Influence of Diblock Copolymer on the Morphology and Properties of Polystyrene/Poly(dimethylsiloxane) Blends

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ABSTRACT: Blends of polystyrene (PS) and poly(dimethylsiloxane) (PDMS), with and without diblock copolymers (PS-*b*-PDMS), were prepared by melt mixing. The melt rheology behavior of the blends was studied with a capillary rheometer. The morphology of the blends was examined with scanning electron microscopy. The miscibility of the blends was studied with differential scanning calorimetry. The morphology of PS/PDMS blends was modified by the addition of PS-*b*-PDMS copolymers and investigated as a function of the molar mass of the diblock copolymers, viscosity ratios and the processing conditions. As investigated, the observed morphology of the melt-blended PS/PDMS pair unambiguously supported the interfacial activity of the diblock copolymers. When a few percent of the diblock copolymers blended together with the PS and PDMS homopolymers, the phase size was reduced and the phase dispersion was firmly stabilized against coalescence. The compatibilizing efficiency of the copolymers was strongly dependent on its molar mass. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2747–2757, 2004

Key words: morphology; diblock copolymers; polystyrene; polysiloxanes; blends

INTRODUCTION

About 30% of all polymers sold today contain more than one polymer, and this fraction continues to increase each year.[1,2] Nearly all of these polymer–polymer blends are immiscible.[1–5] These samples are characterized by a two-phase morphology, a narrow interface, and poor physical and chemical interactions across the phase boundaries. As a consequence of this, immiscible blends often exhibit poor mechanical properties. Because these immiscible blends are thermodynamically unstable, control of the phase morphology during blend processing is a key issue for the production of new materials with improved properties compared with those of the constitutive immiscible polymers. The shape, size, and spatial distribution of the phase result from a complex interplay between viscosity of the phases, interfacial properties, blend composition, and processing conditions. To be used for many applications, the blend morphology must be stabilized during melt processing to prevent coalescence of the dispersed phase at high concentrations.[6] This process of stabilizing polymer blends is commonly called compatibilizing. A compatibilization strategy that is frequently proposed is the addition of a premade block copolymer composed of blocks that are each miscible with one of the homopolymers.[7] Theory suggests that block copolymers will prefer to span the interface.[8,9] Most experimental studies were carried out by casting from solution[10–12]; however, commercially, polyblends are prepared by melt mixing.

The efficacy of block copolymers in the compatibilization of immiscible polymer blends has been well established for several years, and has been proven through thermodynamic models[13–18] and experimentally.[19–24] In such a capacity, they are often known as interfacial agents, compatibilizers, or emulsifying agents because of their tendency to locate at the blend interface, to prevent coalescence between minor phase particles, and to improve the adhesion between phases.

There are several problems in compatibilizing multiphase structures with block copolymers in the melt. The viscosity of block copolymers is high, thus making them difficult to disperse.[25] These copolymers are typically expensive so it is desirable to minimize their concentration. Finally, block copolymers prefer to reside at the interface rather than form micelles or a separate phase.[26]

TABLE I
Characteristics and Sources of the Raw Materials

Sample code	$\overline{M}_w$[a] (kg/mol)	$\overline{M}_n$[a] (kg/mol)	$\overline{M}_z$[a] (kg/mol)	$\overline{M}_w/\overline{M}_n$	Density[b] (kg/m^3)	Grade and source
PS$_{N2000}$ (PS$_1$)	176.3	89.3	284.3	1.97	0.9795	N2000, Shell
PS$_{N3000}$ (PS$_2$)	242.7	121.8	365.8	1.99	0.9795	N3000, Shell
PS$_{N7000}$ (PS$_3$)	329.1	133.1	534.6	2.47	0.9795	N7000, Shell
PDMS-Bayer (PDMS$_1$)	260.6	164.2	373.2	1.60	0.84	BaysiLone-OEL, Bayer
PDMS-Dow (PDMS$_2$)	533.1	347.6	680.6	1.53	0.84	SGM-36 GUM, Dow Corning
PS-b-PDMS[c]						
B$_1$	9.79	9.28	10.3	1.05	—	Risø Laboratory
B$_2$	12.1	11.1	13.0	1.09	—	Risø Laboratory
B$_3$	22.7	19.7	26.0	1.08	—	Risø Laboratory
B$_4$	69.4	57.1	85.0	1.22	—	Risø Laboratory
B$_5$	157.2	130.5	183.3	1.20	—	Risø Laboratory

[a] Measured at Risø by SEC and the standard deviation on the molar mass was ± 3%.
[b] Derived from reference 28 at 180°C.
[c] The PS-b-PDMS diblock copolymers were symmetrical, 50 : 50 wt %.

Very recently, we carried out a systematic experimental investigation on the evolution of blend morphology, by SEM, during melt blending of two immiscible homopolymers in an internal mixer. The purpose of this study was to investigate the effect of adding small amounts of diblock copolymer in melt blends on the resulting morphology. We chose three polystyrenes (PS) and two poly(dimethylsiloxane)s (PDMS), which are available from commercial sources and studied the effect of the viscosity ratio (η_1/η_2) on the blend morphology. We observed the morphology of PS/PDMS blends melt-mixed with five symmetric diblock copolymers (PS-b-PDMS) having molar mass ranging from 10 to 157 kg/mol in this study. The block molar mass was varied so that we could determine whether an optimum block molar mass existed for minimizing the dispersed-phase drop size. A minimum drop size would be expected to provide the maximum interfacial area for block copolymer adsorption. By examining the nature of the block copolymers, we intended to produce well-dispersed stable blends of PDMS in a common thermoplastic such as PS with premade diblock copolymers and understand if and how these diblock copolymers functioned as compatibilizers. The miscibility and the melt rheology behavior of the blends in this study were investigated as well.

EXPERIMENTAL

Materials

The blends investigated in this study were based on three polystyrenes, supplied by Shell, two liquid silicone rubbers, poly(dimethylsiloxane) (PDMS) supplied by Dow Corning (Midland, MI) and Bayer (Leverkusen, Germany); and five diblock copolymers of styrene and dimethylsiloxane containing 50 wt % styrene (PS-b-PDMS), supplied by Risø National Laboratory of Denmark (Risø). The five diblock copolymers of PS-b-PDMS were synthesized by standard anionic polymerization techniques described elsewhere.[27] The properties and sources of these materials used in this study are shown in Table I. The five diblock copolymers are denoted B1, B2, B3, B4, and B5, respectively.

