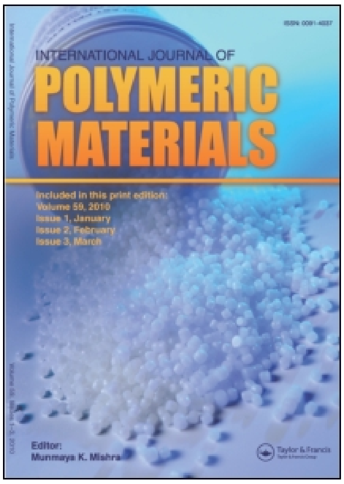

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Compatibilizing Effect of Poly(Styrene-block-2-Vinylpyridine) Copolymer on Polystyrene/Ethylene-Based Ionomer Resin Blends

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To cite this Article Guo, Tianying , Hao, Guangjie , Song, Moudao and Zhang, Banghua(2005) 'Compatibilizing Effect of Poly(Styrene-block-2-Vinylpyridine) Copolymer on Polystyrene/Ethylene-Based Ionomer Resin Blends', International Journal of Polymeric Materials, 54: 3, 199 — 211

To link to this Article: DOI: 10.1080/00914030390246261

URL: http://dx.doi.org/10.1080/00914030390246261

International Journal of Polymeric Materials, 54:199–211, 2005
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ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030390246261

COMPATIBILIZING EFFECT OF POLY(STYRENE-BLOCK-2-VINYLPYRIDINE) COPOLYMER ON POLYSTYRENE/ETHYLENE-BASED IONOMER RESIN BLENDS

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The effect of adding the diblock copolymer poly(styrene-block-2-vinylpyridine) P(S-b-2VP] to immiscible blends of polystyrene (PS)/ethylene based ionomer resin [zinc salt of poly(ethylene-co-methacrylic acid)] on the morphology, dynamic mechanical, and mechanical properties of the blends has been investigated. The diblock copolymer was synthesized by sequential anionic copolymerization and was melt-blended with PS and ionomer. Scanning electron microscopy (SEM) showed that the added block copolymer reduced the domain size of the dispersed phase in the blends. Dynamic mechanical analysis (DMA) revealed that the extent of compatibility between PS and ionomer affected the values tan δ and glass transition temperature Tg of the blends. Notched impact strength, tensile strength, and elongation at break were determined as a function of different amounts of added P(S-b-2VP) in the blends. The compatibilizing effect of the diblock copolymer is most probably the result of its location at the interface between the PS and the ionomer phases and penetration of the blocks into the corresponding phases, that is, the polystyrene block enters the PS matrix, and the poly(2-vinylpyridine) block interacts with ionomer through ion-ligand interaction.

Keywords: blending, compatibilization, polystyrene, ionomer, diblock copolymer

Received 11 June 2003; in final form 21 June 2003.

This work was supported by the National Science Foundation of China (Proj. 59373141).

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INTRODUCTION

Blending of polymers has been the subject of intensive research in both academic and industrial laboratories [1–2]. It is a successful way in which new materials can be produced to have a wide range of properties [3–4]. However, the majority of polymers are immiscible at the molecular level as given by laws of thermodynamics, because of their small combinatorial entropy and their mostly positive enthalpy of mixing [5], which is reflected in a two-phase morphology, poor interactions across the phase boundaries and, therefore, poor mechanical properties. It is possible to obtain a compatible phase structure by bond-formation (physical or chemical) whereby the excellent blend properties may be achieved in the final materials. Such compatibilization can be created in a variety of ways, the most common of which is the introduction of a third component to the blend, which could then promote interactions across the interface of matrix and dispersed phase. Block or graft copolymers are suitable as compatibilizers, because these copolymers could ensure a finer dispersion during melt blending by decreasing interfacial tension, could provide stabilization against phase structure-coarsening during the processing, and could improve adhesion between phases [6–11]. Therefore, in order to get excellent properties of the final material, it is crucial to improve the compatibility of the immiscible polymer pairs. One main procedure applied for this purpose is incorporation of a suitable compatibilizer into a multiphase system that enhances the physical bonding of dissimilar polymers. In recent years, the specific interaction between components in the blending system has attracted much interest due to its unique effectiveness [12–13]. The most common interactions are: acid-base interactions [14], charge-transfer completing [15], $\pi-\pi$ complex formation [16], dipole-dipole interaction [17], $\pi-$hydrogen bond [18], ion-ion [19–20], ion pair-ion pair [21–22], ion-dipole [23–24], ion-ligand [25–26] and so on. The choice of the particular blending pairs was based on the fact that although structure consideration suggests immiscibility, both components possess reactive groups that may react under the mixing condition [27].

