

Compatibilization by Sulfonate Ionomers in Polyblends with Thermotropic Liquid Crystalline Polymers

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Received 18 February 1997; accepted 22 June 1997

ABSTRACT: It is shown by differential scanning calorimetry (DSC) measurements that lightly sulfonated polystyrene (SPS) is partially miscible with polysulfone (PSF), polycarbonate (PC), polyetherimide (PEI), and a thermotropic liquid crystalline polymer (LCP). Fourier transform infrared analysis confirms that the miscibility of SPS and PSF, and of SPS and PC, comes from the ion–dipole interaction between the sulfonate groups of SPS and the polar groups of PSF and PC, respectively. After the addition of SPS to LCP/PSF, LCP/PC, and LCP/PEI blends, this specific interaction leads to the compatibilization of SPS in these blends, which is revealed by inward glass transition temperature shifts of component polymers in DSC and dynamic mechanical analysis thermograms and by a much finer dispersion of the minor LCP phase in these matrix polymers. The utilization of SPS as the compatibilizer results in a stronger interfacial adhesion between LCP and matrix phases and improves the mechanical performances of LCP/PSF, LCP/PC, and LCP/PEI blends as well. Compared with ternary LCP/PSF, LCP/PC, and LCP/PEI blends with polystyrene as an inert third component, the ternary LCP/SPS/PSF, LCP/SPS/PC, and LCP/SPS/PEI blends have significantly enhanced tensile strengths and moduli, with acceptable processabilities at the same time. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 67: 2141–2151, 1998

Key words: liquid crystalline polymers; sulfonate ionomers; compatibilization

INTRODUCTION

So-called *in situ* composites are a group of multi-phase polymeric materials,¹ obtained by physically melt-blending thermoplastic polymers and thermotropic liquid crystalline polymers (LCPs). The fibrillation of LCPs fulfilled *in situ* in the matrix resin makes LCP microfibrils a reinforcing agent, like carbon fibers and glass fibers in fiber-reinforced plastics. Compared with the conventional composites, *in situ* composites not only have enhanced properties, but also have their distinctive characteristics. Among the most important

advantages are their improved processability and dispersion due to the introduction of LCP.^{1–5} However, the final properties of *in situ* composites are not as high as those expected by the rule of mixtures, although each component polymer is chosen for its respective function in the whole composite system. For synergistic performances of LCP/polymer blends, two requirements should be met. One is the formation of LCP fibrils with large aspect ratios in the matrix resin.^{2,6–8} The other is the presence of strong interfacial adhesion between the dispersed microfibrillar LCP phase and the continuous resin phase.^{9,10} The fibrillation of LCPs depends on the characteristics of LCPs themselves¹¹ and their processing conditions, such as shear rate, melt drawing,^{2,3} LCP concentration,^{2,6} and viscosity ratio of the LCP to the matrix.^{2,12} By matching the LCP and the matrix resin and selecting proper processing parameters,

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 59373137.

Journal of Applied Polymer Science, Vol. 67, 2141–2151 (1998)
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reinforcing fibrils can be generated in extruded or injection-molded blends. Most polymer pairs, including the LCPs and the matrix resins, are immiscible, so that the interfacial adhesion between the LCP fibrils and the matrix polymer is usually poor.^{1,13–15} However, strong interfacial adhesion favors effective stress transfer at the interfacial region, which results in enhanced mechanical properties of the polyblends. So compatibilization of blends containing LCPs is of practical importance.

Most polymer pairs are immiscible. A polymer blend homogeneous down to the molecular level associates with a negative value of the free energy of mixing. In thermodynamic terms, $\Delta G_m = \Delta H_m - T\Delta S_m \leq 0$, where ΔG_m is the Gibbs molar free energy and ΔH_m and ΔS_m are the molar enthalpy and entropy of mixing, respectively. In most cases ΔH_m is positive, which does not favor mixing, and ΔS_m is positive, which favors mixing. Homogeneous mixing at the molecular level depends on whether the entropy increase, $T\Delta S_m$, is large enough to offset the hindrance of the enthalpy factor. However, the entropy increase caused by the polymers mixing is too small to meet the requirement of homogeneous mixing. Dominated by the enthalpy contribution, most polyblends are immiscible.

