Effects of Thermal History on the Interfacial Layer of PS/HDPE/SBS Blends

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ABSTRACT: Polystyrene (PS), high-density polyethylene (HDPE), and a triblock copolymer of styrene, butadiene, and styrene (SBS) were melt-mixed and quenched from the melt state into liquid nitrogen, ice water, room-temperature water, and boiling water. Several specimens quenched into liquid nitrogen were annealed at elevated temperatures. The samples that underwent different thermal histories were examined with TEM, and the effects of cooling rate, annealing time, and annealing temperature on the interfacial layer structure were investigated. In the melt-mixed PS/HDPE/SBS blend a mixture of SBS and PS was situated between the PS and PE phases, forming an interfacial layer encapsulating the PE particles. In the sample prepared by quenching the melt into liquid nitrogen, the interfacial layer between the PS and HDPE phases was about 200 nm thick. Two thin SBS layers on the both sides of the interfacial layer were observed. The SBS separated from the PS and PE phases, forming a thinner interfacial layer under slow cooling or annealing conditions. The interfacial layer improved the interfacial bonding of PE to PS; however, the slow cooling rate or the long annealing time resulted in weakening of the bonding between the PE particle and the interfacial layer.

Introduction

Polymer blends are multiphase materials and are normally produced by melt mixing of two or more polymers.[1,2] Polymer blending has become a prosperous commercial practice because it can produce materials with excellent physical properties at low costs. In multiphase polymeric blends, the interfacial layer plays an extremely important role because it controls the adhesion between the different phases, the morphology of the dispersed phase, and the mechanical properties of the blends. Most polymers are mutually immiscible because of the large dimension of their molecules and weak mutual interaction. A multiphase material without strong interfacial bonding will exhibit inferior mechanical properties because stresses cannot be efficiently transferred between the phases. Thus, different compatibilization techniques have been developed for the production of immiscible polymer blends.

One way to compatibilize immiscible polymer blends is the addition of a block or graft copolymer.[3−6] Ideally, the copolymer possesses two different blocks that are identical to or miscible with the two components to be blended. It is believed that the block copolymer at the interface will promote the interfacial interaction and reduce the interfacial tension of the immiscible components and therefore improve the interfacial bonding. It is normally accepted that the compatibility of a block copolymer depends on its molecular weight, block composition, and molecular architecture. To achieve sufficient cohesive forces at the interface, the segments of the block copolymer should be long enough to penetrate into the domains of the homopolymers.[3,4] In polymeric blends the interface between different phases should have a certain thickness and is often referred to as an interfacial layer or a transition layer.

It has been shown that a compatibilizer can reduce the size of the dispersed phase, produce a uniform distribution of the dispersed phase, and stabilize the morphology of the blend.[5−12] However, in some cases, the effect of compatibilizers was found to be temperature dependent. In a blend of polypropylene (PP), polystyrene (PS), and a styrene−butadiene−styrene triblock copolymer (SBS), Fortelny and Michalkova[13] found that the addition of SBS reduced the average size of the dispersed particles but did not enhance the uniformity of the dispersed phase when the processing temperature was 190 °C. The uniformity of the phase structure was improved as the processing temperature was elevated, and the blends with a uniform phase structure could be achieved at a mixing temperature of 250 °C. It was also found that postforming processes, such as annealing, would strongly affect the mechanical properties of PS/PE/poly(styrene−ethylene−butylene−styrene) copolymer (SEBS) blends.[14] The variation of dimensions of the dispersed phases with annealing time has been observed in several polymer blends.[5,7,15]

The miscibility of polymers is temperature dependent. The structure of the interfacial layer of a polymer blend is thus also expected to be temperature dependent. However, owing to the high viscosity of polymer melts, the morphology of the polymer blend will depend on its thermal history. In a study of a linear low-density PE and PS blend compatibilized by a hydrogenated poly(butadiene-*b*-isoprene-*b*-styrene) triblock copolymer, Fayt et al.[16] observed that the interfacial layer measured by transmission electron microscopy (TEM) was about 10 nm thick. For a blend of ethylene−propylene copolymer (EP) and polypropylene (PP) compatibilized by EP-*g*-iPP,[17] the thickness of the interfacial layer determined by TEM was about 20 nm. In a blend of Nylon, poly(styrene-*co*-maleic anhydride), and poly(styrene-*co*-acrylonitrile), Yokioka and Inoue[18] observed that the thickness of the interfacial layer varied with annealing

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time, and at the late stage, the thickness of the interfacial layer could vary from 10 to 50 nm. Recently, Zhao and Huang[15] investigated solution-cast films of blends of poly(butylene) (PB) and poly(methyl methacrylate (PMMA) compatibilized by a PB-*b*-PMMA copolymer. After the PB homopolymer was selectively removed from the PMMA matrix with a solvent, the TEM results indicated that the average dimension of the interfacial layers was on the order of 25 nm. In the annealed films, Zhao and Haung found that the dispersed PB phase coalesced and became coarse, but the variation of the interfacial layer structure caused by annealing has not be reported. The objective of this work was to study the effects of thermal history on the interfacial layer of a PS/HDPE/SBS blend. The stability of the interfacial layer was investigated by annealing the samples at high temperatures because the stability of the interfacial layer is extremely important for reproducibility of the some of the mechanical properties of polymer blends.