Polystyrene (PS) has proven to be a very important commodity polymer. But it has significant shortcomings in properties, such as its high brittleness and poor impact resistance. In order to get a commercial utilization a great many works have been done up to now. One of the most important ways is by blending with other materials, such as polypropylene (PP) [28–30], polyethylene (PE) [31–33], polybutadiene (PB) [34–36], ethylene propylene rubber (EPR) [37–38], ethylene-vinyl acetate copolymer (EVA) [39], polyamide (PA) [40], and so on.

Less information can be found on blends of PS/ethylene based ionomer. Therefore in this work an extensive investigation on compatibilizing behavior of the poly(styrene-block-2-vinylpyridine) [P(S-b-2VP)] for PS/ionomer blend was carried out by means of scanning electron microscopy (SEM), differential scanning calorimeter (DSC), mechanical property measurements, dynamic mechanical analysis (DMA), and FTIR.

EXPERIMENTAL

Materials

Polystyrene was obtained from Beijing Yanshan Petrochemical General Co. (China) in pellet form, with $\rho = 1.05\,\mathrm{g{\cdot}cm^{-3}}$ and $\overline{Mn} = 1.6 \times 10^5$. Ethylene based ionomer resin [zinc salt of poly(ethylene-co-methyl acrylic acid)], Surlyn1652, was supplied by Dupont Co. (USA). All polymer materials were vacuum-dried for 8 h at 60°C.

P(S-b-2VP) was synthesized via sequential anionic copolymerization. All reagents had been strictly purified before use. Dry tetrahydrofuran (THF) and styrene were added to a 500 ml-capped bottle. The bottle was purged with high purity nitrogen (99.999%) and degassed for 0.5 h. n-Butyl lithium in benzene was then added. The fresh red-colored solution was agitated and maintained at –78°C. After the reaction had proceeded for 0.5 h, the 2-vinylpyridine was added. The deep-red solution was agitated to maintain the temperature at –78°C for 2 h. The reaction was quenched with methanol, and the solution was poured into a large amount of deionized water. The precipitate was filtered, washed, and then dried in vacuum. The product was extracted successively with cyclohexane and methanol/water (90/10 v/v) mixture. The final copolymer was characterized by GPC and ^{1}H-NMR. Its $\overline{Mn}$ and $\overline{Mw}/\overline{Mn}$ were 1.06×10^5 and 1.19, respectively, and the content of the PS block was 33 wt%. The P(S-b-2VP) copolymer was dried for 5 days at 40°C under vacuum prior to use.

Blend and Specimen Preparation

Blends of PS/ionomer (90/10 wt/wt) containing appropriate amount of P(S-b-2VP) were prepared in a internal Brabender-like mixer with a rotation rate of 30 rpm, blending temperature 190°C and blending time 5 min. Specimens used for impact and tensile testing were prepared using SL-45 compression-molding machine operated at 190°C and 19 MPa pressure for 4 min, and then allowed to cool to ambient temperature in a press at 5 MPa pressure. The specimens were vacuum-dried for 8 h at 40°C then kept at 21 ± 2°C for at least 2 h before mechanical testing.

Testing and Characterization

Dynamic mechanical analysis (DMA) data were obtained using a Netzsch DMA 242 Dynamic Viscoelastic Spectrograph (German) at a test frequency of 3.3 Hz. The heating rates were 2°C min^{-1}. Samples were cut into rectangular strips with average dimensions of 25 mm (length), 7 mm (width), and 0.6 mm (thickness).

The fracture surfaces of PS/ionomer blends with and without addition of P(S-b-2VP) for SEM observation were prepared by dipping the samples in liquid nitrogen and then fracturing them. The morphology of the surface of the cryogenically fractured samples was observed with a Hitachi S3500N scanning electron microscope (Japan) operating at 20 kV, after coating with gold with E-1010 Sputter.

