Compatibilization of Syndiotactic Polystyrene and a Thermotropic Liquid-Crystalline Polymer Blend with a Zinc Salt of a Sulfonated Polystyrene Ionomer

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ABSTRACT: A zinc salt of a lightly sulfonated (4.5 mol %) polystyrene ionomer was used to compatibilize a 3/1 (w/w) blend of syndiotactic polystyrene and a wholly aromatic thermotropic liquid-crystalline polymer (TLCP). The addition of the ionomer significantly reduced the dispersed TLCP domain size and improved the tensile strength, ultimate elongation, and flexural toughness of the blend. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 564–568, 2003

Key words: blends; compatibilization; ionomers; liquid-crystalline polymers (LCP); syndiotactic; polystyrene

INTRODUCTION

Syndiotactic polystyrene (sPS) is a semicrystalline engineering thermoplastic that has a relatively high modulus, a high melting point ($T_m \sim 270$°C), excellent chemical resistance, and good dielectric properties.[1] A number of research groups have studied the crystal structure,[2–5] thermal properties,[6–8] and blends of sPS with other polymers, including atactic polystyrene (aPS),[9–17] poly(2,6-dimethyl-1,4-diphenylene oxide) (PPO),[4–7,18–22] poly(vinyl methyl ether),[18,23–25] polypropylene,[26] tetramethyl polycarbonate,[27] poly[styrene-(ethylene-*co*-butene)-styrene] triblock copolymer,[28] poly(styrene butadiene styrene) triblock copolymer,[29] and sulfonated atactic polystyrene ionomer (S-aPS).[30]

One deficiency of sPS that has limited its application is its relatively poor toughness. The toughening of thermoplastics is often accomplished by the development of a dispersed phase through blending in another immiscible or partially miscible polymer. That, however, may require the compatibilization of the two polymers, and a number of research groups have addressed this problem with the impact toughening of sPS. For example, block copolymers have been used as compatibilizers for blends of sPS with poly(ethylene propylene) rubber,[31] high-density polyethylene,[32,33] thermoplastic polyurethane,[34] and PPO.[35] Sulfonated syndiotactic polystyrene (S-sPS) was also recently used to compatibilize a blend of nylon 6 and sPS.[36]

This article describes the toughening of sPS with a thermotropic liquid-crystalline polymer (TLCP) and the use of a zinc salt of a sulfonated atactic polystyrene ionomer (Zn-S-aPS) as a compatibilizer. The effects of the concentration of Zn-S-aPS on the morphology, mechanical properties, and rheological properties of the blends were determined.

EXPERIMENTAL

sPS [weight-average molecular weight (M_w) = 613 kg/mol, weight-average molecular weight/number-average molecular weight (M_w/M_n) = 2.2] was provided by the Samsung Advanced Institute of Technology (Kiheung, Korea). It was synthesized by a stereospecific polymerization with a cyclopentadienyl trichlorotitanium/methylene aluminoxane catalyst. The sPS had a T_m of 274°C, as measured by differential scanning calorimetry.

The TLCP used was a commercial copolyester of 73% hydroxybenzoate and 27% hydroxynaphthanoate (Vectra A950) obtained from Ticona Engineering Polymers. The TLCP had a glass-transition temperature (T_g) of 100°C and a T_m of 273°C.

The Zn-S-aPS ionomer was prepared from a commercial aPS (Styron 666) obtained from Dow Chemical Co., Midland, MI (M_w = 280 kg/mol, M_w/M_n = 2.6). The sulfonation reaction was carried out in a 1,2-dichloroethane solution with acetyl sulfate according to the procedure of Makowski et al.[37] The reaction substituted sulfonic acid groups randomly along the

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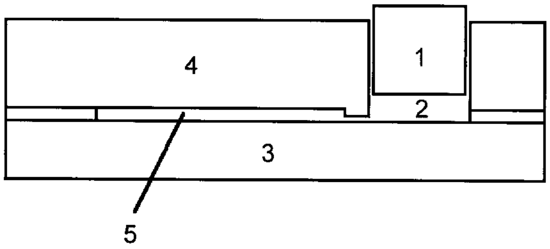

Figure 1 Schematic of the mold used to prepare the tensile specimens: (1) metal piston, (2) reservoir for the molten polymer to be injected into the mold cavity, (3,4) metal blocks, and (5) mold cavity.

chain and primarily at the para position of the styryl ring. The degree of sulfonation was 4.5 mol % (i.e., 4.5 sulfonate groups per 100 styrene repeat units), and the zinc salt was prepared by the neutralization of the sulfonic acid derivative with a 30% excess of zinc acetate. The neutralized 4.5 Zn-S-aPS, hereafter simply called the ionomer, was recovered by precipitation in boiling, deionized water, filtered, washed several times with deionized water and methanol, and dried for several days at 70°C in vacuo. The ionomer was an amorphous plastic with $T_g = 119°C$.