Experimental Section

Materials. The raw materials used in the present work were PS (Dow, USA, PS 685D), HDPE (Philips, USA, HMMPE), and SBS (Yueyang Petrochemical Co., China, SBS 791). The PS and SBS were supplied in granular form while the HDPE was in powder form. The number-average and weight-average molecular weights of HDPE and PS were measured respectively with a high-temperature Waters 150C gel permeation chromatography (GPC) system and a regular GPC. The HDPE was dissolved in 1,2,4-trichlorobenzene at 160 °C. The number-average and weight-average molecular weights were 20 400 and 144 700, respectively, for the HDPE and 92 900 and 297 000, respectively, for the PS. The content of styrene in the copolymer was 30 wt %, and the number-average molecular weight of the PS and PB blocks was 8500 and 39 700, respectively, while the total weight-average molecular weight of the copolymer was 152 600.

Preparation of Samples. A blend consisting of 72 parts (by weight) of PS, 18 parts of HDPE, and 10 parts of SBS was prepared. The compounding was performed on a Haake twin-screw extruder operated at 15 rpm. The temperatures in the three zones of the extruder were 170, 190, and 215 °C, while the die temperature was set at 205 °C. After compounding, the extrudate was cooled in water at 20 °C and pelletized. To ensure that the HDPE and SBS were dispersed uniformly, the pellets were run through the extruder again. After preheating in a hot press at 180 °C for 5 min, the compound was compression-molded into disks of 1.0 mm thick and 20 mm in diameter. The disks were kept at 180 °C for 3 min, and then the compression-molded disks were quenched from the melt state into various temperature baths, including liquid nitrogen, ice water, room-temperature water (20 °C), and boiling water. Finally, the disks were allowed to equilibrate naturally to room temperature in the different cooling baths. A few specimens, which were prepared by quenching into liquid nitrogen, were annealed at 75 or 105 °C for different periods of time in an oven. The annealed specimens were transferred to 400 mL of 75 °C water or boiling water and cooled to room temperature naturally. The specimens after different heat treatment processes were studied by TEM.

Embedding and Trimming. Thin strips with a cross section of about 0.2×0.2 mm^2 were cut from the center of the compression-molded disks. The thin strips were embedded in an epoxy resin and cured at 35 °C for 1 week. The embedded specimens were trimmed first with razor blades by hand then with a glass knife on a Reichert-Jung Ultracut R microtome. After trimming, samples with an extremely smooth surface could be obtained.

Ruthenium Tetroxide Staining. The materials used to prepare the staining agent were sodium periodate ($NaIO_4$) and hydrated ruthenium dioxide ($RuO_2 \cdot 2H_2O$) supplied by Johnson Matthey, USA, in powder form. The solution of ruthenium tetroxide for staining was prepared in situ by the oxidation of ruthenium dioxide by a saturated aqueous solution of sodium periodate.[19,20] For staining, the trimmed specimens were exposed to ruthenium tetroxide vapor in a sealed test tube for 48 h at room temperature. After staining, the specimens were washed in a 3% aqueous solution of sodium periodate and then in distilled water and finally dried in a desiccator.

TEM Examination. A Reichert-Jung R microtome was adopted for ultrathin microtomy. After a top layer of approximately 500 nm was removed from the stained sample, ultrathin sections about 60 nm thick were prepared with a diamond knife at room temperature and a cutting rate of 1.0 mm/s. The ultrathin sections were mounted on 200-mesh copper grids and dried in a desiccator. The TEM study of the stained sections was performed on Philips CM 20 and JEOL JEM-100 CX II transmission electron microscopes. An accelerating voltage of 80 kV was used.

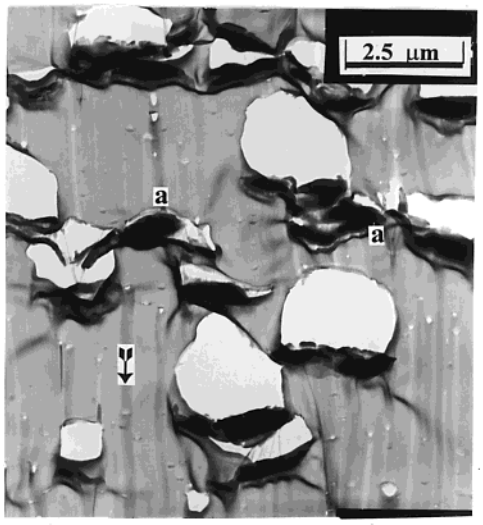
Results and Discussion

After staining with ruthenium tetroxide, the PS, HDPE, and SBS phases in the PS/HDPE/SBS (72/18/10) blend could be distinguished easily under TEM because SBS absorbed more ruthenium tetroxide and thus would appear as the darkest areas in the TEM view. The HDPE phase is identified by its lamellae. Figure 1A shows a micrograph of the blend after staining for 48 h in RuO_4 vapor. The PS and HDPE are the continuous and discrete phases, respectively, whereas SBS is found to be located between the PS and HDPE phases. Figure 1B shows the morphology of a PS/HDPE (82/18) blend without SBS. In this section of the blend, the HDPE particles cannot be observed; instead, many holes are seen. On the bottom side of the holes, a dark area is observed. The knife marks on the micrograph indicate that the microtomy direction was downward, as indicated by the arrow. It is believed that the HDPE particles were present in the same positions as the holes before microtomy. But owing to the poor bonding of the HDPE phase to the PS matrix, the HDPE slices were torn off from the PS matrix during microtoming. They folded up at the bottom of the holes and appear as a dark area in the TEM micrograph because of their larger mass thickness in the viewing direction.