Tensile properties were measured at 21 ± 2°C using a M500-10AX Testometric Universal Tester (U.K). The strain rate was 25 mm/min. And at least 5 dumbbell- shaped specimens were tested for each value given. The average effective dimension of the sample is 25 × 7 × 0.6 mm.

Notched Charpy Impact strengths were determined with a Charpy XCJ-500 impact tester. The average dimension of the sample is 55 × 6 × 4 mm. The average thickness of the notched part of the sample is 2.7 mm.

Differential scanning calorimetry (DSC) of the mixtures prepared by dissolution (see below) was carried out at a heating rate of 10°C/min in a Netzsch DSC 204 calorimeter under a nitrogen atmosphere. The instrument was calibrated with Indium. The glass transition temperature was estimated from the inflexion point in the heat flow curve and from the peak of the heat flow curve derivative.

Infrared spectra were obtained using a Nicolet 5DX FTIR spectrophotometer with a resolution of 2 cm^{-1}.

RESULTS AND DISCUSSION

Binary P(S-b-2VP)/Ionomer Blends

In order to certify further the interaction between side pyridine groups in P(S-b-2VP) and the carboxylate ions in ionomer, P(S-b-2VP)/ionomer binary blends with different compositions were prepared by a solution/precipitation method. Polymer blend, the white flocculent precipitate, appeared when toluene solutions of the P(S-b-2VP) (2% wt) was poured into toluene solution of ionomer (2% wt) slowly at 100°C under agitation. Then the precipitate was dried under vacuum at 60°C for two days.

DSC is a useful tool for studying compatibilization of blends, especially blends containing crystalline polymers, used not only to estimate the compatibilizing effect but also to investigate the compatibilizing location in a blend. The thermal properties of the P(S-b-2VP)/ionomer blends measured by DSC are summarized in Figure 1 and Table 1. DSC results from Figure 1 and Table 1 show that there are two crystalline melting temperatures, Tm_1 and Tm_2, at 77.6°C and 98.6°C for ionomer resin. When the ionomer resin was mixed with P(S-b-2VP)(50/50 wt) in toluene solution, Tm_1 value rises from 77.6°C to 81.3°C, and the Tm_2 value from 98.6°C to 102°C. This result indicates that the interaction between the two blending components probably makes the numbers of physical crosslinking points inside the pristine ionomer decrease, which promotes the ordered arrangements of polymer chains, thus increases Tm. P(S-b-2VP) is amorphous and the morphology is a two-phase structure with microphase

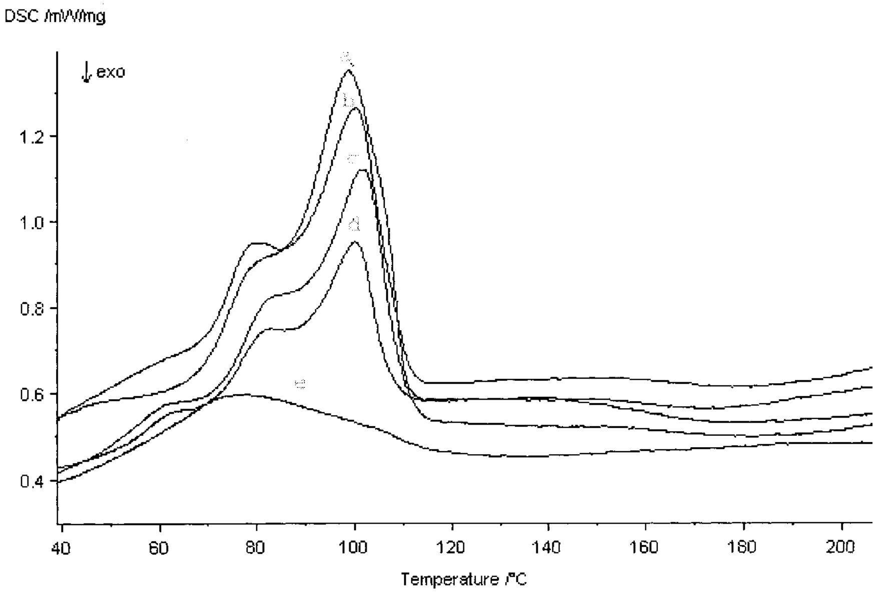


FIGURE 1 DSC spectra of P(S-b-2VP)/ionomer blends; a. ionomer; b. P(S-b-2VP)/ionomer (20/80 wt); c. P(S-b-2VP)/ionomer(50/50 wt); d. P(S-b-2VP)/ionomer (80/20 wt); e. P(S-b-2VP).

