

Thermal Behavior and Properties of Polystyrene/Poly(methyl methacrylate) Blends

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ABSTRACT: The thermal behavior and properties of immiscible blends of polystyrene (PS) and poly(methyl methacrylate) (PMMA) with and without PS-*b*-PMMA diblock copolymer at different melt blending times were investigated by use of a differential scanning calorimeter. The weight fraction of PS in the blends ranged from 0.1 to 0.9. From the measured glass transition temperature (T_g) and specific heat increment (ΔC_p) at the T_g , the PMMA appeared to dissolve more in the PS phase than did the PS in the PMMA phase. The addition of a PS-*b*-PMMA diblock copolymer in the PS/PMMA blends slightly promoted the

solubility of the PMMA in the PS and increased the interfacial adhesion between PS and PMMA phases during processing. The thermogravimetric analysis (TGA) showed that the presence of the PS-*b*-PMMA diblock copolymer in the PS/PMMA blends afforded protection against thermal degradation and improved their thermal stability. Also, it was found that the PS was more stable against thermal degradation than that of the PMMA over the entire heating range. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 609–620, 2004

Key words: diblock copolymers; blends; thermal properties

INTRODUCTION

Simple blends of immiscible polymers usually have weak interphase adhesion, which results in poor mechanical properties. The phase structure of polymer blends reflects the long chain nature in two ways. First, the entropy of mixing for macromolecules is very small, so that most pairs of polymers are immiscible or insoluble in each other because the enthalpy of mixing is usually positive. Second, their viscosity makes the dynamics of phase ripening of these mixtures very slow, so that complete phase separation of a blend takes a very long time. The combination of these two factors means that most polymer blends, made by conventional mixing (e.g., extruders, internal mixers) of either bulk polymers or solutions of polymers, have morphology of phase domains separated on the scale of 0.1–50 μm .

Polystyrene (PS) and poly(methyl methacrylate) (PMMA) are known to be immiscible, exhibiting phase separation,^{1–6} and two glass transition regions are observed. A significant barrier to the development and use of PS/PMMA blends is the inherent lack of

miscibility between PS and PMMA. The favorable polar interaction in PMMA are lost or weakened when polystyrene is used to dilute the poly(methyl methacrylate). This absence of miscibility leads to blends that not always have little adhesion between PS and PMMA phase. The combination of these factors leads to blends that have poor mechanical properties.

A way to control the morphology of polymer blends is through the use of “compatibilizers,” which usually are block or graft copolymers capable of acting as interfacial agents in polymer blends.^{7–10} Therefore, modification of polymer blends by “compatibilization” with interfacially active compatibilizers has been widely investigated and applied in practice. An effective compatibilizer modifies the phase morphology and the interfacial adhesion of a polymer blend by: (1) reducing the interfacial tension between the two phases and hence leading to a finer dispersion of one phase in another, (2) enhancing adhesion by coupling the phases together, and (3) stabilizing the dispersed phase against coalescence.^{11,12}

Various techniques can be used to evaluate the effectiveness of a compatibilizer, compatibilization process, and miscibility of the polymer blend. Locke and Paul,¹³ Heikens et al.,¹⁴ and Fayt et al.^{15–20} reported the beneficial effects on the mechanical properties of polyethylene/polystyrene blends that were compatibilized with different block or graft copolymers. The improvements were attributed to the stronger interfacial adhesion and the smaller particle size of the dispersed phase. With a TEM, Fayt and Teyssie¹⁹ clearly

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TABLE I
Characteristics and Sources of the Raw Materials

Sample code	\bar{M}_w^a (kg/mol)	\bar{M}_n^a (kg/mol)	\bar{M}_z^a (kg/mol)	\bar{M}_w/\bar{M}_n	Density ^b (kg/m ³)	Grade and source
PS ₁	329.1	133.1	534.6	2.47	1030	N7000, Shell
PS ₂	207.6	90.8	358.8	2.29	1030	Polystyol 144C, BASF
PMMA	79.3	43.7	121.1	1.80	1188	Plexiglass 7N, Rohm & Haas
PS- <i>b</i> -PMMA	170.9	162.4	178.2	1.05	—	P719-SMMA, Polymer Source, Inc.

Note: The PS-*b*-PMMA diblock copolymer was symmetrical, 50 : 50 wt %.

^a Measured at DTU laboratory by SEC instrument and the standard deviation on the molar mass was $\leq \pm 3\%$.

^b Derived from reference 38 at 20°C.

demonstrated that a poly(styrene-*b*-ethylene) block copolymer formed a continuous layer around the dispersed phase. The interfacial activity of copolymers has also been characterized by interfacial tension measurements.^{21–26} Some investigators^{1,27–37} have used the glass transition temperature (T_g) and the specific heat increment (ΔC_p) at the T_g to investigate the polymer–polymer miscibility by differential scanning calorimetry (DSC). This method was found to be useful for determining the extent of the miscibility of one polymer in another.

In this study, the effects of adding a PS-*b*-PMMA diblock copolymer in melt blends on the miscibility and the thermal stability of PS/PMMA blends by determining experimentally the glass transition temperature (T_g), the specific heat increment (ΔC_p) at the T_g , and the thermogravimetric analysis (TGA) of the blends were investigated. The morphology of PS/PMMA blends with and without a diblock copolymer was investigated as well.

EXPERIMENTAL

Materials

The characteristics and commercial sources of the polystyrenes (PS), poly(methyl methacrylate) (PMMA), and PS-*b*-PMMA diblock copolymer used in this study are

shown in Table I. Using blends of these polymers we investigated miscibility, thermal stability, and morphology of the PS/PMMA blends with and without the block copolymer during melt blending in a MiniLab twin-screw extruder.

Mixing equipment, torque measurements, and experimental procedures

Blends were prepared using a 5/14 mm diameter conical twin-screw extruder (Haake MiniLab Rheomex CTW5). This extruder can be used in two ways: extrusion (flush), or recycle blends (as shown schematically in Fig. 1). The recycle channel allows recycling the melt for more thorough mixing. The screw length was 109.5 mm and the diameter of the one-hole circular flush die was 2 mm. The screw configuration employed had one 30-mm length-kneading block. The temperature of the extruder was set at 200°C in each zone (flush die, cycle flow channel, and barrel zones), and a screw speed of 30 rpm was used for all blends. A torque trace was recorded for each blending run. The equilibrium torque values, obtained after the set mixing time, and the densities at 200°C of the polymers are given in Table II.

Before a typical blending experiment the PS and PMMA polymers in pellets were dried at 60–65°C

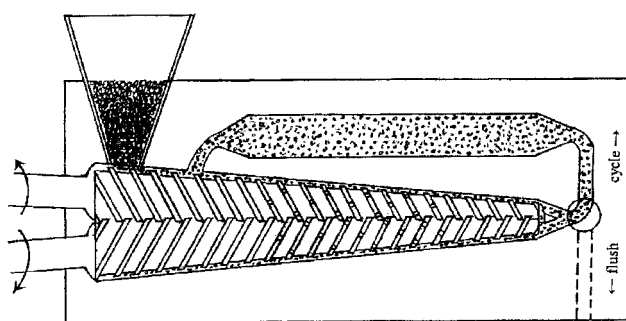


Figure 1 Schematic diagram describing a conical twin-screw extruder, in which a pair of immiscible polymers are extruded under a preset temperature profile along the extruder axis.

TABLE II
Torque, Viscosity and Density Values
of the Raw Materials

Sample code	Torque ^a (Nm)	Viscosity ^b (Pa.s) at 117 s ⁻¹	Density ^c (kg/m ³) at 200°C
PS ₁ (N7000), Shell	32	700	972
PS ₂ (144C), BASF	17	350	972
PMMA (7N), Rohm & Haas	42	2404	1097

^a Measured at DTU laboratory using Haake MiniLab Rheomex CT5 twin-screw extruder for 10-min mixing.

^b Measured at DTU laboratory using Rosand precision capillary extrusion rheometer.