On the basis of the fact the solubility parameter of PS is about 9.0 $[cal/cm^3]^{0.5}$ while that of PE is about 8.0 $[cal/cm^3]^{0.5}$,[21] it would be expected that strong interfacial bonding cannot be achieved when these two polymers are blended together without the addition of a compatibilizer. The SBS comprises PS and PB blocks. The solubility parameter of PB is about 8.3 $[cal/cm^3]^{0.5}$, which is close to that of PE. It is obvious that PS, PE, and SBS are not miscible to form a single phase down to the molecular level. However, it is anticipated that at the processing temperature SBS will form a fine dispersion in both the PE and PS phases. As the melt cools, phase separation will occur—most of SBS will be expelled from the PS and PE phases, forming an interfacial layer or small particles in the PS and PE phases. Therefore, in PS/HDPE blends, the SBS could act as a compatibilizer and improve the adhesion between PS and HDPE. To investigate the fine structure of the interfacial layer in the blends prepared under different cooling conditions, the blends were quenched from the melt into different cooling media, and the morphology of the samples was studied by TEM.

Effect of Cooling Rate. The blend quenched in liquid nitrogen was stained and examined with TEM. Figure 2 shows that the HDPE is dispersed as particles

(A)



(B)

Figure 1. TEM micrographs of (A) PS/HDPE/SBS (72/18/10) blend and (B) PS/PE (82/18) blend, samples stained in a RuO_4 vapor for 48 h. The arrow represents the microtomy direction.

with the dimension of about 2 μm in the PS matrix. The HDPE particles are enveloped with a deep gray interfacial layer. The detailed structure of the PE particles and the interfacial layers are shown in Figure 2B,C at higher magnifications. Inside the PE particles, lamellae about 10 nm thick are observed. The morphology of the lamellae, as shown in Figure 2C, is characteristic of PE lamellae that twist along their length direction.[22] Although the sample was prepared by quenching the melt into liquid nitrogen, crystallization has occurred in the PE phase. This is attributed to the fast crystallization rate and the low glass transition temperature of PE (−100 °C[21]). Therefore, even when the sample was quenched in liquid nitrogen, the PE molecules had enough time to crystallize before reaching the glassy state due to the poor thermal conductivity of polymers.

Inside the PE particles, a few dark spots can be observed, as marked by "b" in Figure 2B. The size of the dark spots varies from 30 to 100 nm in diameter. A few fine dark spots in the scale of several nanometers can also be identified, and they become larger after annealing (cf. later section). Also, some small light gray

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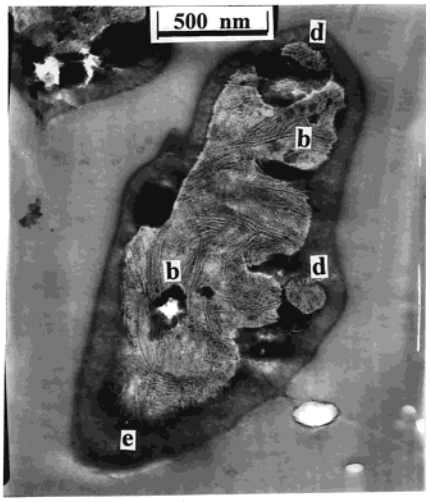

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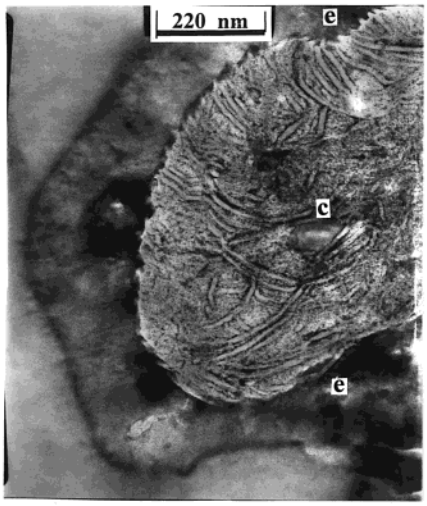


(C)

Figure 2. TEM micrographs of the PS/HDPE/SBS (72/18/10) blend quenched from the melt to liquid nitrogen: (A) a general view; (B) a view of a PE particle and the surrounding interfacial layer; (C) the detailed structure of the interfacial layer.