In general, a small amount of a copolymer is added to compatibilize polymer blends.^{16,17} As a compatibilizer, the choice of a block or graft copolymer is based on its miscibility with the two component polymers, which comes from their identical or similar structures. However, the confined application of this approach is the limited possibility of the copolymer which is miscible with both components in a variety of polymer pairs.

Researchers have demonstrated that the mixing enthalpy of polyblends can be reduced or made negative by specific interactions, such as hydrogen bond, dipole–dipole, ion–dipole, and donor–acceptor interactions. Olabisi¹⁸ studied a miscible blend of poly(vinyl chloride) (PVC) and poly ϵ -caprolactone (PCL). He found that the driving force of miscibility was the hydrogen bond between PVC and PCL. He measured the interaction indices with inverse chromatography.

In recent years more attention has been paid to ionomers, i.e., polymers containing a small amount of bonded ionic groups. Ionic groups, especially acid groups and metal ionic groups, can cause several interactions with polar groups when ionomers are blended with polar polymers. Some possible interactions are dipole–dipole,¹⁹ ion–di-

pole,²⁰ ion–ion,²¹ and hydrogen bond.²² These interactions can serve as physical crosslinks at the interface, so they lead to reduced interfacial energy and improved interfacial adhesion. Eisenberg and Hara²⁰ found that interactions between anions on one polymer and cations on the other resulted in miscibility of otherwise immiscible polymer pairs. A blend of polystyrene (PS) and poly(ethyl acrylate) (PEA) was a typically immiscible blend and was opaque. However, after sulfonic acid groups $-\text{SO}_3\text{H}$ had been introduced into PS and ethyl acrylate had been copolymerized with vinyl pyridine (VP) to form PEA-co-VP, the compatibilization was achieved by the pairwise attractive interactions between the resultant ions. As a result, the blend became transparent. Weiss²³ developed a miscible blend of polyamide 6 (PA 6) and a sulfonated PS (an ionomer, manganese salt of sulfonated polystyrene, Mn-SPS) by using specific interactions, although PA 6 and PS were immiscible. The miscibility over the entire range of composition was evidenced by a single, composition-dependent glass transition temperature (T_g). Infrared spectroscopy confirmed that these specific interactions were hydrogen-bonding, ion–dipole, and complex interactions associated with manganese sulfonates and amide groups.

When studying zinc salts of lightly sulfonated polystyrene (Zn-SPS), Dutta and coworkers²⁴ observed an unusual phenomenon. The unexpected result was that Zn-SPS was miscible with an LCP, a wholly aromatic copolyester of 73% hydroxybenzoate and 27% hydroxynaphthanoate. The LCP/Zn-SPS blends exhibited only a single T_g , measured by differential scanning calorimetry (DSC), which agreed well with the Fox equation prediction. Dynamic mechanical analysis (DMA) results also suggested that the Zn-SPS and LCP were at least partially miscible. Dutta and associates attributed this miscibility to a repulsive interaction within the ionomer, although the origin of miscibility was not yet clear. In addition, they added the Zn-SPS to the blends of LCP/polycarbonate (PC) and LCP/PA66, and found that the Zn-SPS was an effective compatibilizer for both blend systems. The addition of Zn-SPS led to a fine dispersion of LCP in PC or PA66 matrices and to a good adhesion between the phases. As a result, the tensile modulus and strength were increased by the added ionomer.

In the present authors' previous work,²⁵ the compatibilization of Zn-SPS was investigated in PC blends with two different LCPs, a copolyester

of *p*-hydroxybenzoic acid (PHB), poly(ethylene terephthalate) (PET)²⁵ and a wholly aromatic copolyester of PHB, chlorohydroquinone, terephthalic acid, and resorcinol. DSC results indicated that Zn-SPS was at least partially miscible with both LCPs. With the addition of Zn-SPS, T_g s corresponding to a PC-rich phase in LCP/PC blends shifted to lower temperatures with increasing amount of Zn-SPS. Scanning electron microscopy (SEM) also showed that the particle size of the dispersed LCP phase was decreased by the compatibilization in the blends. The present work investigates the miscibility of a zinc salt of lightly sulfonated polystyrene with polysulfone (PSF), PC, and polyetherimide (PEI), and shows the effect of compatibilization of LCP/PSF, LCP/PC, and LCP/PEI blends with this sulfonate ionomer.