^c Derived from ref. 38.

under vacuum for a week to remove moisture. In all experiments a total of 6 g mixtures of PS and PMMA, with or without a PS-*b*-PMMA diblock copolymer, was weighed according to the density of each polymer at 200°C. The diblock copolymer was typically added to the PS/PMMA blends in 3% ratio. The blend was manually premixed by rolling the given blend in a bag for about 10 min before being fed into the hopper of the extruder. A nitrogen blanket was used to minimize polymer degradation. Mixing time was counted from the time when the materials were loaded into the extruder. Typically, 30–40 s were required to load the material. In preparing the blends we varied blend composition and the duration of melt blending.

Size-exclusion chromatography (SEC)

The molar mass of the PS, PMMA, and PS/PMMA blends were measured by size-exclusion chromatography (SEC) in tetrahydrofuran (THF) with PS standards (Polymer Laboratories: EasiCal PS-2 Polystyrene). The SEC instrument equipped with two PS gel (Plgel 5 μm MIXED-D, 300 \times 7.5 mm) columns operated at 25°C. The flow rate was 1 mL/min, the injection volume was 100 μL , and the sample concentration was 1 mg/mL. The SEC columns were calibrated with narrow distribution PS standards using the above-mentioned conditions. The molar mass averages were calculated using the calibration and the “Q factor correction” method. As expected, no significant changes (less than 3%) in molar mass were observed as a result of polymer blending. The experimental data measured by SEC was repeated many times, and was reproducible within approximately 3%.

Rheological measurements

A Rosand Precision Capillary Extrusion Rheometer (Rosand Model RH-7, Rosand Precision Limited) with a capillary rheometer diameter of 1 mm, a length-to-diameter ratio of 16 and an entrance angle of 180° was used to measure the viscosities of the polymers at high shear rates (1–10,000 s^{-1}). Rabinowitsch correction was applied in calculating the wall shear stress. The viscosity values of each polymer are given in Table II.

Annealing

Static annealing of PS₁/PMMA blends was done at 130°C 2°C in a vacuum oven for 54 h. The samples were then removed and quenched to room temperature for analysis.

Dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA)

Dynamic mechanical properties were measured by a TA-Instruments (model DMA-2980). The dynamic me-

chanical testing was performed at a heating rate of 2°C min^{-1} and the frequency of heating was 1 Hz.

Glass transition temperatures (T_g s) of the pure polymers and their blends were determined by a TA-Instruments differential scanning calorimeter (model DSC Q1000). Temperature calibration was performed using indium [$T_m = 156.61^\circ\text{C}$, heat of fusion (ΔH_f) = 28.71 J/g], mercury ($T_m = -38.87^\circ\text{C}$, $\Delta H_f = 11.3$ J/g), and tin ($T_m = 231.928^\circ\text{C}$, $\Delta H_f = 60.6$ J/g).

The heating rate and cooling rate of the samples were 10 and 5°C min^{-1} , respectively, with a sample size between 8 and 12 mg using standard aluminum sample pans. The sample was surrounded by a nitrogen atmosphere. The samples were first heated from 30 to 200°C to remove the effects from previous processing followed by cooling to 30°C and heating again to 200°C. Thermal transition was determined from second DSC scans. The inflection point of the specific jump of a thermal scan was taken as the glass transition temperatures.

The thermogravimetric analysis (TGA) studies were carried out by a TA-Instruments, model TGA Q500, using a standard platinum pan at a heating rate of 10°C min^{-1} under a nitrogen atmosphere over a temperature range from 20°C up to 600°C.

The experimental data measured by DSC and TGA or DMA were repeated many times, and were reproducible within approximately 3%.

Scanning electron microscopy (SEM)

All SEM samples of the extrudates were prepared by cryogenic fracturing in liquid nitrogen. The morphology characterization was carried out in two ways. One was a microscopic observation of the remaining phase with scanning electron microscopy. In this study, selective extraction technique was used to aid in identification of the fractured surface for the morphology observation.^{6,39} Formic acid solvent was used as selective solvent to remove PMMA phase. After extracting, the samples were dried at 60°C under vacuum for 2 weeks. The extraction and drying cycle were repeated several times until a constant weight of remaining polymer was obtained. The other one was a macroscopic observation of the fractured surface of the extrudates without solvent extraction for determining the dispersed state of each phase and the influence of the added block copolymers. All sample surfaces were sputter coated with a 25-nm layer of gold before examination. The morphology of the cross-section of extrudates was examined by SEM in JSM-5900 microscopes at 14-kV accelerating voltages.

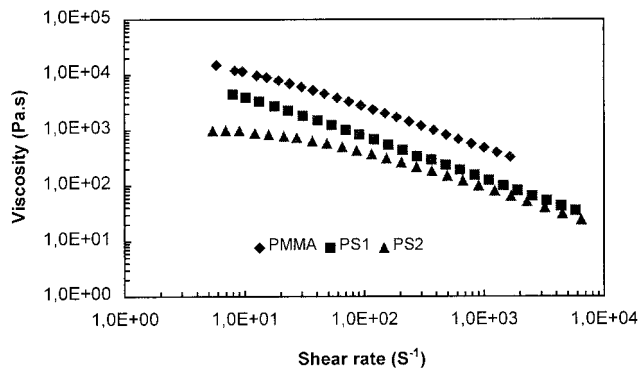


Figure 2 Viscosity as a function of shear rate at 200°C for PS and PMMA from capillary rheometry.

RESULTS AND DISCUSSION

Viscosity and torque of PS, PMMA, and their blends

To investigate the influence of viscosity ratio ($\lambda = \eta_1/\eta_2$), the blends were prepared at two different values of λ . The viscosity of the components, PMMA, PS₁ (N7000) and PS₂ (144C), were measured at 200°C for $\dot{\gamma} = 1\text{--}10,000\text{ s}^{-1}$ by using a capillary rheometer (Fig. 2). The viscosity of PMMA is much higher than that of PS₁ and PS₂ over the entire range of shear rates tested, and the viscosity of PS₁ is higher than that of PS₂, especially at low $\dot{\gamma}$. At low shear rate, the viscosity of PS₂ seems to have a Newtonian plateau-like behavior.

Figure 3 gives the torques during blending for the three blends of PS₂/PMMA system without PS-*b*-PMMA diblock copolymer at the PS weight fractions: $\omega_{\text{PS}} = 0.20$, $\omega_{\text{PS}} = 0.50$, and $\omega_{\text{PS}} = 0.80$, and three blends with the diblock copolymer at the weight fractions: $\omega_{\text{PS-}b\text{-PMMA}} = 0.03$, and $\omega_{\text{PS}} = 0.194$, $\omega_{\text{PS}} = 0.485$, and $\omega_{\text{PS}} = 0.776$. It is seen that excluding a very short period in the beginning each blend exhibits a time-independent torque, and that the addition of the diblock copolymer does not influence the recorded values.

T_g s for pure PS_{*i*}, PMMA, PS-*b*-PMMA, and PS₁/PMMA blends

A typical DSC thermogram of glass transition temperatures (T_g s) of pure polymers and PS₁/PMMA (50/50) blends is shown in Figure 4. From this figure, we can see that only one T_g is exhibited for the sample of PS₁/PMMA (50/50) blends before annealing [Fig. 4(c)], indicating possible miscibility. However, two T_g s are exhibited for the same blends after annealing [Fig. 4(d)]. The reason for the single glass transition between the T_g s of the components may be that the T_g s of PS₁ (102.60°C) [Fig. 4(b)] and PMMA (108.26°C) [Fig. 4(e)] are too close to each other. To judge the extent of miscibility of polymer blends from DSC mea-

surements a difference in components, T_g s approximately 20°C⁴⁰ or larger are needed. The PS₁/PMMA blends before annealing were not truly thermodynamically miscible. Thus, we use PS₂ ($T_g = 86.39^\circ\text{C}$) [Fig. 4(a)] instead of PS₁ for the investigations. For the PS-*b*-PMMA diblock copolymer in Figure 4(f), two glass transition regions are observed, $T_{g,\text{PS}} = 107.27^\circ\text{C}$, associated with PS-rich regions, and $T_{g,\text{PMMA}} = 132.04^\circ\text{C}$, associated with PMMA-rich regions. DMA also showed two glass transitions of the PS-*b*-PMMA diblock copolymer at 110.79 and 132.48°C corresponding to PS and PMMA blocks, respectively (Fig. 5).