Blend preparation

The polymers were dried under vacuum at 60°C for 1 week. For each interfacial agent investigated, a series of blends was produced, with interfacial agent concentrations of 1–4% in volume. A series of PS/PDMS blends, with and without the diblock copolymers varying from 10 to 90 vol %, were prepared. Blends were prepared using a Brabender batch internal mixer (Brabender Plasticorder; C. W. Brabender Instruments, South Hackensack, NJ) at a temperature of 180°C for 15 min mixing at a rotor speed of 50 rpm (using a Walzerkneter Type-60 mixing head having a chamber volume of about 60 mL). In all experiments a total of 60 mL mixtures of PS/PDMS blends, with and without a PS-b-PDMS diblock copolymer, was weighed according to the density of each component at 180°C. The PS, PDMS, and interfacial agent (PS-b-PDMS) were gradually loaded into a preheated internal mixer. After mixing, the material was quenched in cool water to freeze in the morphology. Samples were cut into a cubic shape. The length, width, and thickness of the cubic specimens were about 6, 6, and 5 mm, respectively. An extraction technique was required to remove the PDMS phase from the samples to provide contrast for most of the SEM observations. By morphological characterization of these samples and an-

nealing (at 180°C for 30 min annealing in a vacuum oven) we studied the effects of long-time coalescence.

Size-exclusion chromatography

The molar mass average of the PDMS was measured using size-exclusion chromatography (SEC) in toluene with PDMS standards, whereas PS and PS/PDMS blends were measured in tetrahydrofuran (THF) with PS standards. A Viscotek 200 SEC (Viscotek, Houston, TX) was used at 25°C with two Waters columns (2 × HT 6E; Waters Chromatography Division/Millipore, Milford, MA). The product concentration was 2 mg/mL, the flow rate was 1 mL/min, and the injection volume was 100 μL. The molar mass average was calculated using the calibration and the "Q-factor correction" method.

Rheological measurements

A Rosand precision capillary extrusion rheometer (Model RH-7, Rosand Precision Ltd.) 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}) in the double-bore mode. The Rabinowitsch correction was applied in calculating the wall shear stress. Additional data related to the melt viscosities were equilibrium torque values measured for all the blends after the set mixing time during their melt blending in the Brabender mixer.

Scanning electron microscopy

The morphology characterization was carried out in two ways.

1. Microscopic observation of the remaining phase with scanning electron microscopy (SEM). In this study, a selective extraction technique was used to provide contrast for the morphology observation of the continuous or dispersed state of each phase. Hexane was used as selective solvent to dissolve the PDMS phase. After extracting, the samples were dried at 45°C under vacuum for 1 week. It would be pointless to remove the PS phase because PDMS is a liquid above its T_g temperature (–127°C). In the present study, the microstructure of the PDMS phase was judged only by results of the selective dissolution of the PDMS phase and microstructure observation of the PS phase.
2. Macroscopic observation without extraction for determining the dispersed state of each phase and the influence of the added block copolymers. The fracture surfaces were prepared at liquid nitrogen temperature and observed by
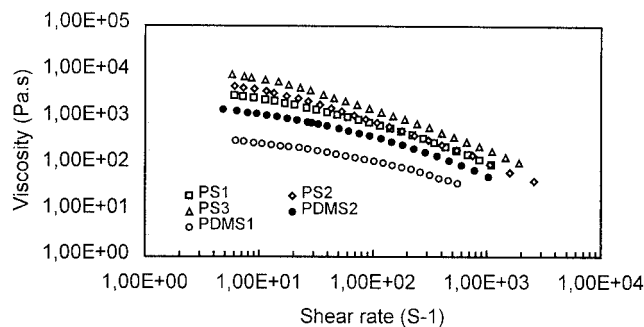

Figure 1 Viscosity as a function of shear rate at 180°C for PS and PDMS from capillary rheometry.

SEM. No preferential staining was necessary because of the higher electron density of the silicon in the PDMS, which caused the siloxane segments to appear dark under brightfield SEM condition.[29] After coating the samples with a 25-nm gold layer to prevent charge build-up at the surface, the morphology was observed using a JEOL Model JSM-5900 microscope (JEOL, Tokyo, Japan) at accelerating voltages of 10 and 15 kV. Scale bars are given at the bottom of each micrograph.

Differential scanning calorimetry

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; TA Instruments, New Castle, DE). Temperature calibration was performed using indium [T_m = 156.61°C, heat of Fusion (ΔH_f) = 28.71 J/g], mercury (T_m = −38.87°C, ΔH_f = 11.3 J/g), and tin (T_m = 231.928°C, ΔH_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 180°C to remove the effects from previous processing followed by cooling to −150°C and heating again to 180°C. Thermal transition was determined from the second DSC scan. The inflection point of the specific jump of a thermal scan was taken as the glass-transition temperature.

RESULTS AND DISCUSSION

Binary PS/PDMS blends

The melt viscosity of pure polymers at 180°C, as measured with a capillary rheometer, is given in Figure 1. The dependencies of the torque on the components of the blends are seen in Figure 2. Comparing these two
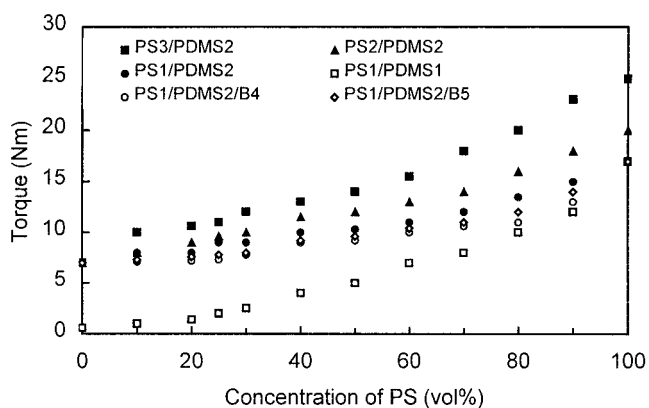
Figure 2 Dependency of the torque at the end of mixing on concentration of PS for $PS_i/PDMS_i$ and $PS_1/PDMS_2/B_i$ blends.

characteristics, it is evident that the component PS_3 has the highest viscosity, whereas $PDMS_1$ has the lowest viscosity. The blends of $PS_1/PDMS_2/B_4$ and $PS_1/PDMS_2/B_5$ have nearly identical torques.