Blends of sPS and TLCP containing 0–15 parts of ionomer per hundred parts of the sPS/TLCP polymer blend (php) were compounded in a Brabender plasticorder (South Hackensack, NJ) intensive mixer with a 50-cm^3 mixing head. The ratio of sPS/TLCP was fixed at 3/1 (w/w) for all the blends. Pellets of TLCP were first fluxed for 2 min in the Brabender at 320°C and at a rotor speed of 50 rpm. When a uniform TLCP melt was achieved, the temperature was reduced to 290°C, and a dry blend of the sPS and ionomer was added to the mixer. The compound was then mixed for an additional 7 min at 290°C and at a rotor speed of 50 rpm. The initial heating of the TLCP to 320°C was used to completely melt any residual high-temperature crystals in the TLCP at the higher temperature,[38] and 290°C was used to better match the viscosities of the TLCP and the sPS melts to facilitate the dispersion of the TLCP in the sPS. The blend melt was removed from the mixer, quenched in a water bath, ground into small pieces, and dried in vacuo for several days at 70°C.

The blends were compression-molded into 3.2-mm-thick plaques and then fractured in liquid nitrogen. The morphology of the fractured surface was examined with an Philips ESEM 2020 electron microscope (Peabody, MA) operated at 20 kV; the specimens were coated with a gold/platinum alloy to avoid charging of the specimens.

Tensile specimens (type V, ASTM Standard D 638) were prepared by compression molding with the mold fixture shown in Figure 1. The fixture was preheated at 290°C for 30 min between 30.5-cm platens in a Carver (Wabash, IN) hot press. A measured amount of the polymer was added to the reservoir of the mold [Fig. 1(1)] and was heated for 5 min at 290°C. The molten polymer was injected into the mold cavity [Fig. 1(5)] with the Carver press to apply a force of approximately 100 kN to the piston [Fig. 1(1)]. The mold was then removed from the hot press and quenched to room temperature with water. Rectangular bars (30 mm × 9 mm × 3.2 mm) for flexural testing were prepared via compression molding at 290°C.

Uniaxial tensile tests and three-point-bending flexural tests were performed with an Instron model 1011 universal testing machine (Canton, MA). The tensile measurements were made at a crosshead speed of 5 mm/min. For the flexural measurements, a span length of 24 mm was used, and the crosshead speed was 500 mm/min. The toughness was calculated from the area under the stress–strain curve with the three-point-bending data. The arithmetic average and standard deviation of the mechanical properties were calculated with a minimum of five test specimens.

The dynamic mechanical properties were measured over a range of frequencies from 0.1 to 100 rad/s at 290°C with an ARES mechanical spectrometer (Rheometric Scientific, Piscataway, NJ) with a 25-mm parallel-plate fixture. The strain was kept at 0.1, and this ensured linear viscoelastic behavior. The sample was blanketed with dry nitrogen during the measurements to prevent oxidative degradation.

RESULTS AND DISCUSSION

The morphology of a melt-blended, immiscible polymer blend depends on a variety of factors, including the interfacial tension, the viscosity ratio of the blend components, the volume fraction, and the shear and extensional stresses encountered during processing.[39–43] In general, an immiscible blend has high interfacial tension, which results in a coarse morphology and a relatively large domain size for the minor component. Compatibilizers are interfacially active compounds that lower the interfacial tension between immiscible materials and reduce the domain size. A compression-molded sPS/TLCP (3/1 w/w) blend exhibited a coarse two-phase morphology [Fig. 2(a)] with TLCP domains ranging from 5 to 13 μm in diameter and a relatively smooth fracture surface. Those characteristics are typical of a relatively brittle blend with high interfacial tension and poor interfacial adhesion.