EXPERIMENTAL

Materials

PS was PS 666D ($M_w = 243,000$, measured by gel permeation chromatography) obtained from Yanshan Petrochemical Co., Shanghai, China. The lightly sulfonated polystyrene ionomer (SPS) was prepared by sulfonating PS with acetyl sulfate in a dichloroethane solution following the procedure of Makowski and colleagues.²⁶ This method has relatively little effect on the polymer backbone and the molecular weight, and results in a random placement of sulfonic acid groups at the *para* position on the phenyl ring of PS. The sulfonation level, determined by sulfur elemental analysis, was 2.7 and 3.4 mol %. The zinc salt was prepared by neutralizing the solution of SPS with a methanol solution of excess zinc acetate with stirring. The salt was precipitated, filtered, washed, and dried. In this context, these zinc salts of SPS are referred to as 2.7 SPS and 3.4 SPS, respectively, according to their sulfonation levels.

The thermotropic LCP used was a copolyester of PHB/PET obtained from Chengdu Silicone Research Center, Chengdu, China. Its PHB content was 70 mol %. PSF with an intrinsic viscosity (IV) of 0.54 was obtained from Shuguang Chemical Factory, Shanghai, China. PC with $M_n = 26,000 \pm 1,000$ was obtained from Zhonglian Chemical Factory, Shanghai, China. PEI was obtained from General Electric (Ultem 1000, U.S.A.).

Blending

Before melt-blending, all materials were dried at 120°C under vacuum for at least 12 h. Binary

blends of 3.4 SPS/PSF and 2.7 SPS/PC were prepared by solution mixing. First, the SPS and PSF were dissolved separately in tetrahydrofuran, and PC was dissolved in dichloromethane. Then the 3.4 SPS solution was added dropwise into a stirred PSF solution to make 3.4 SPS/PSF blends of 20/80, 40/60, and 80/20 compositions (by weight). The 2.7 SPS solution was added dropwise into a stirred PC solution to make 2.7 SPS/PC blends of 20/80, 40/60, and 80/20 compositions (by weight). Blend films were cast from these mixed solutions onto glass plates and dried at 100°C under vacuum for 1 wk. Ternary LCP/3.4 SPS/PSF blends were prepared by melt-mixing with a Haake Rheomix 600 mixer at 350°C for 8 min at a rotor speed of 50 rpm. Ternary LCP/2.7 SPS/PC blends were prepared by melt-mixing with a CS-194 Max Mixing extruder at 270°C for 1 min at a rotor speed of 180 rpm. Ternary LCP/3.4 SPS/PEI blends were prepared by melt-mixing with a Haake TW100 twin-screw extruder at screw speed of 40 rpm with a temperature profile of 330–350–370–360°C from the feeder to the die. All the blends had a fixed ratio of LCP/matrix polymers 1 : 4 by weight, with different amounts of the ionomer added.

The processability of blend melts was evaluated by torque values recorded during melt-processing. This measurement was conducted at the rotor speed of 50 rpm on a Haake Rheomix 600 equipped with a Haake RC90 Rheocord.

Observation and Characterization

DSC measurements were conducted on a Perkin-Elmer DSC-7. The weight of all samples was approximately 10 mg. Samples were scanned from 50 to 200°C with a heating rate of 20°C/min under an atmosphere of circulating dry nitrogen.

DMA was carried out with a Perkin-Elmer DMA-7 from 50 to 200°C. All measurements were conducted in the dual cantilever mode with a frequency of 1 Hz and heating rate of 5°C/min.

The fracture surface of the blends was observed with a Hitachi S-530 scanning electron microscope. The fracture surface was obtained by immersing and breaking the sample in liquid nitrogen and coating with gold.

Infrared spectroscopic (IR) characterization was performed with a Perkin-Elmer FTIR 2000 spectrophotometer. The IR specimens were prepared by dissolving 0.5 g solid of the samples in 20 mL solvent, followed by casting onto KBr

Table I T_g s of the Starting Materials and Their Binary Blends

Sample	A = PS		A = SPS	
	Starting Material (°C)	Binary Blend (°C)	Starting Material (°C)	Binary Blend (°C)
PSF	190	—	190	—
PSF/A (80/20)	188	97	169	116
PSF/A (60/40)	188	96	154	114
PSF/A (20/80)	187	98	141	112
A	—	97	—	109

T_g 's values are obtained by DSC measurements.

plates. All traces of the solvent were removed by the radiation of an infrared lamp for 20 min.