The high immiscibility of PS and PDMS impedes a fine dispersion during melt blending, whatever the characteristics of the homopolymers used (Table I). Figure 3(a)–(d) show the SEM images of the PS phase in $PS_3/PDMS_1$ blends after hexane extraction of the PDMS phase, wherein the viscosity of PS_3 is much

higher than that of PDMS1 (see Figs. 1 and 2). When the morphology was investigated after melt blending in a Brabender laboratory mixer at 180°C for 15 min, a cocontinuous phase structure was observed in all four blends inn the range $0.20 \leq \varphi_{PS3} \leq 0.70$ indicating phase cocontinuity in this volume fraction interval (where φ_i is the volume fraction of component i). That situation is quite general and largely independent on the viscosity characteristics of the commercial PS and PDMS used. In that respect, Figure 3 shows the continuous PS phase that is left in $PS_3/PDMS_1$ blends after the selective solubilization of PDMS by hexane; indeed it means that, even at low PS and PDMS contents, both PS and PDMS form a cocontinuous phase after 15 min of melt blending. The cocontinuous morphologies are formed not in a single volume fraction but rather over a wide range of volume fractions; the range of the volume fraction depends on the viscosity ratios and the processing conditions of the blend compositions. The investigation that we examined, on the evolution of phase continuity and inversion of PS/PDMS blends, is described elsewhere.[30]

Figure 4(a) and (b) show the SEM images of the $PS_3/PDMS_1$ (90/10) blends before and after annealing, showing the PS phase after the extraction of the PDMS phase. It can be seen from Figure 4(a) that $PS_3/PDMS_1$ (90/10) blend morphology, in the absence of any block copolymer, developed rapidly into PDMS droplets
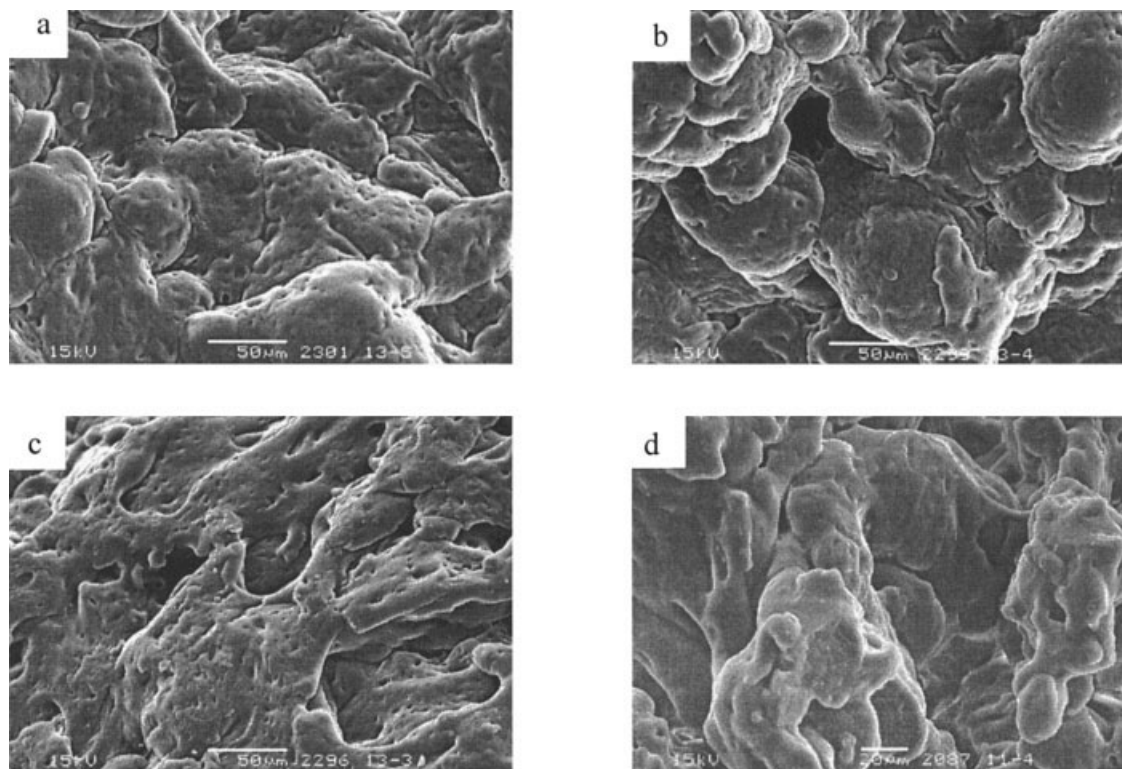

Figure 3 SEM images of PS phase after PDMS extraction in 15 min mixed $PS_3/PDMS_1$ blends: (a) $\varphi_{PS3} = 0.2$, (b) $\varphi_{PS3} = 0.3$, (c) $\varphi_{PS3} = 0.5$, (d) $\varphi_{PS3} = 0.7$.
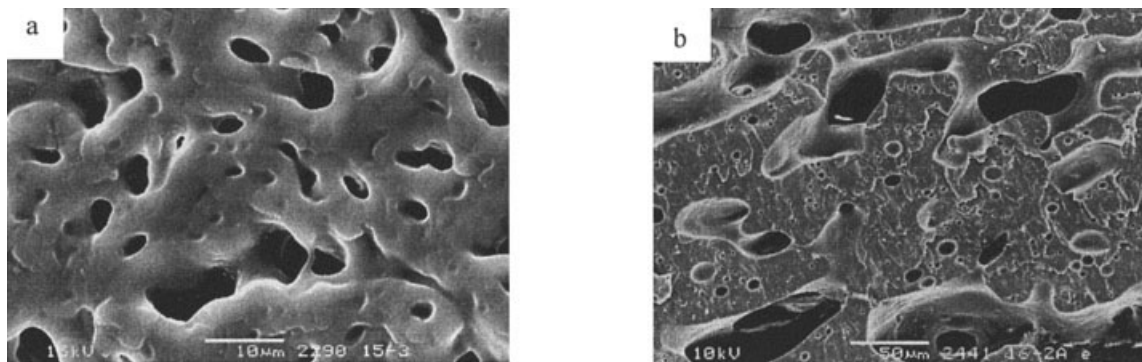
Figure 4 SEM images of PS phase after PDMS extraction in 15 min mixed $PS_3/PDMS_1$ (90/10) blend before and after annealing: (a) before annealing, (b) after annealing.