Glass transition behavior

To investigate how the miscibility is affected by a diblock copolymer, we added 3% PS-*b*-PMMA diblock copolymer to the PS₂/PMMA blend system. Thirty minutes of blending time was used both for the PS₂/PMMA blends with and without the diblock copolymer. Two-, 10-, and 30-min blending times were used to study the effect of the duration of mixing. The results for the T_g s of PS₂ and PMMA for the various compositions are presented in Figures 6 and 7. From Figure 6, we can see that the T_g s of PMMA do not change appreciably with composition of PS for 2, 10, and 30 min blending without the diblock copolymer. Some small changes are within the range of experimental error. In this figure, we can also see that the T_g s of the 30-min mixing blends with the diblock copolymer have a slight decrease with an increase in the PS weight fraction.

The T_g s of polystyrene for 2-, 10-, and 30-min mixing blends of PS/PMMA without the block copolymer and the 30-min mixing blends with the block copoly-

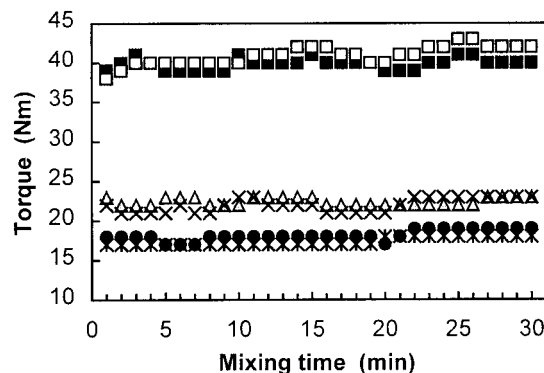


Figure 3 Torque as a function of mixing time for PS₂/PMMA blends ($\omega_{\text{PS}} = 0.20$, $\omega_{\text{PS}} = 0.50$, and $\omega_{\text{PS}} = 0.80$) with and without diblock copolymer: (■) $\omega_{\text{PS}} = 0.20$, $\omega_{\text{PS-}b\text{-PMMA}} = 0.00$; (□) $\omega_{\text{PS}} = 0.194$, $\omega_{\text{PS-}b\text{-PMMA}} = 0.03$; (△) $\omega_{\text{PS}} = 0.50$, $\omega_{\text{PS-}b\text{-PMMA}} = 0.00$; (x) $\omega_{\text{PS}} = 0.485$, $\omega_{\text{PS-}b\text{-PMMA}} = 0.03$; (*) $\omega_{\text{PS}} = 0.80$, $\omega_{\text{PS-}b\text{-PMMA}} = 0.00$; (●) $\omega_{\text{PS}} = 0.776$, $\omega_{\text{PS-}b\text{-PMMA}} = 0.03$.

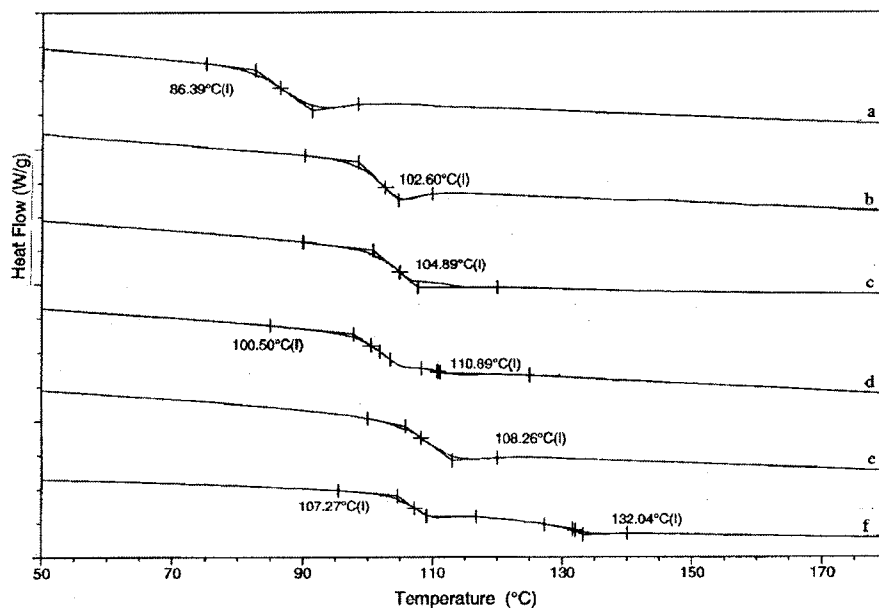


Figure 4 DSC thermograms showing the glass transition temperature (T_g): (a) PS₂; (b) PS₁; (c) PS₁/PMMA blend ($\omega_{PS1} = 0.5$) before annealing; (d) PS₁/PMMA blend ($\omega_{PS1} = 0.5$) after annealing; (e) PMMA; and (f) PS-*b*-PMMA. Vertical scale and placements are arbitrary.

mer are shown to increase with PMMA weight fraction in Figure 7. For a composition of 0.1 weight fraction of PS, the T_g is seen to increase by about 3°C for 2-min blending, about 4°C for 10-min blending, about 5°C for 30-min blending without the block copolymer, and about 6°C for the 30-min blending with the block copolymer. In this figure, it seems that the T_g s increase slightly more at 30-min blending with the

block copolymer than at either 2- or 10- or 30-min blending without the block copolymer.

From the study of glass transition temperatures of PMMA and PS in the PS/PMMA blends, we estimate that the PMMA is dissolving in the PS phase, while the PS does not appear to be dissolving in the PMMA phase. From the above results, we can conclude that the miscibility increases in the presence of the diblock

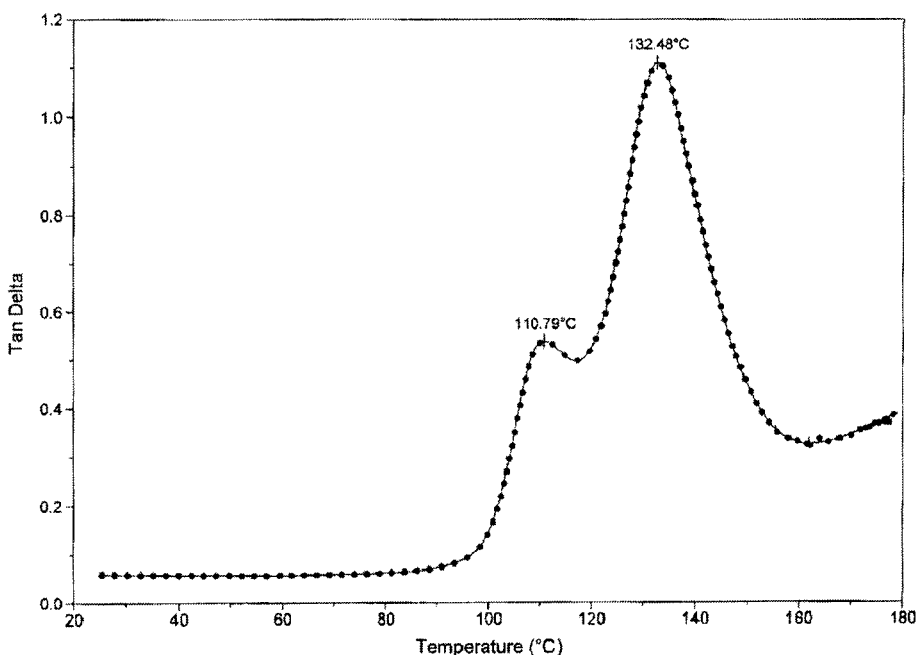


Figure 5 DMA showing the glass transition temperature (T_g) of the PS-*b*-PMMA.