Materials Testing

Tensile strengths and moduli of the blends were measured with a CS-183 TE Mini Max Tensile Tester at ambient. Dumbbell-shaped samples were injection-molded with a CS-183 MMV Mini Max Moulder. Tensile tests at an elongation rate of 1.58 mm/min were performed on cylindrical dumbbell samples with an overall length of 22.22 mm and a narrow-section diameter of 1.58 mm.

RESULTS AND DISCUSSION

Polysulfone Blend Systems

Binary Blends

Detecting T_g s is one of the most effective methods for characterizing the miscibility of blends, when the component polymers have a T_g difference larger than 20°C. The T_g s of the starting materials—PSF, PS, 3.4 SPS, and their blends—are summarized in Table I. The T_g s of PSF, PS, and 3.4 SPS are about 190°C, 97°C, and 109°C, respectively. For PSF/PS blends, two distinct T_g s of non-composition dependence correspond to T_g s of the component polymers. This means that PSF and PS are immiscible and phase separated in these blends.

The partial miscibility of PSF and the ionomer 3.4 SPS is demonstrated by DSC thermograms. PSF/3.4 SPS blends have two composition-dependent T_g s. For PSF/3.4 SPS 80/20, the upper-temperature T_g was depressed by 21°C from the T_g of PSF, and the lower-temperature T_g was increased

by 7°C over the T_g of 3.4 SPS. With increasing 3.4 SPS concentration in the blends, the upper-temperature T_g s decreased much more; shifts in PSF/3.4 SPS 60/40 and 20/80 were 36°C and 49°C, respectively. In other words, the difference between T_g s of PSF and 3.4 SPS was 81°C, however, this T_g difference in PSF/3.4 SPS 20/80 became only 29°C. The transition regions also became broader, indicating the presence of interactions. The lower-temperature T_g s had no significant shifts: only 3°C in PSF/3.4 SPS 20/80. This T_g could be attributed to the existence of an ionomer-rich phase. The aggregation of ionic groups in SPS made most of the SPS molecules form a separated phase having a little-changed lower-temperature T_g . The rest of the SPS molecules were mixed well with PSF to form a PSF–SPS phase. This phase had a changing composition and a decreasing T_g with increasing SPS concentration, which was revealed by changes in upper-temperature T_g s. In conclusion, a partial miscibility of PSF and SPS was confirmed by two composition-dependent T_g s of PSF/3.4 SPS blends and inward shifts of T_g s with increasing SPS concentration.

The miscibility of SPS and PSF came from an intermolecular interaction between ions of $-\text{SO}_3$ and Zn^+ in SPS and polar groups of PSF, as confirmed by the Fourier transform infrared (FTIR) spectra. FTIR spectra are shown in Figures 1 and 2. Figure 1 shows the IR spectra of 3.4 SPS, PSF, and a PSF/3.4 SPS 60/40 blend. The characteristic absorbencies of PSF were the stretching vibration of the C—O band at 1245 cm^{-1} , the asymmetric stretching vibration of S=O at about 1152 cm^{-1} , and the symmetric vibration of S=O at 1014 and 836 cm^{-1} . For 3.4 SPS these vibration bands were located at 1240, 1152, and 1012 cm^{-1} ,

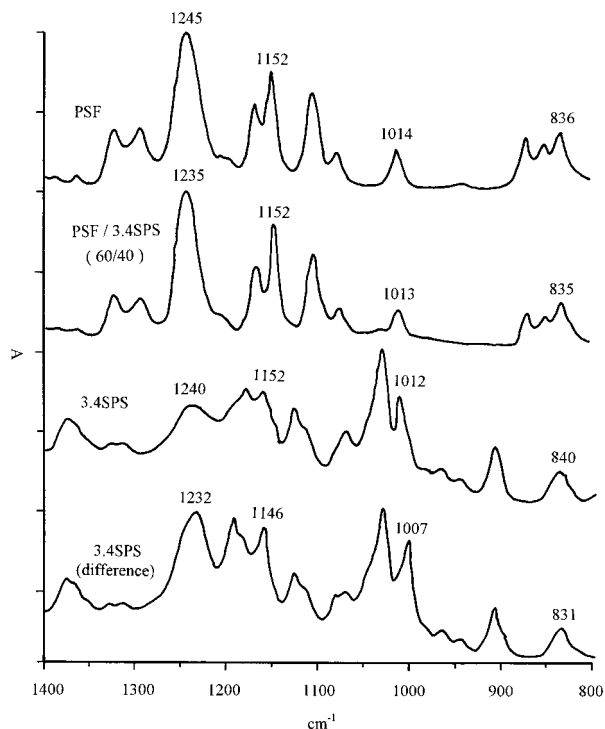


Figure 1 FTIR spectra of 3.4 SPS, PSF, and PSF/SPS 60/40, and a difference spectrum of 3.4 SPS obtained by subtracting the PSF spectrum from that of the PSF/SPS blend.