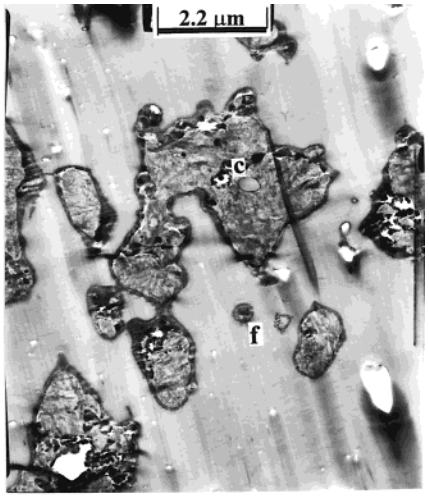
domains of about 100 nm wide have been found in some PE particles, as marked by "c" in Figure 2C. The dark spots are believed to be small SBS particles while the

light gray domains are attributed to a mixture of PS and SBS. The fine SBS particles inside the PE phase suggest that SBS forms a very fine dispersion (smaller than a few nanometers) in HDPE at the processing temperature. SBS was expelled from the PE phase during the subsequent cooling process due to crystallization of PE and the decrease of the temperature. Some of the larger dark spots have a void in their centers. The formation of the voids probably resulted from the contraction of volume in the sample during quenching. In the quenching process, no molding pressure was applied on the specimens as temperature decreased and crystallization took place. Voids might thus emerge inside the PE particles. In Figure 2C, PE lamellae are shown to penetrate into the interfacial layer, as marked by "e". The interaction of the PE lamellae with the interfacial layer may help to improve the adhesion between them.

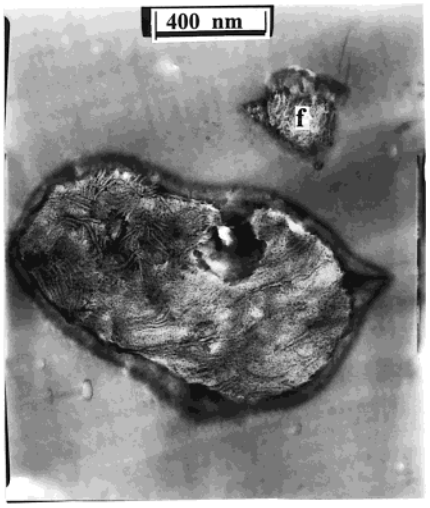
An interfacial layer between the PE particles and the PS matrix, which varies from 100 to 250 nm in thickness, is identified. The color of the interfacial layer is not uniform. The interfacial layer consists of two outer dark layers sandwiching a middle gray layer. These two dark layers are identified as a region of the highest SBS concentration in the interfacial layer. As the temperature decreases, the SBS is expelled from the mixture of PS and SBS as well as from the mixture of HDPE and SBS, producing two darker layers. However, whether these thin SBS layers were formed during quenching or embedding (at a temperature of 35 °C for 7 days) has yet to been determined. The middle portion of the interfacial layer is darker than the PS matrix but lighter than the SBS phase. We posit that the interfacial layer is a mixture of SBS and PS because we cannot see any possibility of having PE in this region owing to the absence of PE lamellae. In some interfacial layers PE particles less than 100 nm can be found (marked by "d" as shown in Figure 2B).

Figure 3 shows TEM micrographs of the sample of the PS/HDPE/SBS (72/18/10) blend prepared by quenching the melt into ice water. The overall morphology of the sample is similar to that of the sample prepared by quenching the melt into liquid nitrogen. The HDPE is dispersed as particles in the PS matrix and is encapsulated by an interfacial layer. A few small deep gray spots (marked by "f" as shown in Figure 3A) can be found in the PS matrix. They should not be taken as evidence that another new phase or domain of PS and SBS have been generated in the blend. They were formed when the cutting plane passed near the top of a PE particle, and the mixture of SBS and PS as an encapsulating layer over the PE particle was sectioned. This small region of a mixture of PS and SBS appears as a deep gray spot in the section.

Although the thickness of the interfacial layer, as shown in Figure 3, still ranges from 100 to 250 nm, the SBS layers on the two sides of the interfacial layer seem to become thicker and darker, especially for the layer adjacent to the PE phase. At a high magnification (cf. Figure 3C) it was found that the interfacial layer consists of a large number of extremely fine black and white dots. The density of the black dots decreases gradually while moving from the PE phase to the PS phases. In Figure 3C, the black dots represent the PB-rich domains while the white dots represent the domains of a mixture of the PS blocks of the SBS and PS. It is a well-known fact that PB is immiscible with PS



(A)



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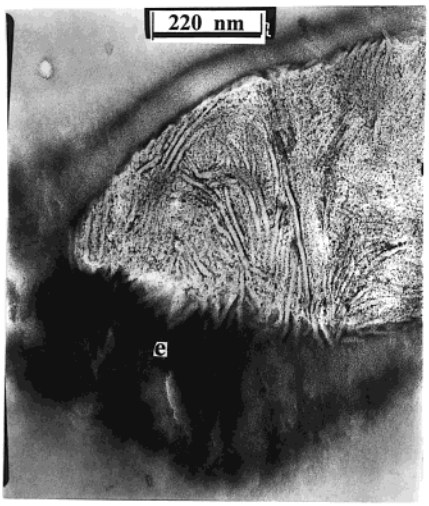