TABLE 1 Thermal Properties of P(S-b-2VP)/Ionomer Blends

P(S-b-2VP)/ionomer. wt	Tm_1(°C)	Tm_2(°C)	Tg(°C)	ΔHm(J/g)
100/0	—	—	77	—
80/20	82.9	100	64.7	16.7
50/50	81.3	102	64.6	26.3
20/80	80.2	101	—	33.1
0/100	77.6	98.6	—	49.7

separation. Therefore there should be an independent glass transition temperature (Tg) for the two blocks of P(S-b-2VP) diblock copolymer. But DSC spectra show that there is only one glass transition temperature at about 77°C, because the Tgs for the two blocks are rather close in the diblock copolymer. The Tg of the P(S-b-2VP)/ionomer (50/50 wt) blend shift in low temperature direction, from about 77°C to 64.6°C. This phenomenon indicates that there is some compatibility between the two blending components, P(S-b-2VP) and ionomer resin. But it is still only a partially compatibizing system.

FTIR spectra of ionomer, P(S-b-2VP) and P(S-b-2VP)/ionomer blend are shown in Figure 2. Here, the peaks at 1591.7 cm^{-1} and 1568.6 cm^{-1} for P(S-b-2VP) spectrum are the C=N (in pyridine ring) asymmetric extension vibration absorption bands. The C=N symmetric extension vibration absorption band appear at 1597.7 cm^{-1} and 1571.4 cm^{-1} for the P(S-b-2VP)/ionomer blending system. This result is most probably attributed to the ion-ligand interaction between Zn^{++} in the ionomer (with a strong complex ability) and –N= in P(S-b-2VP) (an electron donor). Thus, from the DSC and FTIR results it shown earlier, it can be presumed that the ion-ligand interaction between Zn^{++} and –N= of pyridine circle should exist.

Morphology of PS/ionomer/P(S-b-2VP) Blends

For polymer blend systems, one of the most important factors for getting the desired final properties is a control of the morphology. The morphology of polymer blend results from distortion, disruption, and aggregation of polymer-melt drops during the melt processing [41]. Thus, when the compositions of polymer blend and processing condition are fixed, the morphology of the blend should be determined by the nature of components. SEM observation was made on the surface of cryogenically fractured samples of the PS/ionomer (90/10 wt/wt) blends with various levels of P(S-b-2VP) (Figure 3) to

