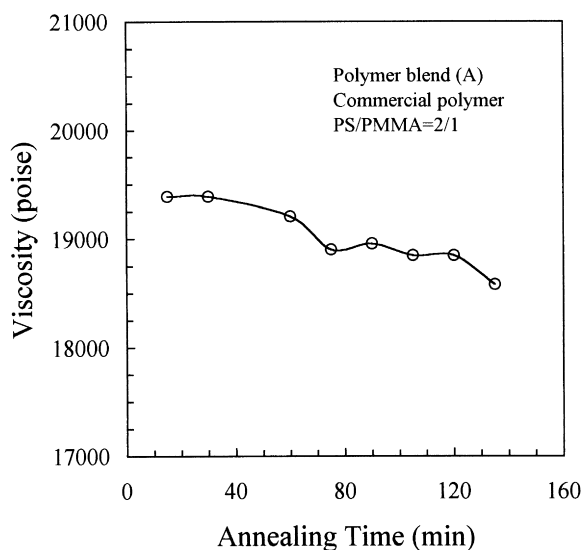


Fig. 7. Influence of thermal annealing time on the viscosity of PS/PMMA commercial polymer blend (polymer blend (A)).

### 3.3. Viscosity properties of polymer blends

Fig. 7 shows the viscosity of polymer blend (A) under the effect of thermal annealing, at the shear rate of  $69.44 \text{ s}^{-1}$ . It showed that the viscosity would decrease with increasing the thermal annealing time. The reasons were due to the fact that the morphology structure of the polymer blend (A) would be influenced by the thermal annealing, so the effect of thermal annealing on the viscosity of polymer blend (A) was significant. Besides, the effect of thermal annealing on the viscosity property of polymer blend (B) showed that with increasing the thermal annealing time, the viscosity would increase first and then decrease as shown in Fig. 8. It was due to the fact that with increasing the thermal annealing time, the interpenetration structure would appear. The interpenetration structure would increase the viscosity of polymer blend (B). After thermal annealing for a longer time, the interpenetration structure disappeared, so that the viscosity of polymer blend (B) would decrease. Moreover, the influence of thermal annealing on the viscosity of polymer blend (C) was insignificant. Because the morphology of polymer blend (C) was stable, the viscosity would not be influenced by the effect of thermal annealing.

## 4. Conclusion

The morphology structure of the commercial grade polymer blend (polymer blend (A)) was unstable. After thermal annealing, the morphology of polymer blend (A) appeared phase separation structure. The mechanical properties and viscosity properties would be influenced by the effect of thermal annealing.

The PMMA/PS core-shell composite latex particles (polymer blend (B)) synthesized by the method of soapless seeded emulsion polymerization have the morphology of core-shell structure. There was an interpenetration layer between the PMMA core and PS shell. The interpenetration layer contained PMMA/PS graft copolymer and physical interpenetration of the polymer chains. The behavior of the interpenetration layer was the same as compatibilizing agent that had the ability to improve the miscibility of the components of the polymer blends. The effect of thermal annealing on the morphology of core-shell polymer latex showed the interpenetration structure first and then formed the co-continuous phase. The tensile strength, Young's Modulus and viscosity of the core-shell polymer latex would increase first and then decrease with increasing the thermal annealing time.

When the commercial polymer blended with the core-shell composite polymer latex, the interpenetration layer of the core-shell composite latex played the role of compatibilizing agent which could reduce the interfacial tension of the polymer-polymer interface and stabilize the morphology structure of the polymer blends. So the influence of thermal annealing on the morphology of the