Previous work[44,45] has shown that S-aPS ionomers are effective compatibilizers for a variety of polymer blends, including blends containing liquid-crystalline polymers with polyamide and polycarbonate. Figure 2(b–d) shows that the ionomer is also an effective compatibilizer for sPS/TLCP blends. As the ionomer concentration increased, the TLCP domain size de-

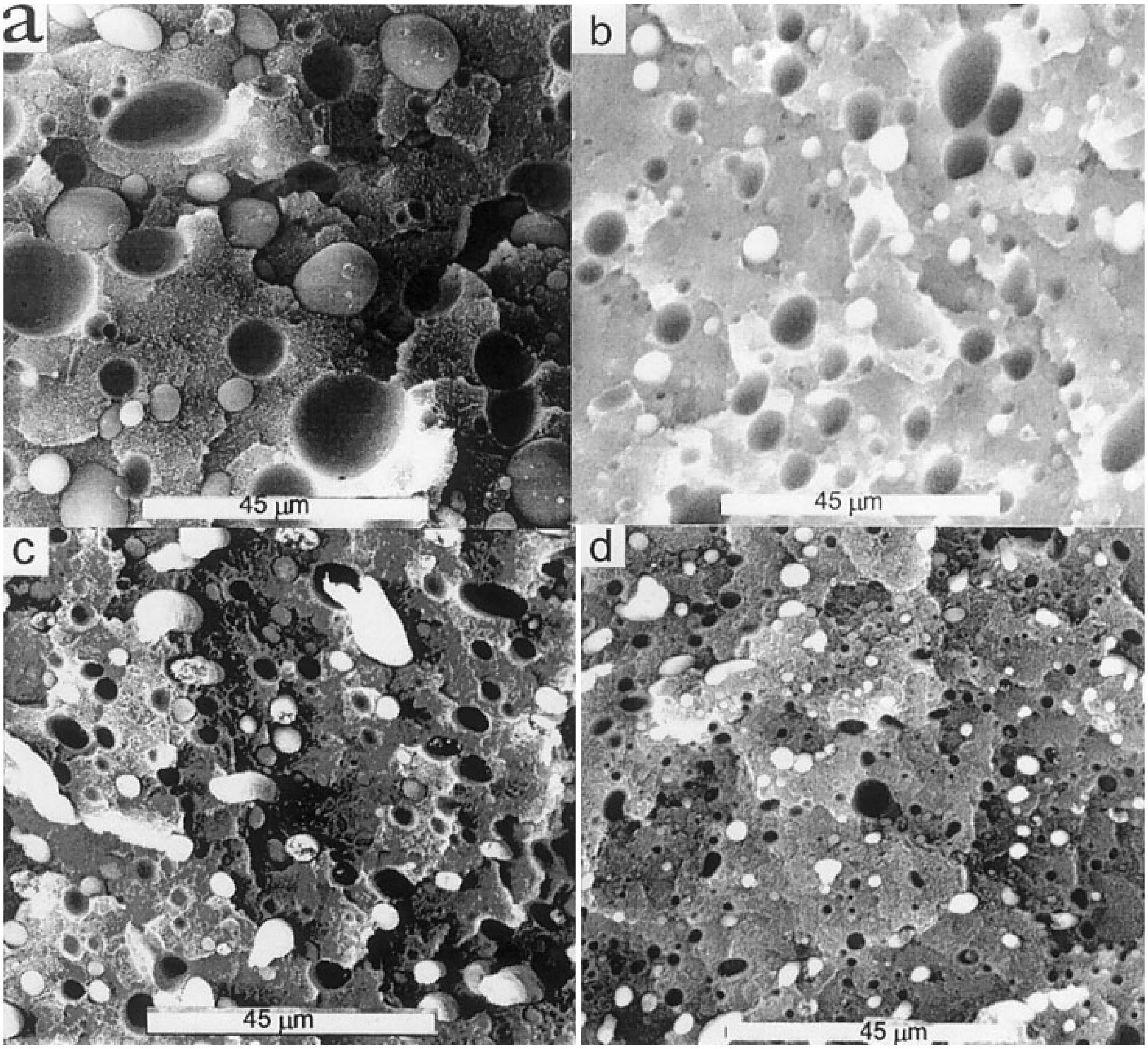

Figure 2 Scanning electron micrographs of fracture surfaces from compression-molded sPS/TLCP (3/1 w/w) blends containing (a) 0, (b) 5, (c) 10, and (d) 15 pph ionomer.

creased, and this is a good indication that the ionomer effectively reduced the interfacial tension. The addition of 5 php ionomer [Fig. 2(b)] reduced the number of very large domains, but the particle size was still rather large, approximately 3–7 μm. The addition of 10 pph ionomer [Fig. 2(c)] reduced the domain size to approximately 2–4 μm, and for 15 pph ionomer [Fig. 2(d)], the domain sizes were approximately 1–3 μm. It is clear from the micrographs in Figure 2 that the ionomer affects the interfacial properties of the sPS and TLCP, although the mechanism of the compatibilization has not been confirmed. The ionomer has previously been reported to be miscible with both sPS[46] and TLCP,[47] and this probably explains the interfacial activity in the sPS/TLCP blend system.