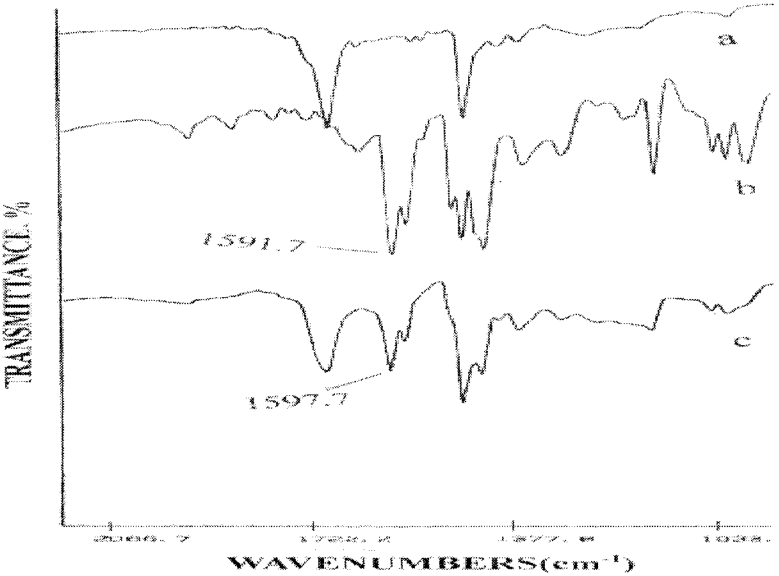
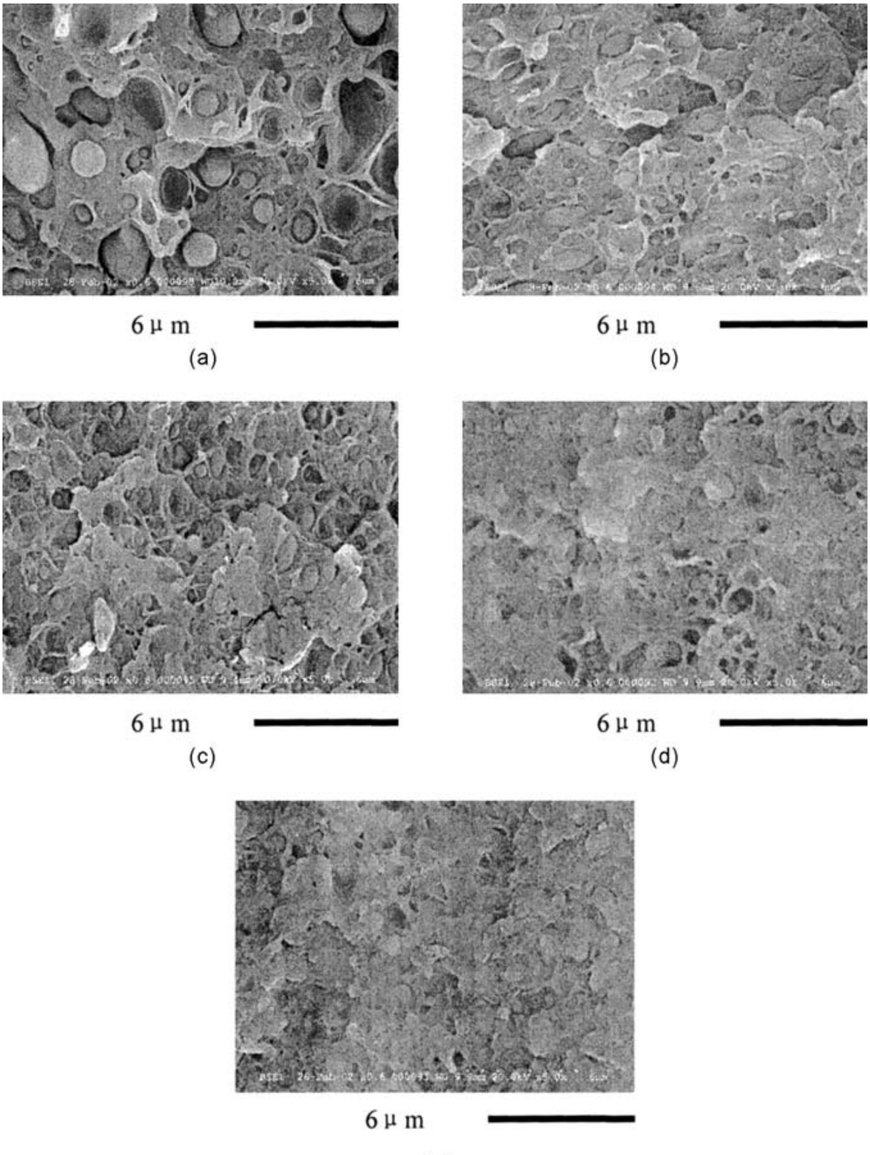


FIGURE 2 FTIR spectra of P(S-b-2VP)/ionomer blends; a. ionomer; b. P(S-b-2VP); c. P(S-b-2VP)/ionomer (50/50 wt).

examine the morphology of the compatibilized blends, especially the compatibilizing effect of the block copolymer on the blends.

The PS/ionomer without P(S-b-2VP) blend shows the typical characteristics of an immiscible blend (Figure 3a). The spherical domains of the dispersed ionomer phase are large, non-homogeneous, and the interface between the PS matrix and the ionomer is smooth and clean, indicating high interfacial tension, coalescence, and a poor interfacial adhesion between the two phases. The average particle diameter of the dispersed phase in 90/10 (wt%) blend was approximately 1.5 μm. The addition of P(S-b-2VP) diblock copolymer resulted in a significant reduction in the size of the dispersed ionomer particles compared to that observed in the non-compatibilized blends. When 0.9 wt% of the block copolymer is added, the domain diameter for the dispersed phase clearly decreased (Figure 3b). Additionally, a more uniform size distribution is obtained when the amount of the block copolymer is up to 2.9 wt%, the interface between the PS and the ionomer phase becomes rough (Figure 3d), indicating an enhanced interfacial adhesion, and the domain size of the dispersed phase becomes even smaller, from 1.5 μm to 0.3 μm. This indicates that the addition of P(S-b-2VP) diblock copolymer may reduce the interfacial tension between the dispersed ionomer phase and the PS matrix [42].