within the PS matrix after 15 min of mixing. Subsequent static annealing of the blend for 30 min at 180°C resulted in a dramatic coarsening of the PDMS droplets. In the SEM image of Figure 4(b), a remarkable growth of the phase domain was found in $PS_3/PDMS_1$ (90/10) blends after annealing compared to that of the nonannealed blends [Fig. 4(a)]. The mean size of the dispersed PDMS phase was increased four- to fivefold [the scale bar of Fig. 4(b) is fourfold that of Fig. 4(a)] to reach approximately 40 μm or more when the blend was annealed at 180°C for 30 min, which means that the morphology of $PS_3/PDMS_1$ blends is obviously quite unstable and strongly dependent on the thermal history after melt blending.

Effect of PS-*b*-PDMS copolymers on the particle dimensions

The investigation of PS/PDMS blends supports the need to improve the interfacial situation. It has been well established in the literature that the addition of suitable block or graft copolymers to immiscible polymer blends is responsible for a significant decrease of the particle dimensions.[31] In our study PS-*b*-PDMS copolymers can confirm that general behavior, as evidenced by the strong decrease of the particle size in blends of PS with PDMS. Figure 5(a)–(h) show the continuous PS phase with and without the diblock copolymer B_4 that remains in $PS_i/PDMS_2$ (80/20) blends after the selective solubilization of PDMS by hexane. Compared to the blends of $PS_1/PDMS_2$ [Fig. 5(a)], $PS_2/PDMS_2$ [Fig. 5(c)], and $PS_3/PDMS_2$ [Fig. 5(e)], in the absence of any block copolymer, the mean particle size of the dispersed PDMS phase is reduced six- to tenfold to reach approximately 4 μm or less for blends of $PS_1/PDMS_2$ [Fig. 5(b)], 2 μm or less for $PS_2/PDMS_2$ [Fig. 5(d)], and 6 μm or less for $PS_3/PDMS_2$ [Fig. 5(g)] when 2% of B_4 copolymer is added to the blends. That beneficial effect is observed in each blend, although its extent depends on the viscosity

ratios (η_{PS}/η_{PDMS}) of the blends and the content of the block copolymer.

As a rule, the particle size decreases when the relative amount of the diblock copolymer increases. It is noteworthy that the major effect is observed at the addition of 1% of the B_4 copolymer in $PS_3/PDMS_2$ blend [Fig. 5(f)], whereas addition of 4% of the B_4 copolymer [Fig. 5(h)] no significant modification results, which means that addition of a diblock copolymer as low as 1% is sufficient to modify the particle size and the interfacial boundary region. Added in such very small amounts, the block copolymer may form bridges between the two phases.

Stabilization effect provided by PS-*b*-PDMS copolymer against coalescence

As previously discussed, the melt blending of PS and PDMS results in unstable dispersions of phase, which coalesce upon subsequent static annealing at 180°C for 30 min [Fig. 4(b)]. To prevent the coalescence of the PDMS droplets, we added 3% B_1, B_2, B_3, B_4, and B_5 diblock copolymers to the $PS_1/PDMS_2$ (77.6/19.4) blends. Figures 6(a)–(j) and 7(a) and (b) show morphologies of the PS phase, respectively, extracted from $PS_1/PDMS_2/B_i$ and $PS_1/PDMS_1/B_4$ blends by hexane. After 15 min of mixing, addition of B_3 [Fig. 6(e)] and B_5 [Fig. 6(i)] altered the blend morphology with respect to the $PS_1/PDMS_2$ blend containing no block copolymer [Fig. 5(a)]. Addition of B_1 [Fig. 6(a)], B_2 [Fig. 6(c)], or B_4 [Fig. 6(g)] produced significantly smaller PDMS particles. However, by adding B_4 to the $PS_1/PDMS_1$ (77.6/19.4) blend the PDMS particle size was reduced only slightly [Fig. 7(a)].