The effect of the addition of the ionomer compatibilizer on the tensile properties of sPS/TLCP blends is shown in Figures 3 and 4. The ionomer had no effect on the modulus, but the tensile strength and elongation to break increased with increasing ionomer content up to approximately 10 php. The addition of more than 10 php ionomer did not result in further improvements in strength or elongation. In all cases, the stress–strain curves were nearly linear, and all the samples exhibited brittle fracture. The improvements in the ultimate tensile properties are consistent with the smaller dispersed TLCP domain size seen in Figure 2 for the samples containing ionomer. The decrease in domain size would be expected to lower the stress concentrations because of the dispersed phase. The lack of improvement of the properties for the highest ionomer concentration used, that is, 15 php, may be a result of the formation of ionomer micelles within one or both of the sPS or TLCP phases, the limited solubility of the ionomer in the blend, or the limit on how much ionomer can migrate to the interface during processing. The insensitivity of the modulus of the blend to the compatibilizer concentration

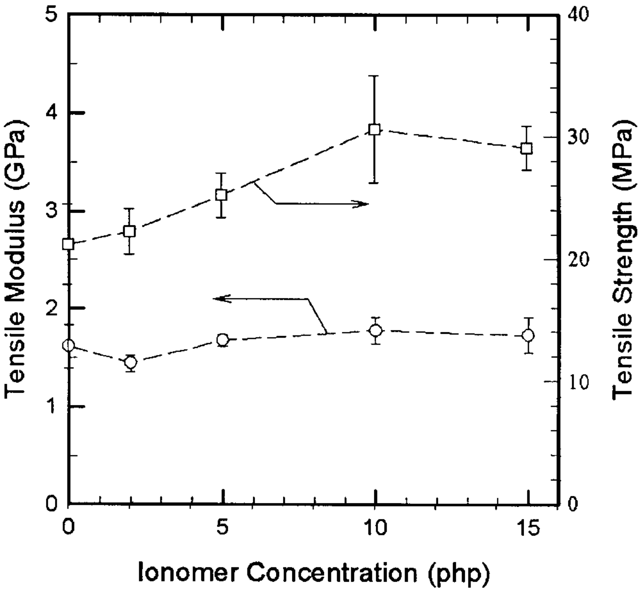

Figure 3 Effect of the ionomer compatibilizer concentration on the stiffness and tensile strength of sPS/TLCP (3/1 w/w) blends at 25°C.

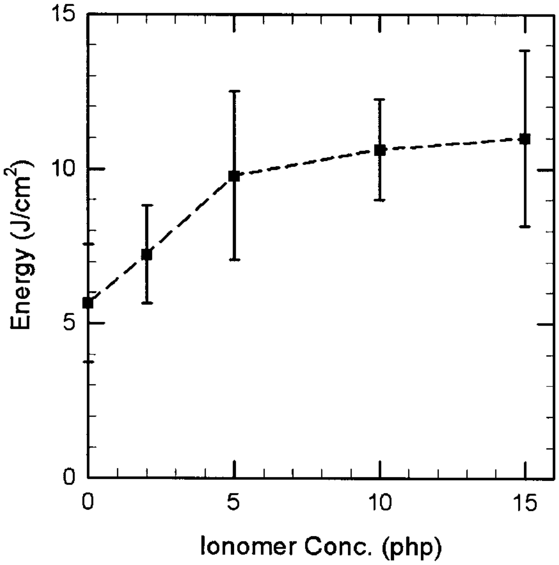

Figure 5 Effect of the ionomer compatibilizer concentration on the toughness in the three-point bending of sPS/TLCP (3/1 w/w) blends at 25°C.

(Fig. 3) is expected because the modulus is defined at infinitesimal strains and should be independent of the dispersed phase particle size and the extent of interfacial adhesion as long as there is sufficient wetting of the TLCP by the sPS.