(C)

Figure 3. TEM micrographs of the PS/HDPE/SBS (72/18/10) blend quenched from melt to ice water: (A) a general view; (B) a view of a PE particle and the surrounding interfacial layer; (C) the detailed structure of the interfacial layer.

at room temperature, and phase segregation of PS and PB exists within the SBS. In the solution-cast sample of SBS with 30 wt % of PS component,[23] the PS component may be present as spheres, cylinders, or

lamellae in the PB matrix in the scale of 10 nm, depending on the solvent, thickness, thermal history, and other factors. On the basis of the TEM results in the present work, it is difficult to predict the morphology of the blend in the melt state. One may suggest that the SBS molecules are aligned with the PB segments toward the PE phase and the PS segments toward the PS phase in melt state. But this suggestion needs more experimental evidence to support. Nevertheless, if phase segregation exists in the melt state, the dimension of the phases should not be larger than a few nanometers because the PB domains that are smaller than this dimension have been imaged in the sample. Similar fine black and white dots are found in the sample prepared by quenching the melt into liquid nitrogen, but they are not as clear as those found in the sample prepared by quenching the melt into ice water. Evidently, in the case of cooling in ice water, the PB and PS blocks had more time to segregate before the movement of molecular chains was frozen; therefore, the segregated phase structure of SBS is more obvious. Similarly, SBS had more time to diffuse out from the PE and PS phases, forming a thicker SBS layer on both sides of the interfacial layer.

When the blend is put into 20 °C water, the cooling rate is further reduced. As shown in Figure 4, the interfacial layer becomes much darker due to the segregation of SBS from the PS and PE phases. In the previous samples, darker layers are present on the both sides of the interfacial layer. In this sample, however, only a single dark layer of about 50−100 nm in thickness between the PE and PS phases is observed. It should be pointed out that the PB and PS blocks of SBS still separate in this interfacial layer; however, the individual PB domains cannot be imaged when their number is large in the viewing direction. Only when the concentration of the PB domain is low and when the PB domains do not overlap in the viewing direction can the segregated PB domains be distinguished. Figure 4C shows that the interfacial layer becomes lighter when moving from the PE to PS phases, indicating a decrease in the concentration of the PB domains. As the concentration of the PB domain decreases, the fine individual PB domains are visible in the regions near the PS matrix. In this sample, the segregated PB domains could still be found in some regions where the dimension of the interfacial layer is large, as marked by "g" in Figure 4C. In this region, fine black PB domains and white PS domains can be clearly seen. Several larger white spots can also be found in this region. These large white spots are strong evidence that PS precipitated from a mixture of SBS and PS when the sample was cooled in 20 °C water. Figure 4B,C shows that the interfacial layer consists of not only SBS and PS but PE lamellae as well, as marked by "e". Some of these PE lamellae are extended from the PE phase. The detailed structure of this interfacial layer offers an explanation that SBS can be used as a compatibilizer for PE and PS blends, improving the interfacial bonding.

Figure 5 shows the morphology of the sample prepared by putting the melt into boiling water and then was cooled naturally to room temperature in a beaker. At such a slow cooling rate, HDPE crystallized into thicker lamellae. The thickness of the lamellae is about 25 nm while that of the lamellae in the sample quenched by liquid nitrogen or ice water is about 10 nm. In this sample, larger SBS domains with a hole in their center