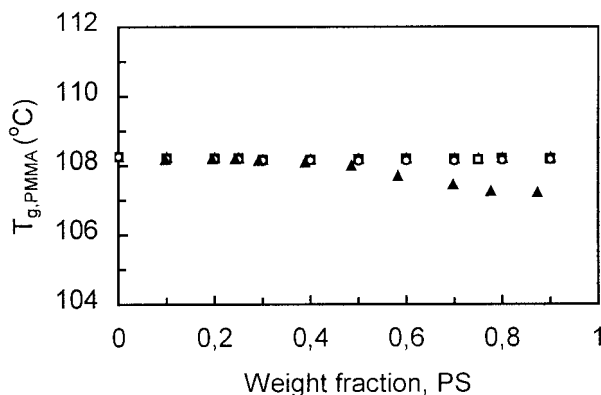


Figure 6 Effect of blend composition on the $T_{g,PMMA}$ for PS₂/PMMA blends with and without diblock copolymer. Differential mixing time: (Δ) 2 min, $\omega_{PS-b-PMMA} = 0.00$; (□) 10 min, $\omega_{PS-b-PMMA} = 0.00$; (○) 30 min, $\omega_{PS-b-PMMA} = 0.00$; (▲) 30 min, $\omega_{PS-b-PMMA} = 0.03$.

copolymer addition in the PS/PMMA blends, but it is very limited.

Morphology of PS/PMMA and PS/PMMA/PS-*b*-PMMA blends

The morphology of PS/PMMA and PS/PMMA/PS-*b*-PMMA blends by MiniLab twin-screw extrusion was studied using scanning electron microscopy. Figure 8 shows SEM micrographs of the cryogenically fractured cross-section surfaces of 90/10 PS₂/PMMA [Fig. 8(a)] and 87.3/9.7/3 PS₂/PMMA/PS-*b*-PMMA [Fig. 8(b)] extrudates. From Figure 8(a), we can see that the lack of adhesion between PS₂ and PMMA is obvious, wherein dispersed particles do not adhere to the PS matrix and leave cavities with a smooth surface. This phase morphology is strikingly modified by addition of a diblock copolymer [Fig. 8(b)]. The phase separation between PS and PMMA phases is more pro-

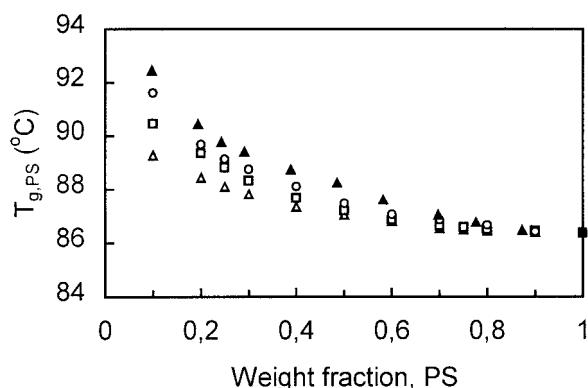


Figure 7 Effect of blend composition on the $T_{g,PS}$ for PS₂/PMMA blends with and without diblock copolymer. Differential mixing time: (Δ) 2 min, $\omega_{PS-b-PMMA} = 0.00$; (□) 10 min, $\omega_{PS-b-PMMA} = 0.00$; (○) 30 min, $\omega_{PS-b-PMMA} = 0.00$; (▲) 30 min, $\omega_{PS-b-PMMA} = 0.03$.

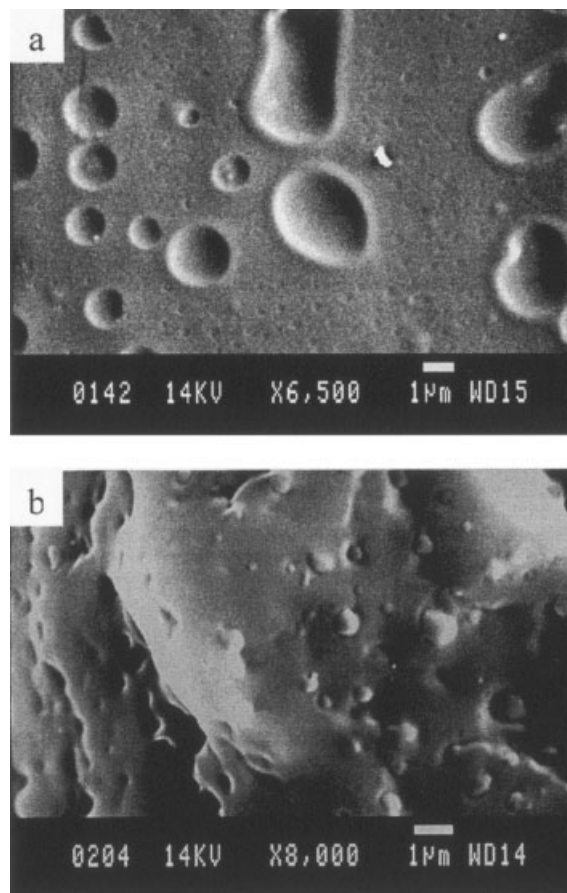


Figure 8 SEM images obtained from the cryogenically fractured cross-section surfaces of PS₂/PMMA blends with and without diblock copolymer after 30 min of mixing: (a) PS/PMMA (90/10) blends; (b) PS/PMMA/PS-*b*-PMMA (87.3/9.7/3) blends.

nounced in the case of absence of the diblock copolymer than in the case of presence of the diblock copolymer.

Figure 9 shows SEM micrographs of the PS₂ phase after PMMA extraction in PS₂/PMMA/PS-*b*-PMMA (87.3/9.7/3) blends for 2 min [Fig. 9(a)] and 30 min [Fig. 9(b)] of mixing. The SEM has revealed many block copolymer micelles in the PS matrix. The white spots correspond to micelles, whereas the dark holes correspond to PMMA particles that have been removed after extraction using formic acid solvent. The micelles of the blends after 2 min of mixing [Fig. 9(a)] appear slightly larger than those of the blends after 30 min of mixing [Fig. 9(b)]. The SEM image reveals micelles in the PS matrix, in the case after only 2 min of mixing. Apparently, the energy minimum of the interface was not sufficient to trap the block copolymer.

Block copolymers are often known as interface agents or compatibilizer, because of their tendency to locate at the blend interface rather than form micelles or a separate phase. The small effect of the diblock

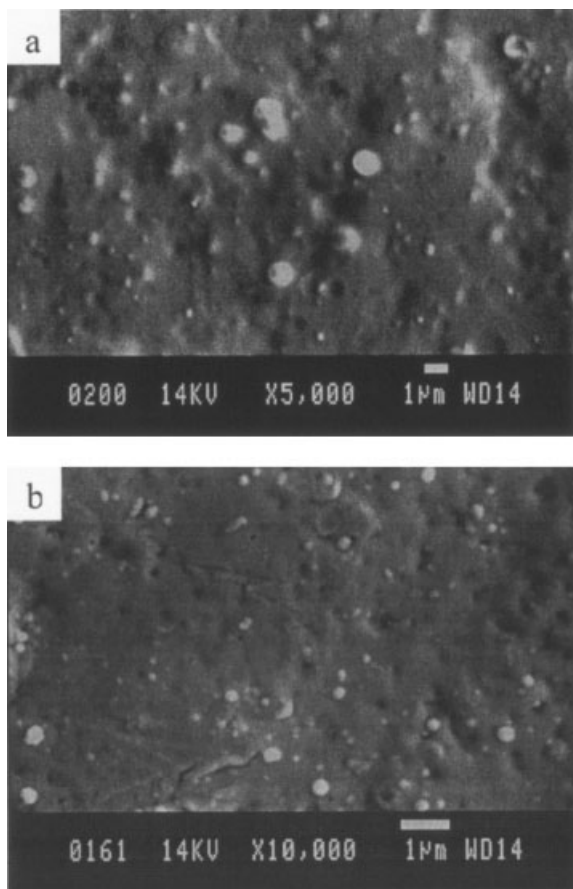


Figure 9 SEM images of the PS phase after PMMA extraction in 2 min and 30 min mixed PS₂/PMMA/PS-*b*-PMMA (87.3/9.7/3) blends: (a) 2 min of mixing; (b) 30 min of mixing.

copolymer may indicate that the diblock copolymer forms its own mesophase. However, the efficiency of a diblock copolymer strongly depends on its molar mass.^{6,39,41-42} The diblock copolymer with low molar mass can reduce the interfacial tension, but cannot form entanglements with homopolymer. If the molar mass of the diblock copolymer is too large, it is difficult to be dispersed. Therefore, much of the diblock copolymer might be wasted in micelles or in a separate phase during melt blending.