After annealing, the $PS_1/PDMS_2/B_1$ blend [Fig. 6(b)], $PS_1/PDMS_2/B_2$ blend [Fig. 6(d)], and $PS_1/PDMS_1/B_4$ blend [Fig. 7(b)] morphologies coarsened significantly. The mean particle size of the dispersed PDMS phase increased very approximately to 40 μm or more for the $PS_1/PDMS_2/B_1$ blend, 35 μm or more
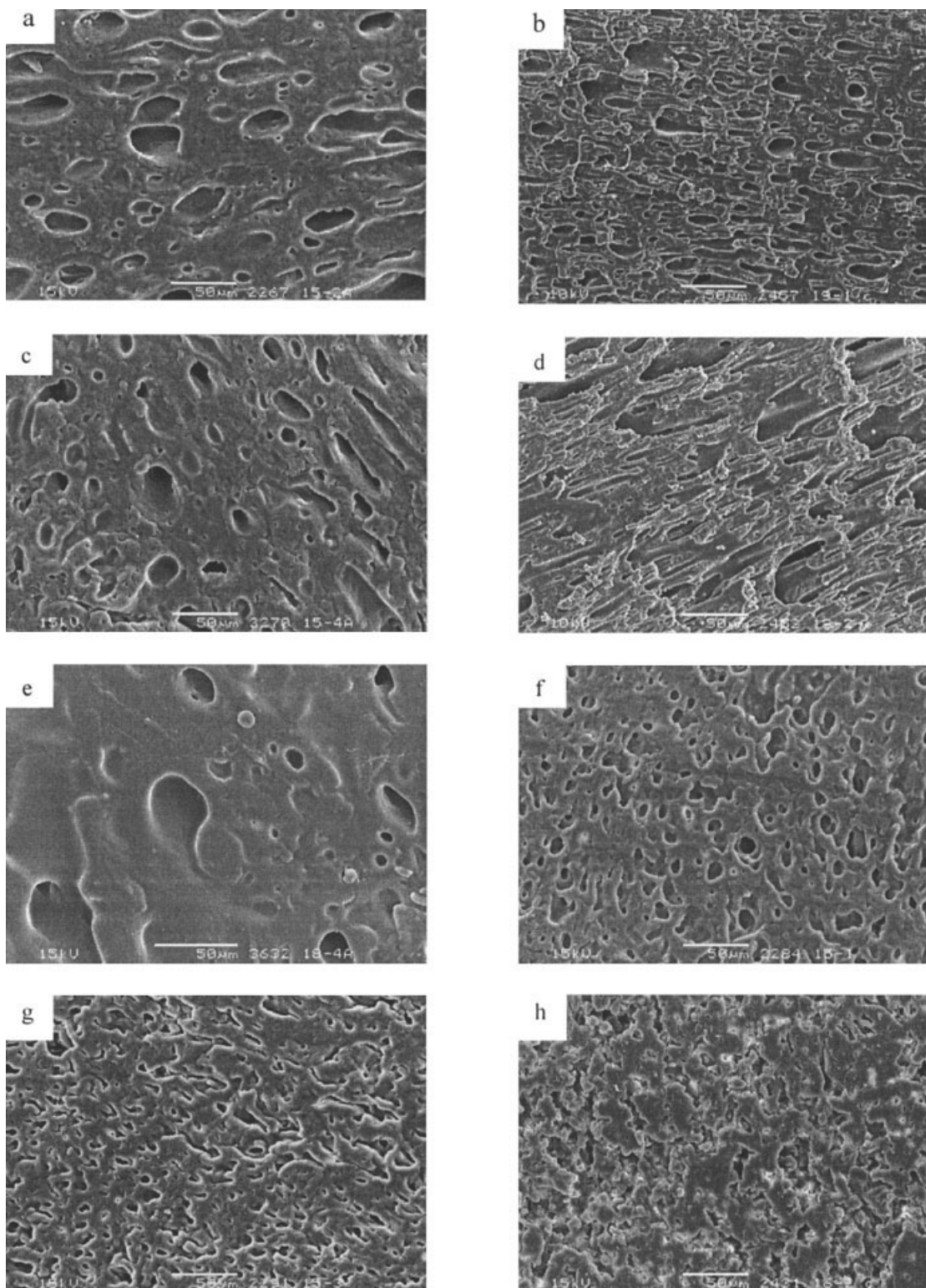
Figure 5 SEM images of PS phase after PDMS extraction in 15 min mixed $PS_i/PDMS_2$ and $PS_i/PDMS_2/B_4$ blends: (a) $PS_1/PDMS_2$ (80/20), (b) $PS_1/PDMS_2/B_4$ (78.4/19.6/2), (c) $PS_2/PDMS_2$ (80/20), (d) $PS_2/PDMS_2/B_4$ (78.4/19.6/2), (e) $PS_3/PDMS_2$ (80/20), (f) $PS_3/PDMS_2/B_4$ (79.2/19.8/1), (g) $PS_3/PDMS_2/B_4$ (78.4/19.6/2), (h) $PS_3/PDMS_2/B_4$ (76.8/19.2/4).

for the $PS_1/PDMS_2/B_2$ blend, and 50 μm or more for the $PS_1/PDMS_1/B_4$ blend. The $PS_1/PDMS_2$ blends containing B_1 and B_2 consisted of rough interfaces

after annealing [Fig. 6(b), (d)]. This may indicate that B_1 and B_2 exhibited interfacial activities in preventing dynamic coalescence during melt blending. However,