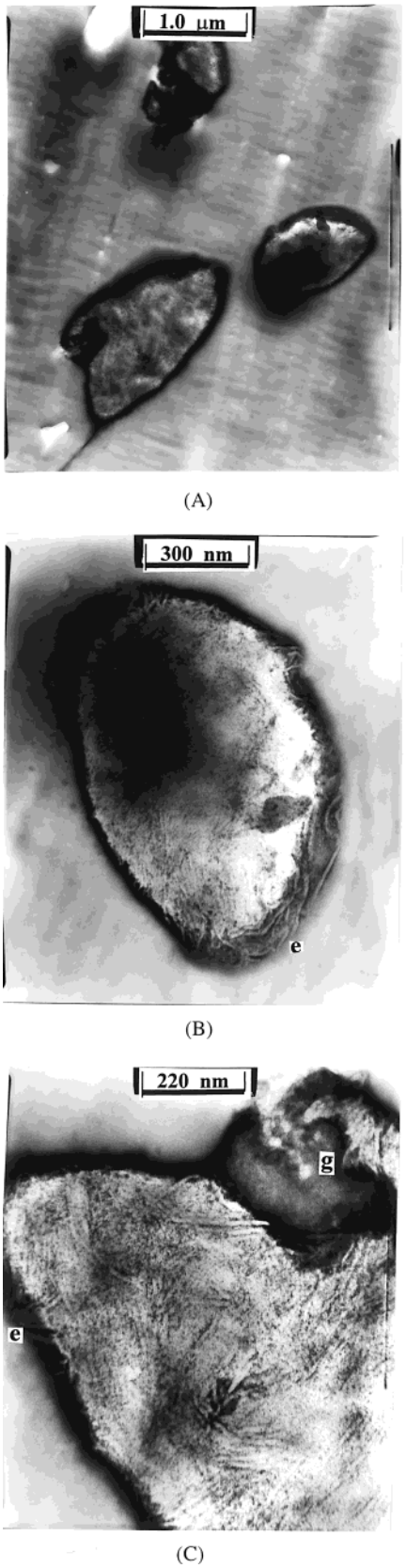
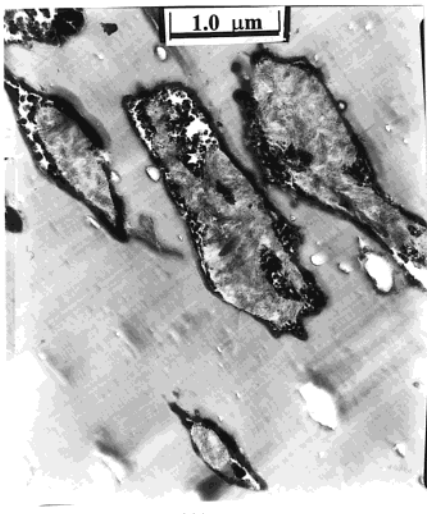
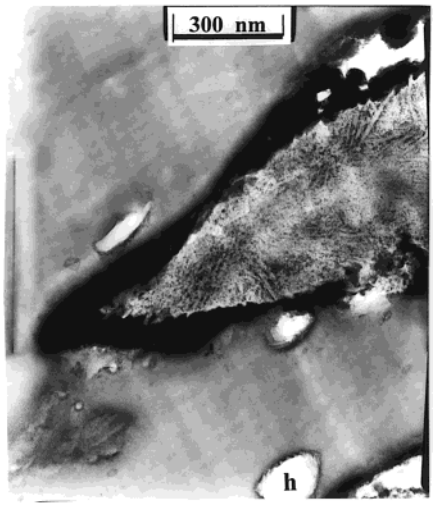


Figure 4. TEM micrographs of the PS/HDPE/SBS (72/18/10) blend quenched from the melt to water at 20 °C: (A) a view of PE particles and the surrounding interfacial layer layers; (B) and (C) the detailed structure of the interfacial layer.

are observed in the PE phase, marked by "b" in Figure 5C. During crystallization, less dense domains or voids were formed within the PE phase due to the contraction of volume as a result of crystallization. The SBS



(A)



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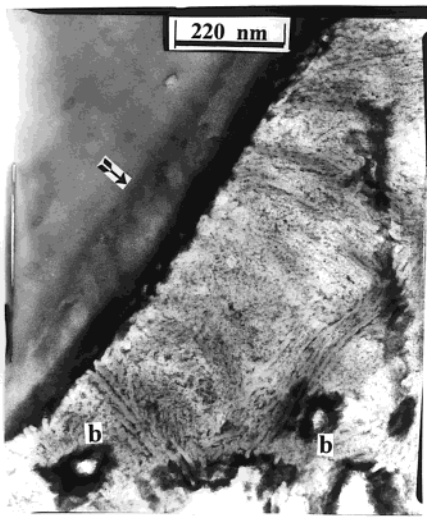

(C)

Figure 5. TEM micrographs of the PS/HDPE/SBS (72/18/10) blend transferred from the hot press to boiling water and cooled naturally: (A) a view of PE particles and the surrounding interfacial layers; (B) and (C) the detailed structure of the interfacial layer.

separates from the PE phase as the temperature decreases, leading to the formation of a SBS layer around the voids. The voids in the interfacial layer can also be caused by the contraction stress.

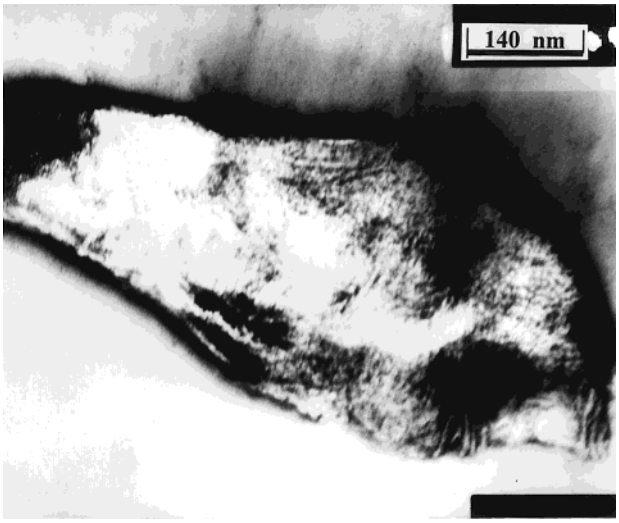

Figure 6. TEM micrographs of the PS/HDPE/SBS (72/18/10) blend quenched from the melt to liquid nitrogen and annealed at 75 °C for 48 h.