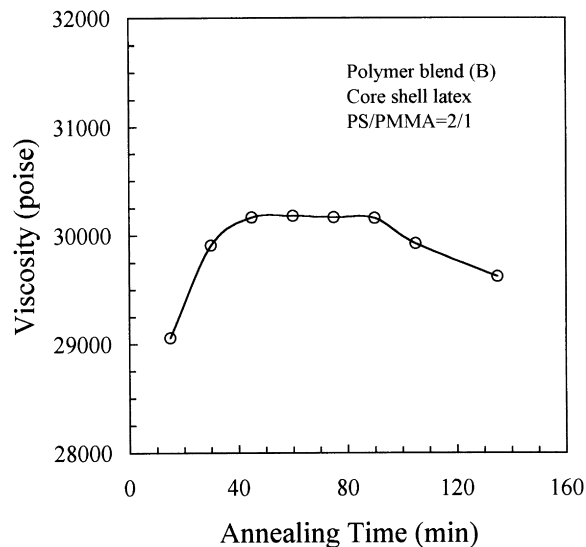


Fig. 8. Influence of thermal annealing time on the viscosity of PS/PMMA core-shell composite latex (polymer blend (B)).

polymer blend (C) was insignificant. Because the morphology was stable, the effect of thermal annealing on the mechanical properties and viscosity property of polymer blend (C) was unimportant.

In this study, we found that the interpenetration layer of the core-shell composite latex had the ability to improve the miscibility of the components of the polymer blends. The miscibility of the components would increase with increasing the concentration of interpenetration layer. So that the effect of thermal annealing on the morphology structure of polymer blend (B) that has the higher concentration of interpenetration layer appeared the co-continuous structure.

Moreover, the effect of thermal annealing on the morphology of polymer blend (C) that has a lower concentration of the interpenetration layer would retain the original structure, and not appear in the co-continuous structure.

## References

- [1] Chen CC, White JL. *Polym Engng Sci* 1993;33:923.
- [2] Shay Jr. RM, Caruthers JM. *Polym Engng Sci* 1990;30:1266.
- [3] McMaster LP. *Adv Chem Ser* 1975;142:43.
- [4] Nishi T, Wang TT, Kwei TK. *Macromolecules* 1975;8:227.
- [5] Voigt-Martin IG, Leister KH, Rosenau R, Roningsveld R. *Polym Sci: Polym Phys Ed* 1986;24:723.
- [6] Andradi LN, Hellmann GP. *Polymer* 1993;34:925.
- [7] Siggia E. *Phys Rev A* 1979;20:595.
- [8] Lifshitz JM, Slyozov VV. *Phys Chem Solids* 1961;19:35.
- [9] Binder K, Stauffer D. *Phys Rev Lett* 1974;33:1006.
- [10] Brown HR, Char K, Deline VR, Green PF. *Macromolecules* 1993;26:4155.
- [11] Char K, Brown HR, Deline VR. *Macromolecules* 1993;26:4164.
- [12] Dai CA, Dair BJ, Dai KH, Ober CK, Kramer EJ, Hui CY, Jelinski LW. *Phys Rev Lett* 1994;73:2472.
- [13] Norton LJ, Smigolova V, Pralle MV, Hubenko A, Dai KH, Kramer EJ, Hahn S, Berglund C, Dekoven B. *Macromolecules* 1995;28:1999.
- [14] Brown HR. *Macromolecules* 1989;22:2859.
- [15] Brown HR, Deline VR, Green PF. *Nature* 1989;341:221.
- [16] Creton CF, Kramer EJ, Hui CY, Brown HR. *Macromolecules* 1992;25:3075.
- [17] Washiyama J, Creton CF, Kramer EJ, Xiao F, Hui CY. *Macromolecules* 1993;26:6011.
- [18] Creton CF, Brown HR, Deline VR. *Macromolecules* 1994;27:1774.
- [19] Creton C, Kramer EJ, Hadziioannou G. *Macromolecules* 1991;24:6.
- [20] Xu Z, Jandt KD, Kramer EJ, Edgcombe BD, Frechet JMJ. *Polym Sci: Polym Phys* 1995;33:2351.
- [21] Lee CF, Chiu WY, Chern YC. *Appl Polym Sci* 1995;57:591.
- [22] Lee CF, Lin KR, Chiu WY. *Appl Polym Sci* 1994;51:1621.