Before annealing

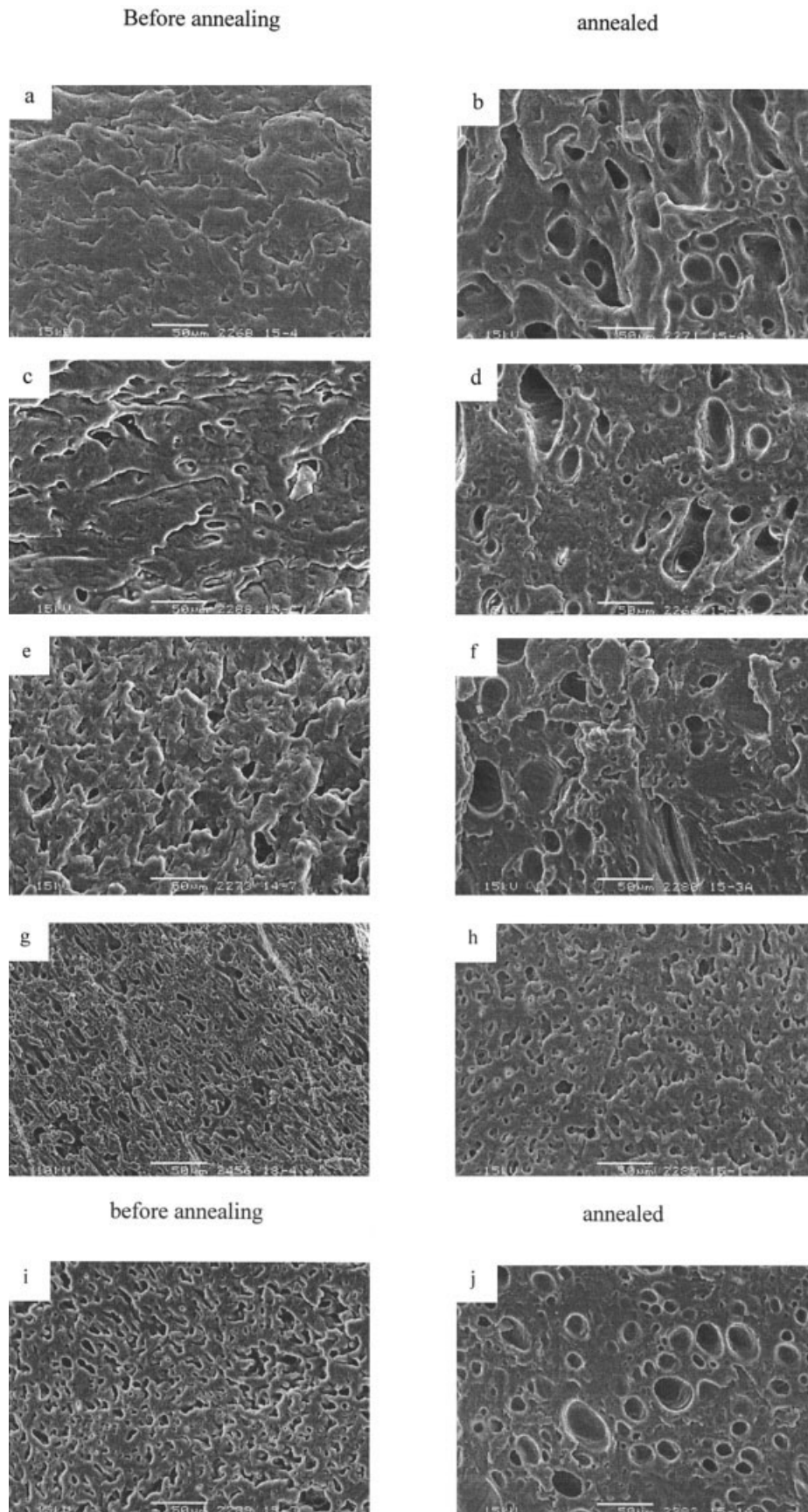annealed

before annealing

annealed

Figure 6 SEM images of PS phase after PDMS extraction in 15 min mixed $PS_1/PDMS_2/B_i$ (77.6/19.4/3) blends before and after annealing: (a) and (b) $PS_1/PDMS_2/B_1$, (c) and (d) $PS_1/PDMS_2/B_2$, (e) and (f) $PS_1/PDMS_2/B_3$, (g) and (h) $PS_1/PDMS_2/B_4$, (i) and (j) $PS_1/PDMS_2/B_5$.
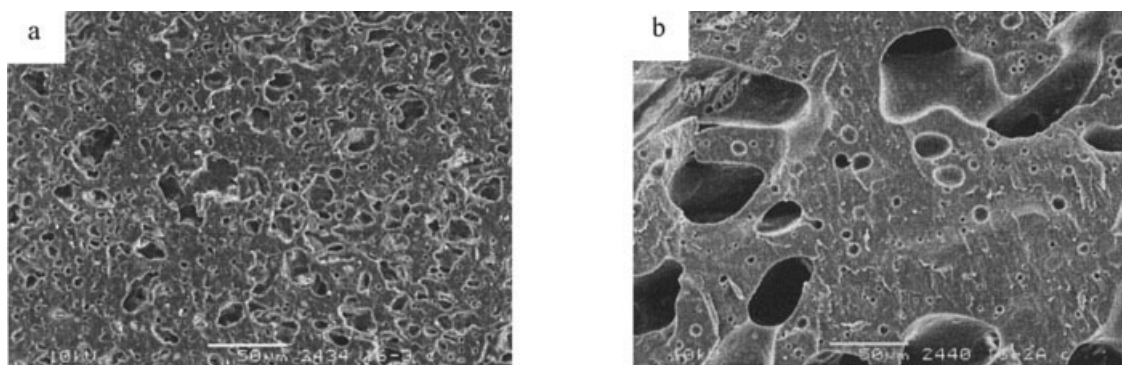
Figure 7 SEM images of PS phase after PDMS extraction in 15 min mixed $PS_1/PDMS_1/B_4$ (77.6/19.4/3) blends before and after annealing: (a) before annealing, (b) after annealing.

because of their low molar mass, they are not sufficient to be entangled with the constitutive chains and may be squeezed out from the interface during annealing. The $PS_1/PDMS_1/B_4$ blend marginally coarsened [Fig. 7(b)], whereas the $PS_1/PDMS_2/B_4$ blend was stable [Fig. 6(h)], although its as-mixed morphology was relatively coarse. It suggests that the morphologies of the blends very depend on viscosity ratios of the blends and the molar masses of the diblock copolymers. The morphology of the $PS_1/PDMS_2/B_3$ blend [Fig. 6(e)] was similar to that of the $PS_1/PDMS_2/B_5$ blend [Fig. 6(i)] after 15 min of mixing, although both blends coarsened significantly after annealing [Fig. 6(f), (j)]. The mean particle size of the dispersed PDMS phase increase very approximately to 30 μm or more for $PS_1/PDMS_2/B_3$ and 25 μm or more for $PS_1/PDMS_2/B_5$ blends. For the $PS_1/PDMS_2$ blend series, it appears that an optimal diblock copolymer molar mass of approximately 69 kg/mol stabilizes the morphology.

On the other hand, it seems that the other compatibilizers do not stabilize the interface against particle coalescence, at least not during annealing. The probable explanation is that the molecules of the copolymer may move away from the interface during annealing

to form micelles or other structures. This conclusion is supported by the increasing particle size during annealing.