Again the interfacial layer in this sample as marked by the arrow in Figure 5C is similar to that in Figure 4. However, the interfacial layers seem to become weaker, and some broken interfacial layers are observed in the stained sections. On closer examination, it was found there are some remnants of PE lamellae in the broken interfacial layer (marked with "h" as shown in Figure 5B). It is believed that the damage to the interfacial layer was initiated from the noncrystallized materials between the PE lamellae near the interfacial layer. The investigation of the effect of molecular weight of block copolymers on the compatibility of polymer blends indicated that high molecular weight blocks prefer to form fine particles (micelles) in the matrix and low molecular weight blocks prefer to stay at the interface.[4,24] However, only the segments of the block copolymer, which entangle with the homopolymer chains, can provide strong mechanical links between the phases. Perhaps, more low molecular weight SBS was accumulated near the PE side of the interfacial layers at slow cooling rates, leading to the formation of weaker regions in the interfacial layers.

Effect of Annealing. To study the effect of annealing on the interfacial layer, several specimens, which were prepared by quenching the melt in liquid nitrogen, were annealed at elevated temperatures. The structural changes caused by annealing were examined under TEM. Figure 6 shows a TEM micrograph of a sample annealed at 75 °C for 48 h. After annealing, the interfacial layer becomes thinner and its gray color becomes deeper. The thickness reduces from around 200 nm to about 40 nm. The structure of the interfacial layer of the annealed sample is similar to that of the sample quenched from the melt to 20 °C water (cf. Figure 4.). During annealing at 75 °C, the separation of SBS from the mixture of PS and SBS as well as from the mixture of PE and SBS was further enhanced.

Figure 7 shows the structure of the interfacial layer of the specimen annealed at 105 °C for 24 h. A comparison of this sample with the unannealed sample (cf. Figure 2) indicates that the interfacial layer of the annealed sample is thinner, and the boundary of the interfacial layer next to the PS phases appears rather

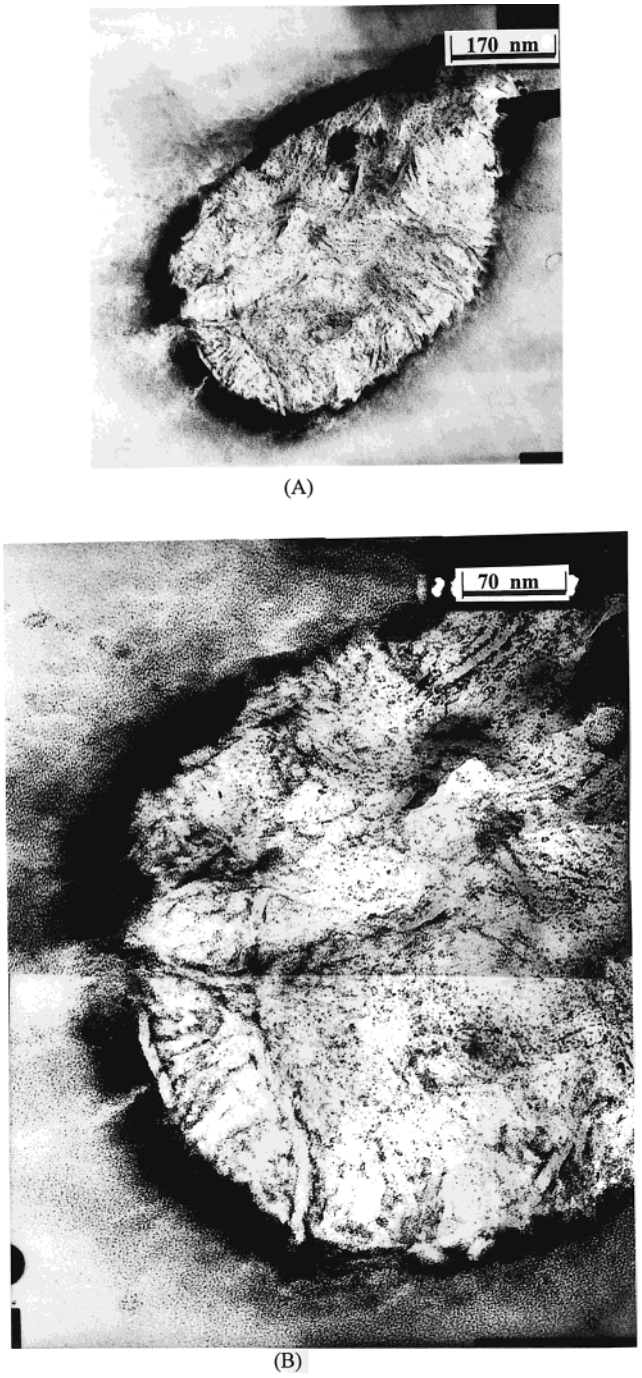

Figure 7. TEM micrographs of PS/HDPE/SBS (72/18/10) blend quenched from the melt to liquid nitrogen and annealed at 105 °C for 24 h: (A) a PE particle and the interfacial layer; (B) detailed structure of the interfacial layer.

blurred. On a closer examination, it has been found that the interfacial layer consists of PB domains and PS domains of 2−3 nm in size, as shown in Figure 7B. The concentration of the PS and PB domains decreases and increases, respectively, moving from the PS matrix toward the PE phase. Near the PE phase, the SBS forms a thin layer. A similar interfacial layer structure has been observed in a PB/PMMA/PB-*b*-PMMA blend.[15] In that solution-mixed blend, the block copolymer (PB-*b*-PMMA) formed a continuous layer around the dispersed PB particles. The thickness of PB-*b*-PMMA layer was about 25 nm. Discrete particles of the copolymer with a particle size ranging from 5 to 15 nm were also found in PMMA matrix. On the basis of Balazs' theory,[24] the