The addition of the ionomer compatibilizer also improved the toughness of the sPS/TLCP blends, as determined from the area under the stress–strain curves from three-point-bending measurements (Fig. 5). The toughness of the blend nearly doubled with the addition of 5 wt % ionomer, and it increased gradually with the further addition of the ionomer. The increase is attributed to the reduction of the domain size (Fig. 2).

Figure 6 shows the dynamic viscosity of the 3/1 sPS/TLCP blends at 290°C as a function of the compatibilizer concentration. All samples showed pseudoplastic behavior, but the viscosity increased significantly with the addition of the ionomer. With the addition of only 2 php ionomer, the zero-shear viscosity (i.e., the asymptote at low frequency) increased nearly an order of magnitude, and for 15 php, the increase was about three orders of magnitude. At the higher frequencies, the changes were somewhat less but substantial nonetheless. Two possible explanations for the viscosity results are that the increase is simply a result of the very high viscosity of the neat

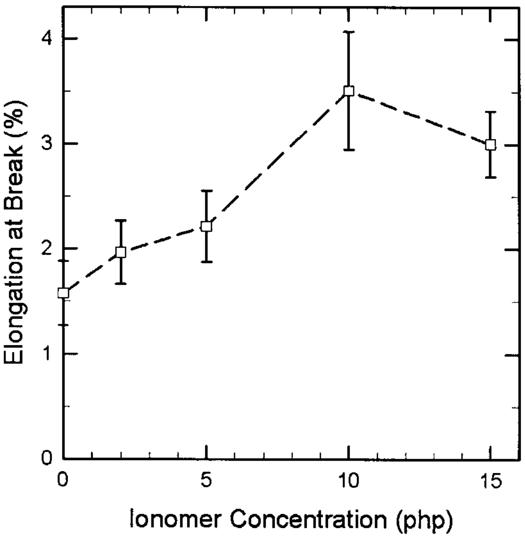

Figure 4 Effect of the ionomer compatibilizer concentration on the ultimate elongation of sPS/TLCP (3/1 w/w) blends at 25°C.

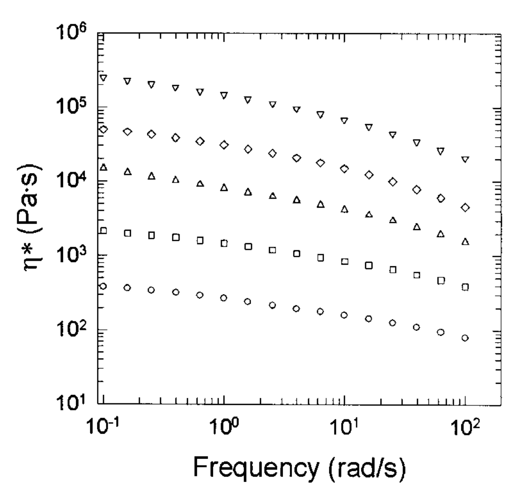

Figure 6 Effect of the ionomer concentration on the dynamic viscosity of sPS/TLCP (3/1 w/w) blends at 290°C: (○) 0, (□) 2, (△) 5, (◇) 10, and (▽) 15 php ionomer.

ionomer or that the ionomer greatly improves the interfacial adhesion between the two phases in the melt. Although the S-aPS ionomers generally have very high melt viscosities because of ionic associations that persist in the melt, it is unlikely that that can explain the substantial changes in the viscosity of the sPS/TLCP blends that were observed here given the relatively low concentrations of ionomer and the high temperature (290°C) used. One is tempted to attribute the viscosity increases to the interfacial activity of the ionomer and specifically to the improved interfacial adhesion, presumably due to the efficient entanglement or complexation of the ionomer with both sPS and TLCP. However, that conclusion is, at this time, mere speculation and requires further experimental verification.

CONCLUSIONS

The zinc salt of a lightly sulfonated (4.5 mol %) aPS ionomer exhibited significant interfacial activity in two-phase blends of sPS and a wholly aromatic TLCP. The addition of the ionomer as a compatibilizer improved the ultimate tensile strength and elongation and the flexural toughness of 3/1 (w/w) blends of sPS and TLCP. Those results are consistent with a lowering of the interfacial tension between sPS and TLCP by the addition of the ionomer, which reduced the dispersed TLCP domain size. A very large increase in the melt viscosity of the blends was also realized by the addition of the ionomer.

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