Phase compositions of PS₂/PMMA blends with and without a copolymer

Glass transition temperatures composition relationships for polymer/small molecule and polymer/polymer blends have been described by several semiempirical equations,⁴⁴⁻⁴⁸ which is often used to describe the dependence of T_g on composition. From the glass transition temperatures of PS and PMMA in the PS/PMMA blends, we can estimate the apparent weight fractions of PS and PMMA dissolved in the PS-rich phase and the PMMA-rich phase, respectively. The

Couchman equation relating the blend glass transition temperature (T_g) to the component weight fraction (ω_1, ω_2), glass transition temperatures (T_{g1}, T_{g2}), and specific heat increments ($\Delta C_{p1}, \Delta C_{p2}$) at the T_g is:⁴⁵

$$\ln T_g = \frac{\omega_1 \Delta C_{p1} \ln T_{g1} + \omega_2 \Delta C_{p2} \ln T_{g2}}{\omega_1 \Delta C_{p1} + \omega_2 \Delta C_{p2}} \quad (1)$$

With T_{g1}/T_{g2} approximately equal to 1, eq. (1) reduces to the Wood copolymer equation:⁴⁶

$$T_g = \frac{\omega_1 \Delta C_{p1} T_{g1} + \omega_2 \Delta C_{p2} T_{g2}}{\omega_1 \Delta C_{p1} + \omega_2 \Delta C_{p2}} \quad (2)$$

If the relation:⁴⁷

$$\Delta C_{p1} T_{g1} = \Delta C_{p2} T_{g2} \quad (3)$$

is satisfied, eq. (2) further reduces to the Fox relation⁴⁸

$$1/T_g = \omega_1/T_{g1} + \omega_2/T_{g2} \quad (4)$$

where ω_1 and ω_2 represent the weight fraction of the components ($\omega_1 = 1 - \omega_2$), and T_g, T_{g1}, T_{g2} are the T_g s of the blend and components 1 and 2, respectively. Equation (4) can be rearranged to

$$\omega_1 = T_{g1}(T_{g1,b} - T_{g2}) / (T_{g1,b}(T_{g1} - T_{g2})) \quad (5)$$

where ω_1 is the apparent weight fraction of PS in the PS-rich phase, $T_{g1,b}$ is the observed T_g of PS-rich phase. Similarly, eq. (4) can also be rearranged to

$$\omega_1'' = T_{g1}(T_{g2,b} - T_{g2}) / (T_{g2,b}(T_{g1} - T_{g2})) \quad (6)$$

where ω_1'' is the apparent weight fraction of PS in the PMMA-rich phase, $T_{g2,b}$ is the observed T_g of PMMA-rich phase.

Applying eqs. (5) and (6) to the T_g values of PS/PMMA blends with and without the block copolymer, the apparent weight fractions of PS in the PS-rich phase (ω_1') and in the PMMA-rich phase (ω_1'') for 30-min blending were calculated. The results are tabulated in Tables III and IV.

From Tables III and IV, we can see that the apparent weight fraction of PS (ω_1') increase more in the PS-rich than that apparent weight fraction of PMMA (ω_2'') decrease in PMMA-rich. For a composition of 0.9 weight fraction of PS, the is seen to increase by about 0.2803 for 30-min blending without the diblock copolymer and about 0.3198 with the diblock copolymer. For a composition of 0.1 weight fraction of PMMA (from 0.9 to 0.1 ω_{PMMA}), the ω_2'' is seen to decrease by about 0.0011 without the diblock copolymer and about 0.0436 with the diblock copolymer. The above data quantitatively estimate that the PMMA dissolves more

TABLE III
Apparent Weight Fraction (ω) of PS and PMMA Components in the PS-Rich Phase and the PMMA-Rich Phase of the Extruded PS/PMMA Blends at 30 min Blending without PS-*b*-PMMA Diblock Copolymer

W_{ps}^a	T_{g1} (°C)	T_{g2} (°C)	PS-rich ^b		PMMA rich ^b	
			ω_1'	ω_2'	ω_1''	ω_2''
1.00	86.39	—	1.0000	—	—	—
0.90	86.42	108.18	0.9982	0.0018	0.0029	0.9971
0.80	86.68	108.16	0.9834	0.0166	0.0037	0.9963
0.70	86.86	108.14	0.9732	0.0268	0.0044	0.9956
0.60	87.08	108.15	0.9607	0.0393	0.0040	0.9960
0.50	87.48	108.14	0.9383	0.0617	0.0044	0.9956
0.40	88.12	108.16	0.9028	0.0972	0.0037	0.9963
0.30	88.76	108.16	0.8678	0.1322	0.0037	0.9963
0.25	89.13	108.19	0.8478	0.1522	0.0026	0.9974
0.20	89.68	108.20	0.8184	0.1816	0.0022	0.9978
0.10	91.61	108.21	0.7179	0.2821	0.0018	0.9982
0.00	—	108.26	—	—	—	1.0000

^a Blend composition given as the overall weight fraction PS in the PS/PMMA blend.

^b Single prime and double prime denote PS-rich phase and PMMA-rich phase, respectively, and subscripts 1 and 2 denote PS and PMMA components, respectively. All ω_1' 's and ω_1'' 's calculated from eqs. (5) and (6), respectively.

in the PS phase than does the PS in the PMMA phase. Also, this data offers an additional proof of the diblock copolymer addition in the PS₂/PMMA blends can slightly promote the solubility of the PMMA phase in the PS phase.

TABLE IV
Apparent Weight Fraction (ω) of PS and PMMA Components in the PS-Rich Phase and the PMMA-Rich Phase of the Extruded PS/PMMA Blends at 30 min Blending with 3% PS-*b*-PMMA Diblock Copolymer

W_{ps}^a	T_{g1} (°C)	T_{g2} (°C)	PS-rich ^b		PMMA-rich ^b	
			ω_1'	ω_2'	ω_1''	ω_2''
1.000	86.39	—	1.0000	—	—	—
0.873	86.48	107.00	0.9948	0.0052	0.0465	0.9535
0.776	86.78	107.26	0.9777	0.0223	0.0368	0.9632
0.697	87.06	107.46	0.9619	0.0381	0.0294	0.9706
0.582	87.62	107.70	0.9305	0.0695	0.0205	0.9795
0.485	88.26	108.00	0.8951	0.1049	0.0095	0.9905
0.388	88.75	108.10	0.8683	0.1317	0.0058	0.9942
0.291	89.41	108.15	0.8328	0.1672	0.0040	0.9960
0.243	89.78	108.20	0.8131	0.1869	0.0022	0.9978
0.194	90.45	108.20	0.7777	0.2223	0.0022	0.9978
0.097	92.46	108.18	0.6750	0.3250	0.0029	0.9971
0.000	—	108.26	—	—	—	1.0000

^a Blend composition given as the overall weight fraction PS in the PS/PMMA blend, $\omega_{PS-b-PMMA} = 0.03$ in all blends.

^b Single prime and double prime denote PS-rich phase and PMMA-rich phase, respectively, and subscripts 1 and 2 denote PS and PMMA components, respectively. All ω_1' 's and ω_1'' 's calculated from eqs. (5) and (6), respectively.