respectively. Figure 1 also shows a difference spectrum obtained by subtracting the PSF spectrum from that of the PSF/3.4 SPS blend. It is clear that the difference spectrum differs from that of the pure 3.4 SPS. The absorbency bands at 1240 and 1152 cm^{-1} shift to 1232 and 1146 cm^{-1} , respectively. The 1012 and 836 cm^{-1} bands also shift to lower frequencies, to 1006 and 831 cm^{-1} , respectively. These are consistent with the results of Lu and Weiss's research.²³ These shifts are evidence for a distinct interaction involving the sulfonate group. Figure 2 shows the IR spectra of PSF and PSF/PS 60/40 and their difference spectrum for keeping the PSF contribution. It is clear that the difference spectrum is almost identical to the spectrum of PSF. This IR result confirms that PSF and PS are immiscible and their blends are phase-separated. It can be concluded that the miscibility of PSF and SPS comes from the ion-dipole interaction between sulfonate groups of SPS and polar groups of PSF.

The miscibility of the LCP and the SPS was confirmed by DSC of the LCP/3.4 SPS 60/40 blend. A single loss peak was observed for the neat ionomer and the blend, corresponding to T_g

values of 107 and 96°C, respectively. The transition for the blend was broad and gradual, which could suggest that the transition might actually be a sum of two transitions, one for an LCP-rich phase and one for an ionomer-rich phase. We had no interest in resolving the two transitions further because of the nearness of transitions of the LCP and 3.4 SPS. If predicted by the Fox equation, the T_g of the LCP should be 87°C, although it was undetectable due to the chain rigidity and structural complexity of the LCP. However, it is clear that the LCP and SPS are at least partially miscible.

Ternary Blends

The T_g s of PSF, LCP/3.4 SPS, LCP/PSF, and LCP/3.4 SPS/PSF blends are summarized in Table II. In an LCP/PSF 20/80 blend, a glass transition corresponding to the PSF phase located at about 187°C, which is near the glass transition of the neat PSF. The inability to resolve the T_g of LCP in this blend, and even in neat LCP, may be due to the rigidity and complicated structure of this LCP. It is accepted that PSF and LCP are completely immiscible. The DSC curve of LCP/3.4 SPS 60/40 exhibited only one T_g , which is 10°C lower than that of the neat ionomer. In addition

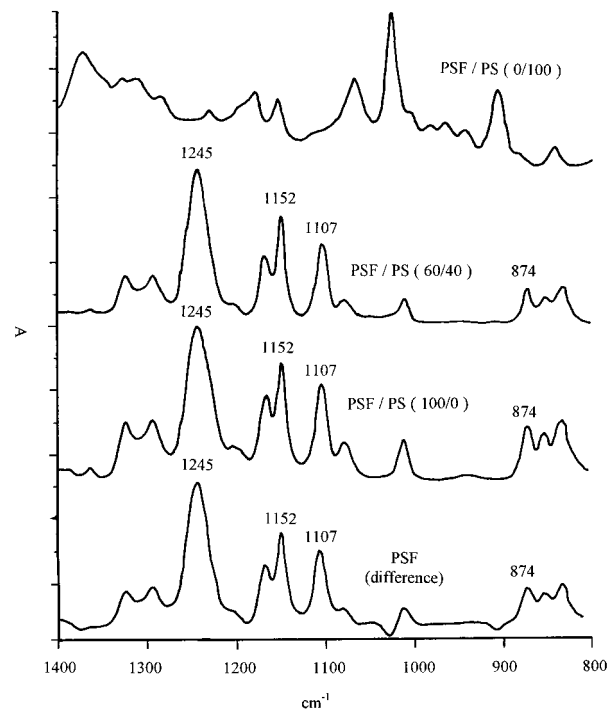


Figure 2 FTIR spectra of PS, PSF/PS 60/40, and PSF, and a difference spectrum of PSF obtained by subtracting the PS spectrum from that of the PSF/PS blend.