(a) (b) (c) (d) (e)

FIGURE 3 Scanning electron micrographs of PS/ionomer (90/10 wt) blends with different amount of P(S-b-2VP) copolymer: (a) 0% wt. (b) 0.9% wt. (c) 1.9% wt. (d) 2.9% wt. (e) 5.0% wt.

Dynamic Mechanical Properties of PS/Ionomer/P(S-b-2VP) Blends

Dynamic mechanical analysis (DMA) is often used to study polymer/polymer miscibility in polymer blends. The glass transition region can be studied using tan δ or the loss modulus curves. The results of dynamic mechanical testing thus provide information on the behavior of the blends and the phase morphology. The DMA results illustrating the temperature dependence of tan δ of the blends are shown in Figure 4.

DMA spectra given in Figure 4 show that the main relaxation of the PS matrix phase is at 114°C and that of the ionomer is at −100.5°C. In Figure 4, the dynamic mechanical properties of PS/ionomer show two sharp tan δ peaks. The presence of two well-defined peaks in the blends thus establishes the immiscibility of the two phases. These facts clearly indicate that PS/ionomer blends are incompatible because of the different polarities between PS and ionomer. On addition of P(S-b-2VP) to the blend, it was found that there appeared

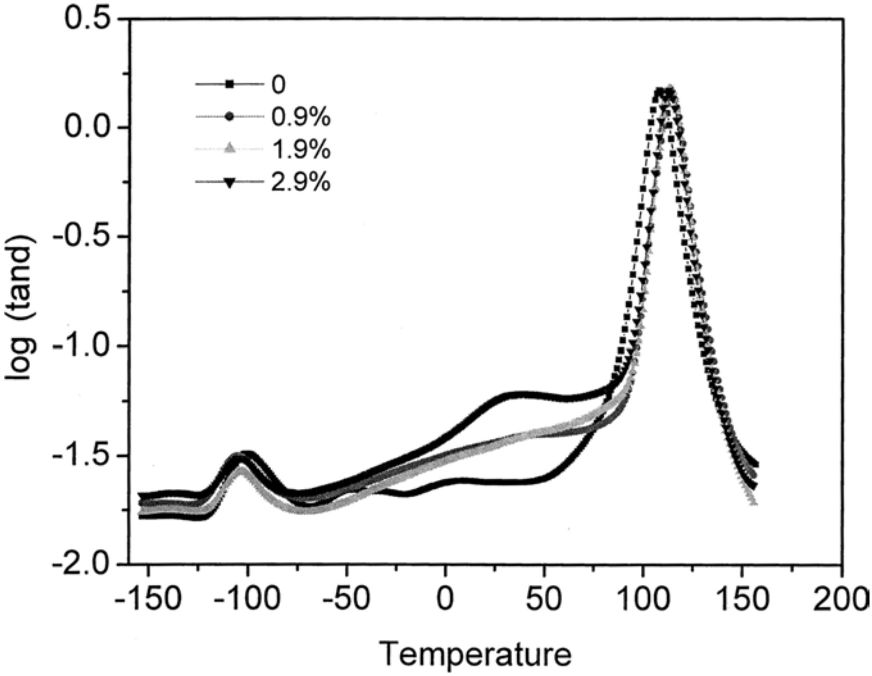


FIGURE 4 Temperature dependence of the tan δ for PS/ionomer (90/10 wt) blends with different amount of P(S-b-2VP) copolymer.

a broad tan δ peak at about 50°C, between the two sharp peaks. This demonstrates that P(S-b-2VP) macromolecules migrate to the interface between the two phases of PS/ionomer blends, forming a third phase (interfacial phase) consisting of PS, ionomer, and P(S-b-2VP). And the interaction between the two incompatible phases was enhanced. Thus more ionomer phase was microdispersed into the PS matrix. Many of the ionomer particles were partly or completely covered with the P(S-b-2VP) diblock layer, with the help of the ion-ligand interaction between Zn^{++} and –N=.