Direct observation of the location of the added block copolymers

The average reduction of the particle diameter of the PDMS and PS phases, respectively, in the phase-separated system agrees with the determinate role that PS-*b*-PDMS copolymers play in the interfacial region. This conclusion is supported by the morphology of PS/PDMS blends modified by PS-*b*-PDMS diblock copolymers. Figure 8(a) and (b) show the images of the PS_1 phase after $PDMS_2$ extraction in $PS_1/PDMS_2/B_i$ (77.6/19.4/3) blends for 15 min of mixing. The white spots in Figure 8 correspond to micelles, whereas the dark holes correspond to PDMS particles that have been removed after extraction using hexane solvent. The micelles of B5 [Fig. 8(b)] appear slightly larger, as expected, than those of B4 [Fig. 8(a)] after 15 min of mixing. The particles observed in Figure 8(a) are nearly all spherical, but the particles observed in Figure 8(b) are nearly all nodular. Unfortunately, it is not possible to observe micelles in the PDMS droplets
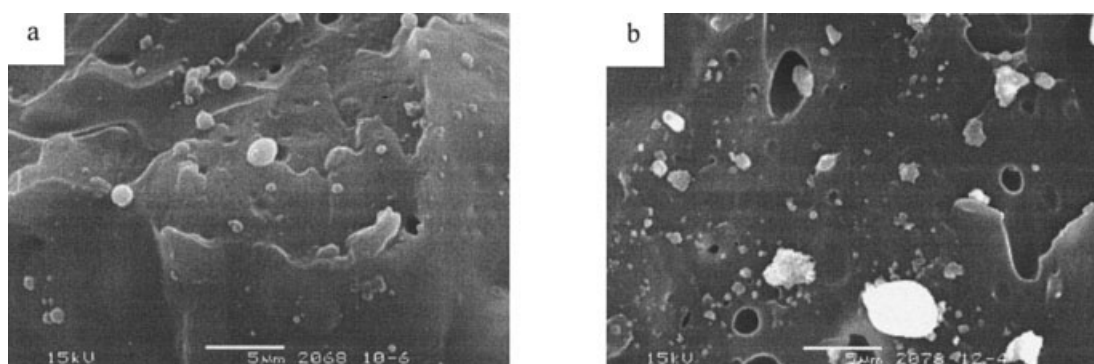

Figure 8 SEM images of PS phase after PDMS extraction in 15 min mixed $PS_1/PDMS_1/B_i$ (77.6/19.4/3) blend: (a) $PS_1/PDMS_2/B_4$, (b) $PS_1/PDMS_2/B_5$.

TABLE II
T_g, T_m, and ΔC_p of PS$_1$/PDMS$_2$ Blends at 180°C for 15 min of Mixing

PS$_1$/PDMS$_2$	T_g of PS phase (°C)	T_g of PDMS phase (°C)	T_m of the blends (°C)	ΔC_p of PS phase (J g^{-1} °C^{-1})	ΔC_p of PDMS phase (J g^{-1} °C^{-1})
100/0	90.54	—	—	0.3482	—
90/10	95.35	−125.37	−41.68	0.3030	0.0180
70/30	100.92	−126.76	−44.70	0.2393	0.0671
50/50	103.34	−125.34	−43.88	0.1480	0.0520
30/70	104.56	−123.80	−44.07	0.1327	0.0889
20/80	107.08	−122.20	−42.43	0.0785	0.1091
10/90	108.72	−122.25	−42.95	0.0332	0.1041
0/100	—	−127.37	−42.87	—	0.1368

because PDMS is a liquid at temperatures above its T_g and seeps out of the samples, appearing as dark cavities in the images.

To our best knowledge, the SEM observation is of great significance with regard to the location and the possible surface activity of the block copolymer. It is observed that a block copolymer cannot penetrate completely into the corresponding homopolymer phases. The extent of penetration of the different copolymers is dependent on their molar mass. Gaylord[32] suggested that, in the case of high molar mass copolymers where the molar mass of the copolymer is >150 kg/mol, macromolecular interactions such as chain entanglements hinder the complete penetration of each segment into the corresponding homopolymer phases. This further suggests that the copolymers cannot penetrate completely into the homopolymer phases and, therefore, it is expected that part of the copolymer may remain at the interface.

Effect of copolymer on blend miscibility

It is clear that adding an AB copolymer to a simple mixture of A and B homopolymers enhances the compatibility but cannot improve the miscibility of the homopolymer mixture. These results in our study obtained by DSC are in good agreement with those in

Patterson and Robard.[33] The main DSC results are summarized in Tables II and III. One can see that, for the blends, two glass transitions to PS and PDMS exist. No significant differences can be observed between the modified and unmodified blends in the same composition of the PS/PDMS blends. The incompatibility of the two systems is substantial and the blends reflect the superposition of the two phases: the glass transition (T_g) and heat capacity (ΔC_p) of PDMS in pure PDMS and in the blends are unchanged. The same observation can be made with the ΔC_p of PS; the glass transition of PS is even higher for the blends than for pure PS. This indicates that addition of the compatibilizer does not alter the level of miscibility. In other words, incorporation of the compatibilizer does not promote molecular level miscibility.

The above results correspond to the investigation made by Paul and Newman,[31] who suggest that, if two polymers are far from being miscible, then no copolymer is likely to make a one-phase system. In a completely immiscible system, the main role of the copolymer is to act as an interfacial agent.

There are two explanations for the increasing T_g values of both PS$_1$ phase and PDMS$_2$ phase with increasing volume fraction of PDMS in the blends. (1) The initial increase in T_g for PS could be attributable to the migration of low molar mass impurities (styrene

TABLE III
T_g, T_m and ΔC_p of PS$_1$/PDMS$_2$/B$_4$ Blends at 180°C for 15 min of Mixing