Table II T_g s of Component Polymers and Their Blends from DSC Measurements

T_g (°C)	PSF	LCP/PSF 20/80	LCP/SPS 60/40	LCP/SPS/PSF				
				19.6/2/78.4	19.2/4/76.8	18.8/6/75.2	18.4/8/73.6	18/10/72
High	190	187	—	181	180	178	178	176
Low	—	—	96	—	111	113	112	114

to this T_g shift, the broader transition suggests that T_g s of LCP and 3.4 SPS locate closely with each other and that LCP and 3.4 SPS are at least partially miscible.²⁴ But with the addition of the ionomer, the situation changed. A 2% 3.4 SPS in a LCP/PSF 20/80 blend caused a T_g shift 6°C lower than that of the LCP/PSF 20/80 blend. The T_g shift of LCP/3.4 SPS/PSF blends increased with addition of increasing amounts of SPS. When the SPS amount reached 10%, the upper-temperature T_g of the blend was about 176°C, 11°C lower than that of LCP/PSF 20/80. These T_g shifts suggest that the compatibilization in LCP/PSF blends is accomplished by the addition of the ionomer, the zinc salt of lightly sulfonated polystyrene, which promotes mixing through intermolecular interactions between LCP and SPS and between SPS and PSF.

DMA probes molecular relaxation arising from local motions of the polymer chain. Generally it is more sensitive than DSC in detecting glass transition and secondary relaxation. The T_g s of LCP, PSF, LCP/PSF, and LCP/3.4 SPS/PSF blends are listed in Table III. A loss peak of the neat PSF was located at about 201°C. The neat LCP had a low, broad transition peak at 103°C. This phenomenon is consistent with the result of DSC measurement. For the LCP/PSF 20/80 blend, two loss peaks were detected, one corresponding to LCP phase at about 104°C and the other corresponding to PSF phase at about 197°C. Similar to the results of DSC measurements, no significant shift, implying miscibility of LCP and PSF, was found. With the addition of 3.4 SPS, the high-temperature loss peaks, corresponding

to PSF, shifted to lower temperatures. The T_g readings were 187, 184, and 182°C for LCP/PSF blends containing 4%, 6%, and 10% of 3.4 SPS, respectively. On the other hand, the low-temperature loss peaks, corresponding to the LCP-rich phase, shifted to higher temperatures. The T_g readings were 118, 123, and 123°C for LCP/PSF blends containing 4%, 6%, and 10% of 3.4 SPS, respectively. Compared with a difference of 93°C between T_g s in LCP/PSF 20/80, the difference between T_g s in LCP/3.4 SPS/PSF 18/10/72 is 59°C, which means a 34°C inward shift of the two T_g s. The stepwise shifts of T_g s with increasing amounts of the ionomer, revealed by DSC and DMA measurements, confirm that the compatibilization in LCP/PSF blends is accomplished by the addition of SPS.

SEM micrographs of fractured blend surfaces are shown in Figure 3. Because all the samples were obtained in a mixer, the lack of field effect made it difficult to generate LCP fibrillar domains in these blends. Figure 3(a) provides direct evidence that phase separation occurred in a binary LCP/PSF 20/80 blend. This sample has a distinct two-phase morphology, i.e., a continuous PSF phase with a dispersed LCP phase. The LCP particles in the form of spheres have diameters in the range of 2 to 13 μm . All the spheres and holes have smooth surfaces, indicating poor interfacial adhesion between the LCP and PSF phases. However, with the addition of the ionomer, the morphologies of fractured surfaces change dramatically. With 6% 3.4 SPS in the LCP/PSF 20/80 blend, the domain size of the minor LCP phase decreased significantly [Fig. 3(b)]. The diameter

Table III T_g s of Component Polymers and Their Blends from DMA Measurements

T_g (°C)	PSF	LCP/PSF 20/80	LCP	LCP/SPS/PSF				
				19.6/2/78.4	19.2/4/76.8	18.8/6/75.2	18.4/8/73.6	18/10/72
High	201	197	—	190	187	184	184	182
Low	—	104	103	112	118	123	121	123