Mechanical Properties

Un-compatibilized PS/ionomer (90/10 wt/wt) blend is a fragile material at ambient temperature. When P(S-b-2VP) was added to the PS/ionomer (90/10 wt/wt) blends, the notched impact strength, ultimate tensile strength, and tensile elongation at break were obviously increased (see Figures 5, 6, and 7). This demonstrates that

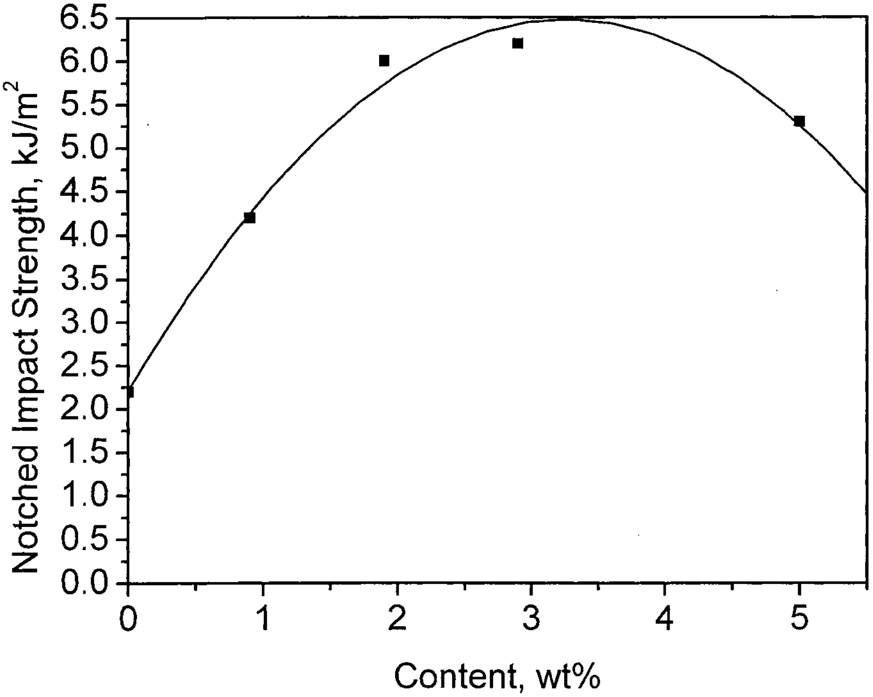


FIGURE 5 Notched impact strength of PS/ionomer (90/10 wt) blends with different amount of P(S-b-2VP) copolymer.

the adhesion between the ionomer dispersed phase and the PS matrix phase was increased. Hence, the stresses generated in impact and tensile tests can be transferred between the two phases, allowing the rigid dispersed phase domains to yield and dissipate the energy. Thus, the blends show toughening and strengthening characteristics of rigid materials to some extent. At the same time it was found that for the PS/ionomer/P(S-b-2VP) blend system, the notched impact strength, tensile strength, and elongation at break reached a top value when the amount of P(S-b-2VP) added was about 3.0 wt%. This indicates that 3.0 wt% of P(S-b-2VP) has acted as an interfacial active agent, and the condition for dispersing the ionomer phase is the best. Furthermore, this result demonstrates that 3.0 wt% is the critical micelle concentration (CMC) of this P(S-b-2VP) copolymer. A part of the P(S-b-2VP) copolymer changes into micelles dispersed in the PS matrix when the concentration of P(S-b-2VP) is more than its CMC. This part of the P(S-b-2VP) copolymer can act not only as the interfacial agent and interfacial adhesive, but also introduces weakness into the blends.