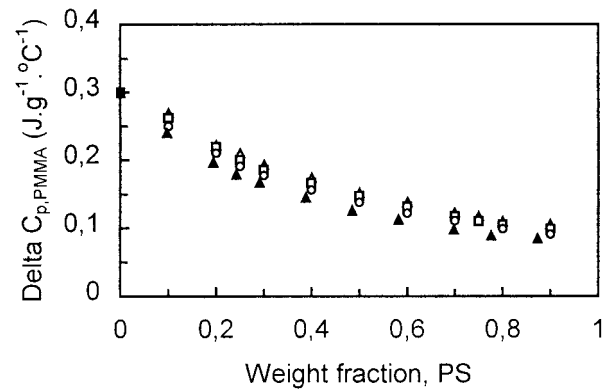


Figure 10 Specific heat increment (ΔC_p) at the T_g of PMMA for PS₂/PMMA blends with and without diblock copolymer. Differential mixing time: (Δ) 2 min, $\omega_{PS-b-PMMA} = 0.00$; (\square) 10 min, $\omega_{PS-b-PMMA} = 0.00$; (\circ) 30 min, $\omega_{PS-b-PMMA} = 0.00$; (\blacktriangle) 30 min, $\omega_{PS-b-PMMA} = 0.03$.

Specific heat increment (δC_p) behavior

The ΔC_p values of PMMA and PS as a function of weight fraction of PS for 2-, 10-, and 30-min blending time without PS-*b*-PMMA diblock copolymer and for 30-min blending time with the block copolymer are presented in Figures 10 and 11, respectively. In Figure 10, the ΔC_p 's of PMMA for 2-, 10-, and 30-min blending with and without PS-*b*-PMMA diblock copolymer are seen to decrease with composition of PS in the PS₂/PMMA blends, whereas the ΔC_p 's of PMMA for 30-min blending with the diblock copolymer decrease slightly more than the blends without the diblock copolymer.

In Figure 11, the values of ΔC_p for PS of the 2-, 10-, and 30-min blends without the block copolymer and 30 min with the block copolymer are presented. From Figure 11, the ΔC_p 's of PS do not appear to increase significantly with composition of PS in PS₂/PMMA blends. The explanation⁴⁹ proposed for the decrease of

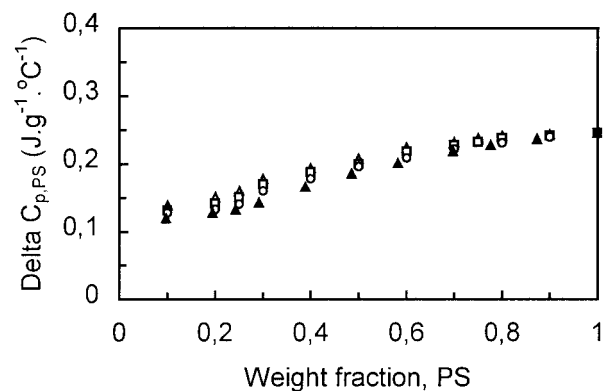


Figure 11 Specific heat increment (ΔC_p) at the T_g of PS for PS₂/PMMA blends with and without diblock copolymer. Differential mixing time: (Δ) 2 min, $\omega_{PS-b-PMMA} = 0.00$; (\square) 10 min, $\omega_{PS-b-PMMA} = 0.00$; (\circ) 30 min, $\omega_{PS-b-PMMA} = 0.00$; (\blacktriangle) 30 min, $\omega_{PS-b-PMMA} = 0.03$.

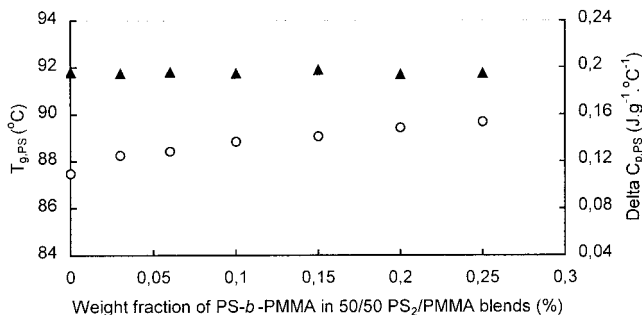


Figure 12 Effect of diblock copolymer concentration on the $T_{g,PS}$ and the $\Delta C_{p,PS}$ at the T_g for $PS_2/PMMA(50/50)/PS-b-PMMA$ blends: (\circ) for T_g ; (\blacktriangle) for ΔC_p .

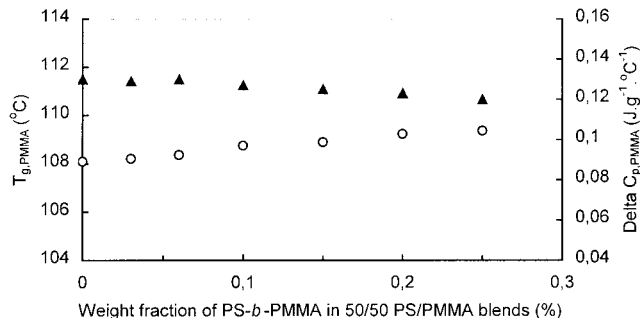


Figure 13 Effect of diblock copolymer concentration on the $T_{g,PMMA}$ and the $\Delta C_{p,PMMA}$ at the T_g for $PS_2/PMMA(50/50)/PS-b-PMMA$ blends: (\circ) for T_g ; (\blacktriangle) for ΔC_p .

ΔC_p at T_g of PMMA or the increase of ΔC_p at T_g of PS is that the size of the dispersed phase is very small so that the magnitude of the specific heat increment (ΔC_p) of each phase is decreased or increased somewhat.

In this study, we can see from Figures 6 and 7 that a decrease of $T_{g,PS}$ with the weight fraction of PS is significant, whereas the $T_{g,PMMA}$ remains essentially unchanged. This behavior can be explained quantitatively in Tables III and IV, which shows that the weight fraction of PMMA dissolved in the PS-rich phase (ω_1') is much higher than that weight fraction of PS component dissolved in the PMMA-rich phase (ω_2''). This result is consistent with the behavior of ΔC_p in Figures 10 and 11. These results suggest that the PMMA dissolves more in the PS phase than does the PS in the PMMA phase.

In this study, we can also see that the effects of the diblock copolymer on the mutual solubility of the PS and PMMA are not significant.

Block copolymer concentration

To investigate the influences of the added diblock copolymer amount on miscibility of $PS_2/PMMA$ blends, 3, 6, 15, 20, and 25% $PS_2-b-PMMA$ diblock copolymers were added into 50/50 $PS_2/PMMA$ blend system for 30-min mixing. The results for the T_g s and ΔC_p s of PS are shown in Figure 12 and of PMMA are shown in Figure 13. In Figure 12, it can be seen that the T_g s of PS increase with increasing weight fraction of $PS-b-PMMA$. However, the T_g s of PS does not appear to increase significantly by increasing the weight fraction of $PS-b-PMMA$ from 0.03 to 0.25. For a composition of 0.03 weight fraction of $PS-b-PMMA$ diblock copolymer, the T_g s of PS is seen to increase by about 1°C, and about 2°C for a composition of 0.25 weight fraction of $PS-b-PMMA$. In Figure 13, it can be seen that the T_g s of PMMA does not decrease with the weight fraction of $PS-b-PMMA$ diblock copolymer, as expected; on the contrary, it increases slightly with the composition. The reason for this result may be due to

the fact that the T_g of the PS and PMMA blocks in $PS-b-PMMA$ copolymer ($T_{g,PS} = 107.27$, $T_{g,PMMA} = 132.04^\circ\text{C}$) is higher than the T_g of PMMA (108.26°C). Therefore, the T_g of PMMA increases with $PS-b-PMMA$ diblock copolymer content in the $PS/PMMA$ blends. From Figures 12 and 13, it appears that the $\Delta C_{p,PS}$ of PS remained essentially unchanged. Some small changes may be within the range of experimental error.