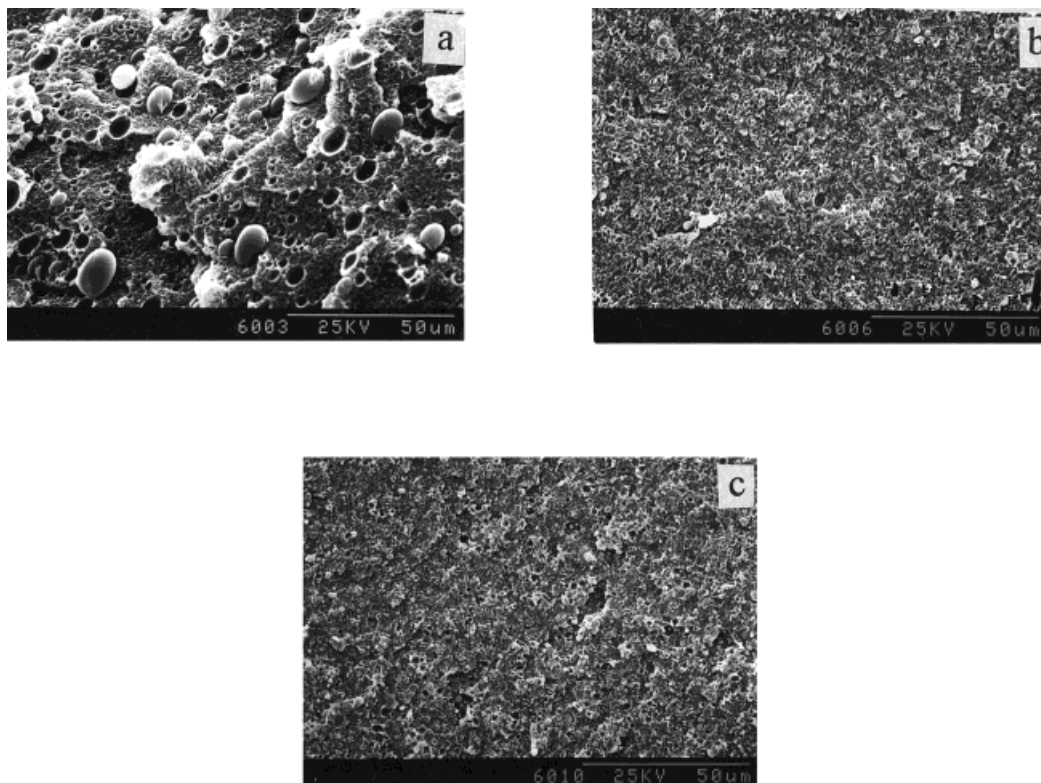


Figure 3 Morphologies of fracture surfaces of blends (a) LCP/PSF 20/80; (b) LCP/3.4 SPS/PSF, 18.8/6/75.2; (c) LCP/3.4 SPS/PSF 18/10/72.

of the largest particles was smaller than $1 \mu\text{m}$. With 10% 3.4 SPS in the blend, the LCP phase was well dispersed in the continuous PSF phase. The LCP particles had uniform diameters below $0.5 \mu\text{m}$ [Fig. 3(c)]. In addition to this, the fractured surface became blurred. From these phenomena, it is evident that the compatibilization of the blends is achieved and the interfacial adhesion between two phases is improved.²⁷ These results verify the expectation that specific interactions between the phases can act as physical crosslinks along the interface and compatibilize polymer blends to a much finer dispersion.

Mechanical measurements were conducted on samples of binary and ternary blends. The tensile strengths and moduli are summarized in Table IV. The tensile strength and modulus of LCP/PSF 20/80 were 50.2 MPa and 0.75 GPa, respectively. The addition of SPS increased the tensile strengths and moduli of ternary blends dramatically. The LCP/3.4 SPS/PSF 19.6/2/78.4 had a strength of 87.8 MPa and a modulus of 1.04 GPa, compared with LCP/PS/PSF 19.6/2/78.4 having 56.8 MPa and 0.78 GPa, respectively. The replacement of PS in LCP/PS/PSF 18.8/6/75.2 by SPS increased the strength from 45.5 to 73.9 MPa and the modulus

from 0.78 to 1.06 GPa. The introduction of SPS with ionic groups gave LCP/PSF blends increased mechanical properties. Together with other results shown above, this means that SPS compatibilizes LCP/PSF blends, improves the interfacial interaction, and enhances the mechanical performances.

However, it should be noted that SPS was not as strong mechanically as PSF and LCP, so that it could be a useful compatibilizer only at a low concentration. A small amount of added SPS will improve the mechanical properties, but SPS-rich domains formed with excess SPS addition will impair the mechanical performances.