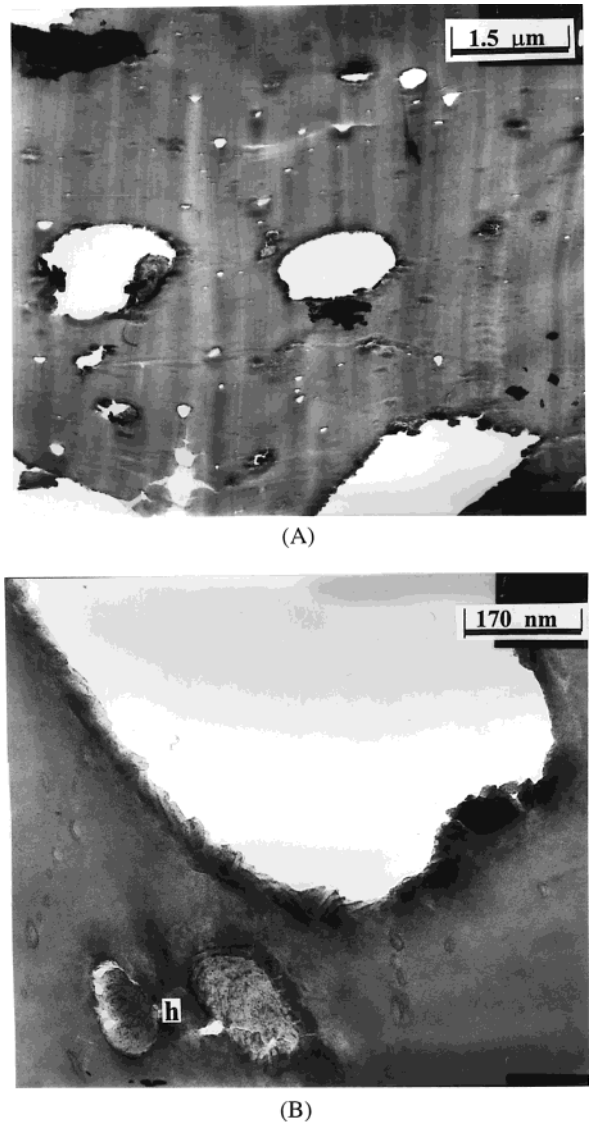

Figure 8. TEM micrographs of the PS/HDPE/SBS (72/18/10) blend quenched from the melt to liquid nitrogen and annealed at 105 °C for 48 h: (A) some PE slices were tore of from PS; (B) a broken interfacial layer.

discrete particles were believed to be the higher molecular weight copolymer. However, the discrete particles of the copolymer in the present work are much smaller than those found in the solution-mixed blend. The difference in the particle size may be attributed to the difference in the molecular architecture or, perhaps, to the different mixing methods. In solution blending the components easily attain the thermodynamic equilibrium state, but in the melt blended system it is more difficult for the polymer components to attain the equilibrium state because of the high viscosity of polymer melt. At this time it is difficult to conclude whether the discrete SBS domains are composed of the copolymer with a higher molecular weight. But this is highly probable because the longer the molecules are, the higher the molecular entanglement is, leading to a slower diffusion rate of SBS.

When the specimen was annealed at 105 °C for a longer period of time, the interfacial layer seems to become weak in some regions. For the sample annealed at 105 °C for 48 h the overall structure of the interfacial layer is similar to that for the sample placed in boiling water (cf. Figure 5), and some interfacial layers are

broken. Furthermore, a few holes appear on the stained sections, as shown in Figure 8. Though these PE slices has been torn off from the PS matrix, the PE lamella blocks could be observed near the ring of the holes at a high magnification, as shown in Figure 8B. In the PE particle marked by "h" in Figure 8B, one can see that the PE particle is being detached from the interfacial layer that is still adhering to the PS matrix. This suggests that adhesion of the interfacial layer to PS matrix is stronger than the adhesion of the interfacial layer to PE. These results suggest that the interface in this system is not stable subject to long-term high-temperature aging. Cross-linking between the PB and PE may be a viable method to stable the interface of this blend.[25]

Conclusion

SBS forms a very fine dispersion (domain size less than a few nanometers) in the PS and PE phases at 200 °C. As temperature decreases, SBS is expelled from the PS and PE phases and migrates toward the interface. In the melt mixed PS/HDPE/SBS blend, a mixture of SBS and PS situates between the PS and PE phases and forms an interfacial layer encapsulating the PE particles. The interfacial layer can be about 200 nm at fast cooling rates. However, the structure of the interfacial layer changes with cooling rate or annealing time, and the interfacial layer coarsens and its thickness decreases under slow cooling or annealing conditions due to segregation and migration of SBS. The interfacial layer improves the adhesion of the PE phase to the PS matrix. But slow cooling rates or long periods of annealing time will result in extensive phase separation between the SBS and PE, resulting in poor adhesion between the interfacial layer and PE phase.

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