The above results suggest that the addition of more amount of a $PS-b-PMMA$ diblock copolymer in the $PS/PMMA$ blends cannot significantly increase the mutual solubility of the PS and PMMA. From the above results, we can conclude that the addition of a small amount of $PS-b-PMMA$ (3%) to $PS/PMMA$ blends is sufficient to improve miscibility of the $PS/PMMA$ blends; if the block copolymer is effective, more interfacial modifier addition is unnecessary.

Thermal decomposition behavior

Figures 14 and 15 show the initial TGA thermograms of pure PS_2 , PMMA, and 70/30, 50/50, 30/70 $PS_2/PMMA$ blends with and without a $PS-b-PMMA$ diblock copolymer. Tables V and VI summarize the

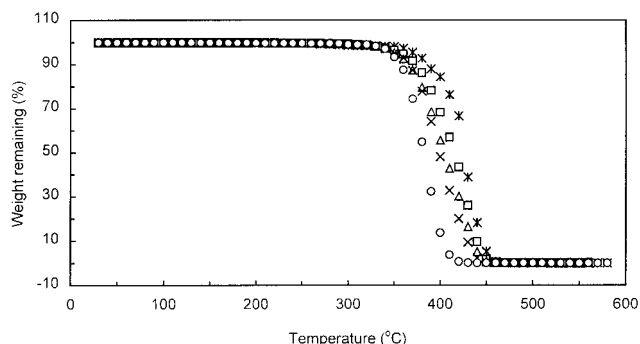


Figure 14 TGA thermograms of PS_2 , PMMA, and $PS_2/PMMA$ blends: (*) PS_2 ; (\square) $PS_2/PMMA$ (70/30) blend; (\triangle) $PS_2/PMMA$ (50/50) blend; (\times) $PS_2/PMMA$ (30/70) blend; (\circ) PMMA.

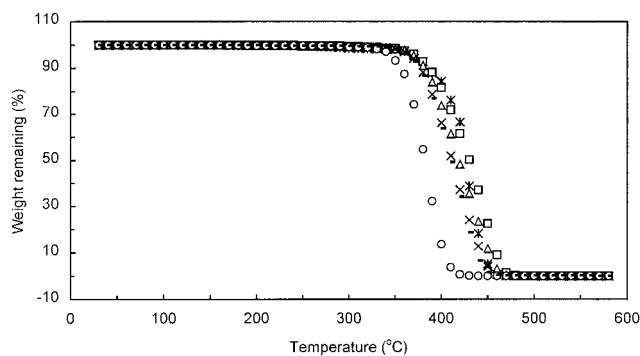


Figure 15 TGA thermograms of PS₂, PMMA, and PS₂/PMMA/PS-*b*-PMMA blends: (*) PS₂; (□) PS₂/PMMA/PS-*b*-PMMA (67.9/29.1/3) blend; (△) PS₂/PMMA PS-*b*-PMMA (48.5/48.5/3) blend; (x) PS₂/PMMA/PS-*b*-PMMA (29.1/67.9/3) blend; (○) PMMA; () PS-*b*-PMMA.

percentage weight loss at different decomposition temperatures for the pure polymers and various ratios of PS₂/PMMA blends with and without the diblock copolymer at 30-min blending time taken from the TGA thermograms. It can be seen from Figure 14 and Table V that pure PS₂ and PMMA lose about 0.03 and 0.29% of weight at 200°C, respectively. This behavior indicates that the initial decomposition reaction for PS begins at a higher temperature than for PMMA. By increasing the heating temperature from 200 to 300°C, the loss in weight of the PS₂ was found to be about 1/3 the loss in weight of the PMMA, and at 400°C the weight loss of the PS₂ was found to be about 1/5 the PMMA weight loss. It can also be observed from Figures 14 and 15 and Tables V and VI that the thermal stability increases over the entire temperature range with increasing PS contents. Thus, it may be concluded that the PS is more stable against thermal decomposition than the PMMA over the entire range of the studied temperature.

Comparing the results of Figure 15 and Table VI with Figure 14 and Table V, it can be observed that the thermal stability of the PS₂/PMMA blends with the PS-*b*-PMMA diblock copolymer at any composition is much higher than those of the blends without the block copolymer over the entire temperature range. For example, the weight loss of the 50/50 PS₂/PMMA blends with the block copolymer at 200, 300, 350, and 400°C are 0.15, 0.6, 1.56, and 26.17%, respectively. The corresponding results for the blends without the diblock copolymer at 200, 300, 350, and 400°C are 0.18, 0.85, 4.58, and 44.45%, respectively. These results suggest that the PS-*b*-PMMA diblock copolymer offered some sort of protection against thermal degradation of the PS₂/PMMA blends.

The thermal stability of any polymer material is largely determined by the strength of the covalent bond between the atoms forming the polymer molecules. The calculated dissociation energy for the different covalent bonds C—H, C—C, C—O, C=O, and C=C in the literature were found to be 98, 81, 87, 174, and 145 kcal/mol, respectively.⁵⁰ The lower complete dissociation energy of PMMA (about 99.1 kcal/mol) compared to PS₂ polymer (about 101.5 kcal/mol) is certainly due to the lack of the C=C bonds of aromatic nuclei in the PMMA molecule. Therefore, it can be concluded that the presence of the PMMA polymer in larger contents in the polymer blends cannot improve the thermal stability. Thus, the respective thermal stability obtained by experimental TGA thermograms of the various PS₂/PMMA blends can be explained on the basis of these theoretical calculations of average dissociation energy of polymer molecules.

By using these thermograms, it is difficult to make a conclusion concerning the thermal stability of PS₂/PMMA/PS-*b*-PMMA blends. Two points may be addressed: (1) incorporating compatibilizer into the PS₂/PMMA blends may have enhanced the adhesion be-

TABLE V
Weight Loss (%) at Different Decomposition Temperatures for Various Ratios of PS₂/PMMA Blends at 30-min Blending

PS ₂ /PMMA	Weight loss (%)							
	200 (°C)	300 (°C)	350 (°C)	400 (°C)	420 (°C)	440 (°C)	450 (°C)	460 (°C)
100/0	0.03	0.31	1.86	15.59	33.34	81.72	94.78	99.30
90/10	0.12	0.78	1.98	16.78	38.53	79.98	95.11	99.38
80/20	0.13	0.82	3.35	25.94	50.58	88.35	97.83	99.45
70/30	0.14	0.83	3.55	31.89	56.54	90.35	98.30	99.58
60/40	0.15	0.85	4.37	38.92	64.16	93.12	98.78	99.59
50/50	0.18	0.85	4.58	44.45	69.81	94.82	99.17	99.78
40/60	0.23	0.85	4.80	47.93	74.65	96.25	99.44	99.85
30/70	0.26	0.86	4.85	51.85	79.88	97.68	99.63	99.88
20/80	0.27	0.87	5.17	56.73	84.95	98.68	99.77	99.92
10/90	0.28	0.88	6.32	81.67	97.95	99.89	99.92	99.93
0/100	0.29	0.89	6.68	86.29	99.30	99.94	99.94	99.94

TABLE VI
Weight Loss (%) at Different Decomposition Temperatures for Various Ratios of PS₂/PMMA/PS-*b*-PMMA Blends at 30-min Blending

PS ₂ /PMMA/ PS- <i>b</i> -PMMA	Weight loss (%)							
	200 (°C)	300 (°C)	350 (°C)	400 (°C)	420 (°C)	440 (°C)	450 (°C)	460 (°C)
100/0.0/0.0	0.03	0.31	1.86	15.59	33.34	81.72	94.78	99.30
87.3/9.7/3	0.06	0.50	1.28	13.44	23.38	46.60	62.78	80.54
77.6/19.4/3	0.07	0.58	1.35	14.86	31.70	56.29	72.10	87.21
67.9/29.1/3	0.07	0.59	1.38	18.41	38.36	62.77	77.37	90.99
58.2/38.8/3	0.08	0.61	1.46	23.35	46.37	71.45	85.10	95.73
48.5/48.5/3	0.15	0.60	1.56	26.17	51.74	76.47	88.22	96.90
38.8/58.2/3	0.15	0.64	1.58	27.94	54.63	80.21	91.32	98.15
29.1/67.9/3	0.16	0.65	1.58	33.61	62.73	87.11	95.83	99.33
19.4/77.6/3	0.16	0.65	1.60	33.99	66.45	91.09	97.58	99.58
9.7/87.3/3	0.18	0.69	1.68	36.76	70.81	94.18	98.71	99.77
0.0/100/0.0	0.29	0.89	6.68	86.29	99.30	99.94	99.94	99.94
0.0/0.0/100	0.19	0.47	1.92	36.24	65.82	93.37	98.44	99.45

tween the two phases. (2) The diblock copolymer may have decreased the phase separation between the PS and PMMA components inside the blends. It is far from complete for the theoretical understanding why the block copolymer protects thermal stability of the PS₂/PMMA blends, which requires greeter attention in the future.