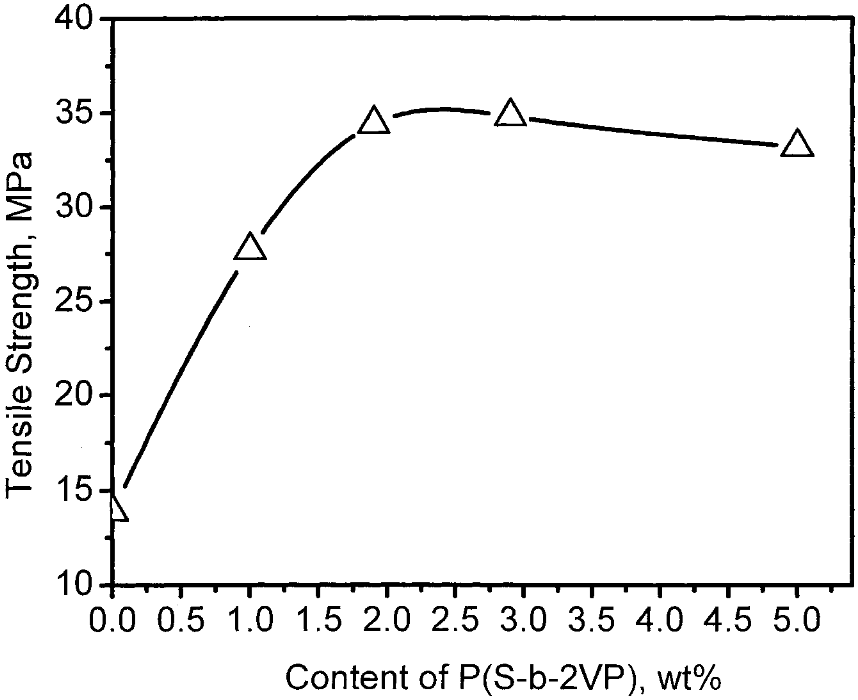


FIGURE 6 Ultimate tensile strength of PS/ionomer (90/10 wt) blends with different amount of P(S-b-2VP) copolymer.

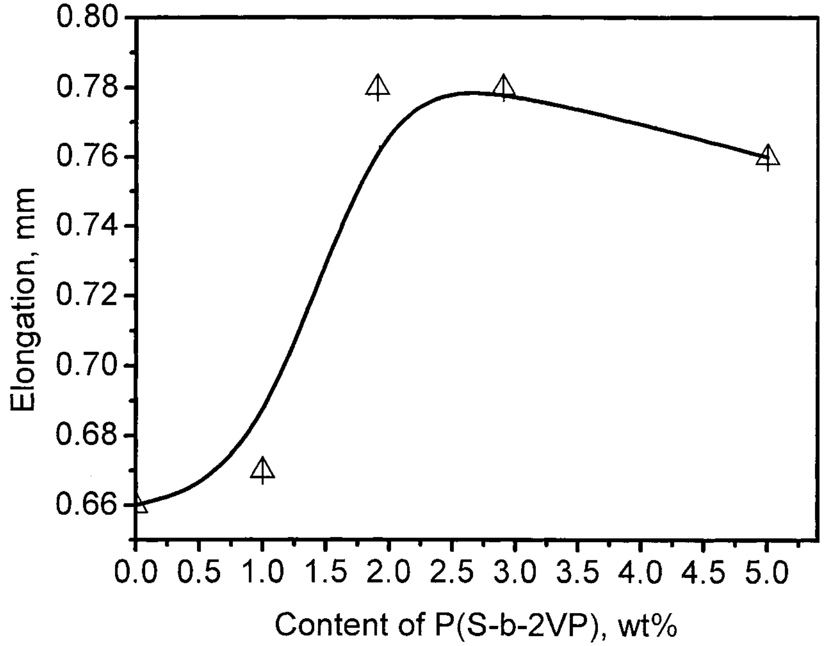


FIGURE 7 Elongation at break of PS/ionomer (90/10 wt) blends with different amount of P(S-b-2VP) copolymer.

Thus the notched impact strength and the tensile strength decreased when the addition amount was up to 5.0%, which is higher than its CMC. These results support the earlier discussion about the dynamic mechanical properties and the morphology of the blends.

CONCLUSIONS

Poly(styrene-b-2-vinylpyridine) [P(S-b-2VP)] is efficient in compatibilizing PS/ionomer blend system. The compatibilizing action of poly(styrene-b-2-vinylpyridine) is most probably coming from the ion-ligand interactions existing between the copolymer and ionomer. Adding 2.9 wt% of P(S-b-2VP) copolymer can raise the impact strength, ultimate tensile strength, and elongation at break of PS/ionomer (90/10 wt/wt) blends substantially.

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