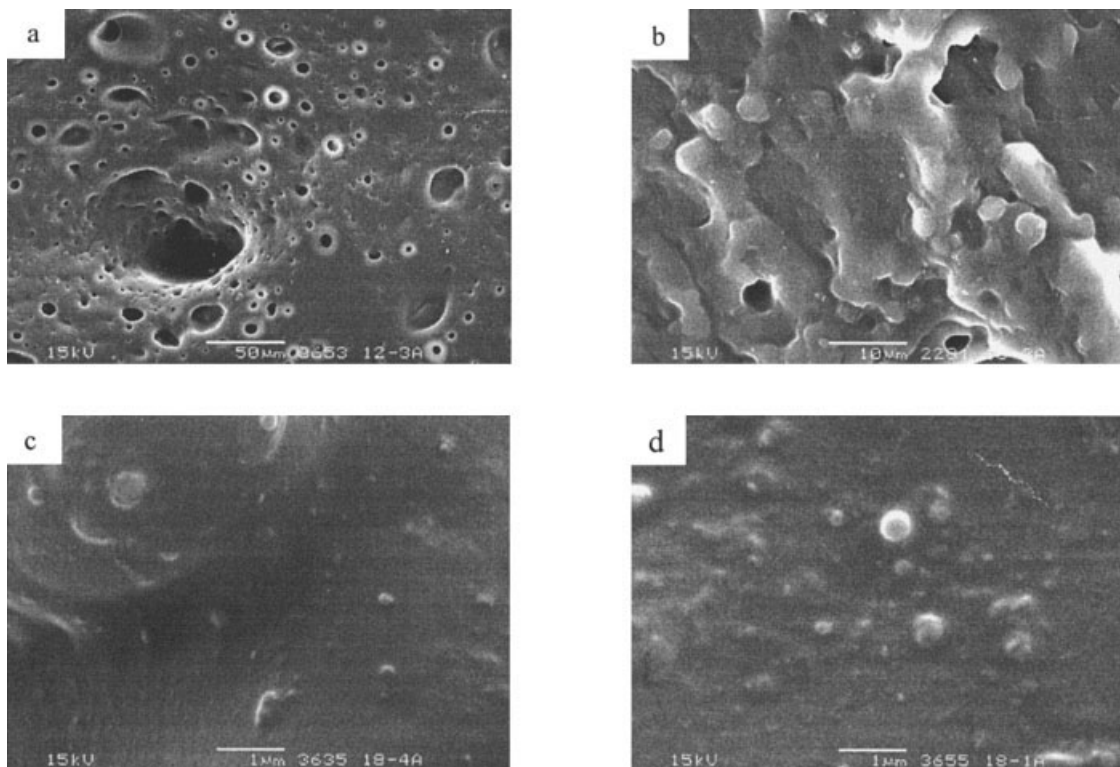| PS$_1$/PDMS$_2$/B$_4$	T_g of PS phase (°C)	T_g of PDMS phase (°C)	T_m of the blend (°C)	ΔC_p of PS phase (J g^{-1} °C^{-1})	ΔC_p of PDMS phase (J g^{-1} °C^{-1})
100/0.0/0.0	90.54	—	—	0.3482	—
87.3/9.7/3	96.19	−126.70	−41.90	0.3145	0.1431
67.9/29.1/3	100.98	−126.45	−44.49	0.2529	0.0871
48.5/48.5/3	103.32	−125.86	−43.20	0.1719	0.0917
29.1/67.9/3	106.23	−126.06	−43.54	0.1037	0.1176
19.4/77.6/3	106.57	−124.13	−44.27	0.0876	0.1406
9.7/87.3/3	103.02	−121.75	−43.00	0.0290	0.1318
0.0/100/0.0	—	−127.37	−42.87	—	0.1368
0.0/0.0/100	94.37	−135.08	−47.67	0.0771	0.1143

Figure 9 SEM images of obtained from the cryogenically fractured surface of $PS_1/PDMS_2$ (80/20) and $PS_1/PDMS_2/B_i$ (77.6/19.4/3) blends: (a) no block copolymer after 15 min mixing, (b) added with 3% B_5 after 15 min mixing, (c) added with 3% B_4 after 5 min mixing, (d) added with 3% B_4 after 15 min mixing.

monomer, antioxidant, etc.) into the PDMS phase. (2) PS_1 is the sample with the lowest number average molar mass. PS_1 has a molar mass distribution with a tailing toward the low molar mass species, whereas $PDMS_2$ has a much higher molar mass. Our interpretation of the observation in Table II is that the PDMS phase simply acts as an extraction medium for low molar mass species from the PS phase, whereas the PDMS is insoluble in the PS phase. Consequently T_g's measured for the PS phase will tend toward the asymptotic limit for PS samples when their molar mass tends to infinity, whereas the T_g's of the PDMS will increase because material with a higher glass-transition temperature is mixed with the PDMS phase.

Interfacial adhesion of the PS/PDMS blends

The immiscibility of PS and PDMS promotes the (desired) segregation of phases but is also responsible for poor adhesion between the phases. The lack of interfacial adhesion is a barrier to efficient transfer of stress between the phases. Thus enhancement in the degree of compatibility between the homopolymers seems necessary and may be sought by addition of a third component that reduces the number of unfavorable contacts between segments of the two polymers. The use of diblock copolymers is now commonly used: (1)

to increase the degree of dispersion of one phase in another; (2) to improve the adhesion at the phase boundaries, thus proving enhanced stress transfer; and (3) to stabilize the dispersed phase against coalescence.[1,11,31,34–36]

A deeper insight into the interfacial situation is provided by SEM micrographs of fracture surfaces prepared at liquid nitrogen temperature. Figure 9(a)–(d) depict the SEM images of the cryogenically fractured surface of $PS_1/PDMS_2$ (80/20) blends, with and without diblock copolymer. The lack of adhesion between PS and PDMS is obvious from the examination of Figure 9(a), wherein dispersed particles do not adhere to the matrix and leave cavities with a smooth (clear) surface. This phase morphology is modified by addition of a diblock copolymer. Just like the phase size reduction, the enhancement of the interfacial adhesion depends on molar mass of the added block copolymer. Figure 9(b)–(d) compare the fractured surfaces of $PS_1/PDMS_2$ (68/29) blends added with 3% diblock copolymers B_4 or B_5. From Figure 9(b)–(d), the SEM images of the fractured surfaces clearly show that block copolymer in an amount as low as 3% is sufficient to modify both the particle size and the interfacial boundary region of $PS_1/PDMS_2$ blends. Added in such very small amounts, the block copolymer may form bridges between the phases to such an extent

that the observed particles are not flung away during the breaking process. Based on morphological observation, one can also see the great influence of the molar mass of the added block copolymers. B_4 appears to be an optimum molar mass of the PS-*b*-PDMS copolymer that gives the smallest particle diameter [Fig. 9(c), (d)] compared to the one with B_5 [Fig. 9(b)].

The conclusion is to be assessed by the extent of the interfacial activity of the diblock copolymers that the particle size of the nodules and their adhesion to the matrix may both change with the addition of quite small amounts of the diblock copolymer.

CONCLUSIONS

The results presented showed that the addition of properly chosen diblock copolymers had a great influence on the morphology of binary PS/PDMS blends. The investigation of the morphology of PS/PDMS blends supported the interfacial activity of PS-*b*-PDMS copolymers. The compatibilizing efficiency of the copolymer was strongly dependent on its molar mass and the viscosity ratios of the blends. As a consequence, the domain size was significantly reduced, the interfacial adhesion was increased, and the phase dispersion with a 69 kg/mol block copolymer was firmly stabilized against coalescence during subsequent thermal annealing.

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