CONCLUSIONS

In the study of PS/PMMA blends, two glass transition temperatures have been found, T_g (PS), associated with PS-rich regions, and T_g (PMMA), associated with PMMA-rich regions, using differential scanning calorimetry.

From the study of the effect of various blend compositions on T_g , ΔC_p , and phase composition, it can be concluded that PMMA dissolves more in the PS phase than does the PS₂ in the PMMA phase and increase the interfacial adhesion between PS and PMMA phases during processing.

From the study of the effect of PS-*b*-PMMA diblock copolymer addition on the miscibility of the PS₂/PMMA blends, the results suggest that the copolymer can slightly promote the solubility of PMMA phase in the PS phase.

From the study of thermal stability of PS₂/PMMA blends, it can be concluded that the PS-*b*-PMMA diblock copolymer offers protection against thermal degradation to PS₂/PMMA blends.

References

- Shultz, A. R.; Young, A. L.; Aless, S.; Stewart, M. J Appl Polym Sci 1983, 28, 1685.
- Lyngaae-Jørgensen, J.; Utracki, L. A. Makromol Chem, Macromol Symp 1991, 48/49, 189.
- Lyngaae-Jørgensen, J. J Macromol Sci-Phys 1998, B37, 239.
- Lyngaae-Jørgensen, J.; Rasmussen, K. L.; Chtcherbakova, E. A.; Utracki, L. A. Polym Eng Sci 1999, 39, 1061.
- Ton-That, C.; Shard, A. G.; Daley, R.; Bradley, R. H. Macromolecules 2000, 33, 8453.
- Chuai, C. Z.; Almdal, K.; Lyngaae-Jørgensen, J. Polymer 2003, 44, 481.
- Washiyama, J.; Kramer, E.; Hui, C. Y. Macromolecules 1993, 26, 2928.
- Maglio, G.; Palumbo, R. In Polymer Blends; Kryszewski, M.; Galeski, A.; Martuscelli, E., Eds.; Plenum: New York, 1982.
- Fayt, R.; Jerome, R.; Teyssie, P. Makromol Chem 1986, 187, 837.
- Noolandi, J.; Hong, K. M. Macromolecules 1984, 17, 1531.
- Paul, D. R. In Polymer Blends; Paul, D. R.; Newman, S., Eds.; Academic Press: New York, 1978; vol. 2, chap. 12.
- Fayt, R.; Jerome, R.; Teyssie, Ph. In Multiphase Polymers: Blends and Ionomers; Utracki, L. A.; Weiss, R. A., Eds.; American Chemical Society: Washington, DC, 1989; Chap. 2.
- Locke, C. E.; Paul, D. R. J Appl Polym Sci 1973, 17, 2719.
- Heikens, D.; Hoen, N.; Barentsen, W.; Peit, P.; Ladan, H. J Polym Sci Polym Symp 1978, 62, 309.
- Fayt, R.; Jerome, R.; Teyssie, Ph. J Polym Sci Polym Lett Ed 1981, 19, 79.
- Fayt, R.; Jerome, R.; Teyssie, Ph. J Polym Sci Polym Phys Ed 1981, 19, 1269.
- Fayt, R.; Jerome, R.; Teyssie, Ph. J Polym Sci Polym Lett Ed 1988, 26, 2209.
- Fayt, R.; Jerome, R.; Teyssie, Ph. Makromol Chem 1986, 187, 837.
- Fayt, R.; Jerome, R.; Teyssie, Ph. J Polym Sci Polym Lett Ed 1986, 24, 25.
- Fayt, R.; Jerome, R.; Teyssie, Ph. J Polym Sci Polym Lett Ed 1989, 27, 481.
- Patterson, H. T.; Hu, K. H.; Crindstaff, T. H. J Polym Sci Polym Symp 1971, 34, 31.
- Gailard, P.; Ossenbach-Sauter, M.; Riess, G. Makromol Chem Rapid Commun 1980, 1, 771.
- Gailard, P.; Ossenbach-Sauter, M.; Riess, G. In Polymer Compatibility and Incompatibility; Principles and Practice; MMI Symposium Series 2; Solc, K., Ed.; Harwood: New York, 1982.
- Anastasiadis, S. H.; Gancarz, I.; Koberstein, J. T. Macromolecules 1989, 22, 1449.
- Elemans, P. H. M.; Janssen, J. M. H.; Meijer, H. E. J Rheol 1990, 34, 131.
- Wahner, M.; Wolf, B. A. Polymer 1993, 34, 1460.

27. Kim, W. N.; Burns, C. M. *J Appl Polym Sci* 1986, 32, 2989.
28. Kim, W. N.; Burns, C. M. *J Appl Polym Sci* 1987, 34, 945.
29. Brinke, G. T.; Karasz, F. E.; Ellis, T. S. *Macromolecules* 1983, 16, 244.
30. Shultz, A. R.; Young, A. L. *J Appl Polym Sci* 1983, 28, 1677.
31. Chuai, C. Z.; Almdal, K.; Johannsen, I.; Lyngaae-Jørgensen, J. *Polym Eng Sci* 2002, 42, 961.
32. Krause, S.; Iskandar, M.; Iqbal, M. *Macromolecules* 1982, 15, 105.
33. Rodriguez-Parada, J. M.; Percec, V. *Macromolecules* 1986, 19, 55.
34. Ellis, T. S.; Karasz, F. E.; Brinke, G. T. *J Appl Polym Sci* 1983, 28, 23.
35. Fried, J. R.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* 1978, 11, 150.
36. Morese-Seguela, B.; Jacques, M. S.; Renaud, J. M.; Prudhomme, J. *Macromolecules* 1980, 13, 100.
37. Gaur, U.; Wunderlich, B. *Macromolecules* 1980, 13, 1618.
38. Orwoll, R. A. *Physical Properties of Polymers Handbook*; American Institute of Physics: Woodbury, 1996.
39. Chuai, C. Z.; Almdal, K.; Alstrup, J.; Lyngaae-Jørgensen, J. *Macromolecules*, submitted.
40. Gedde, U. W. *Polymer Physics*; Chapman and Hall: London, 1995.
41. Koning, C.; Van Duin, M.; Pagnoulie, C.; Jerome, R. *Prog Polym Sci* 1998, 23, 707.
42. Di Lorenzo, M. L.; Frigione, M. *J Polym Eng* 1997, 17, 429.
43. Chuai, C. Z.; Almdal, K.; Alstrup, J.; Lyngaae-Jørgensen, J. *Polymer*, submitted.
44. Couchman, P. R. *Macromolecules* 1978, 11, 1156.
45. Couchman, P. R. *Phys Lett* 1979, 70A, 155.
46. Wood, L. A. *J Polym Sci* 1958, 28, 319.
47. Boyer, R. F. *J Macromol Sci Phys* 1973, B7, 487.
48. Fox, T. G. *Bull Am Phys Soc* 1956, 1, 123.
49. Fried, J. R.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* 1978, 11, 150.
50. Kadariah, F. S.; Marlianti, I. *J Appl Polym Sci* 1983, 28, 3123.