Being one of the advanced engineering plastics, PSF has a high melt viscosity and poor processability as its drawbacks. Higher melt temperatures, higher molding pressures and higher molder temperatures are required during its processing. In a sense, the final performances of PSF materials depend upon the processability of their formulations. The presence of LCPs facilitates the flow of PSF molecules and decreases the melt viscosity, as shown in Table V. Ionomers can compatibilize immiscible polymer pairs and offer strong interfacial interaction; however, they usually worsen the processability of the blends as a result.

Table IV Mechanical Properties of Blends

Sample	Component	Strength (MPa)	Modulus (GPa)
LCP/PSF	20/80	50.2 ± 1.9 ^a	0.75 ± 0.05
LCP/PS/PSF	19.6/2/78.4	56.8 ± 2.1	0.78 ± 0.07
LCP/SPS/PSF	19.6/2/78.4	87.8 ± 3.6	1.04 ± 0.09
LCP/PS/PSF	18.8/6/75.2	45.5 ± 2.3	0.78 ± 0.07
LCP/SPS/PSF	18.8/6/75.2	73.9 ± 2.3	1.06 ± 0.05
LCP/PS/PSF	18/10/72	43.2 ± 2.0	0.73 ± 0.05
LCP/SPS/PSF	18/10/72	70.4 ± 2.8	1.04 ± 0.06
LCP/PC	20/80	54.3 ± 2.8	1.08 ± 0.07
LCP/PS/PC	19.6/2/78.4	56.8 ± 2.1	1.15 ± 0.05
LCP/SPS/PC	19.6/2/78.4	59.7 ± 2.9	1.22 ± 0.07
LCP/PS/PC	18.8/6/75.2	52.7 ± 3.6	1.13 ± 0.04
LCP/SPS/PC	18.8/6/75.2	63.4 ± 3.6	1.19 ± 0.05
LCP/PS/PC	18/10/72	46.8 ± 2.2	0.97 ± 0.05
LCP/SPS/PC	18/10/72	52.3 ± 2.8	1.23 ± 0.04
LCP/PEI	20/80	73.2 ± 3.4	1.23 ± 0.04
LCP/PS/PEI	19.6/2/78.4	75.6 ± 3.1	1.21 ± 0.05
LCP/SPS/PEI	19.6/2/78.4	85.8 ± 3.1	1.43 ± 0.06
LCP/PS/PEI	18.8/6/75.2	71.3 ± 3.4	1.18 ± 0.06
LCP/SPS/PEI	18.8/6/75.2	89.9 ± 3.6	1.47 ± 0.09
LCP/PS/PEI	18/10/72	68.4 ± 2.9	1.24 ± 0.06
LCP/SPS/PEI	18/10/72	80.5 ± 3.3	1.48 ± 0.10

^a Standard deviations.

But the latter does not always happen. Table V shows the torques of LCP/3.4 SPS/PSF formulations at two processing intervals in a Haake Rheomix 600 mixer. For these ternary blends, processing torques are in the range of 3 to 9 Nm, which are a little higher than that of LCP/PSF 20/80 blend but lower than that of neat PSF. The ternary blends containing SPS ionomers have acceptable processabilities and improved mechanical performances.

Polycarbonate Blend Systems

Just like the PSF/3.4 SPS blends, the partial miscibility of PC and 2.7 SPS is also demonstrated

by DSC thermograms. PC/2.7 SPS blends have two composition-dependent T_g s (Table VI). The upper-temperature T_g decreased with increasing SPS amounts from 150°C for PC to 139°C for PC/2.7 SPS 20/80, whereas the lower-temperature T_g increased with increasing PC concentration from 107°C for 2.7 SPS to 114°C for PC/2.7 SPS 80/20. The miscibility of SPS and PC was also confirmed by FTIR spectra. The absorption peak of C=O shifted from 1775 cm⁻¹ in PC to lower wave numbers in PC/2.7 SPS blends, i.e., 1773 cm⁻¹ in PC/2.7 SPS 20/80, 1772 cm⁻¹ in PC/2.7 SPS 40/60, and 1771 cm⁻¹ in PC/2.7 SPS 80/20. The absorption peak of C—O shifted from 1231 cm⁻¹ in PC

Table V Torque Values (in Nm) of Blends Processed in a Mixer

Matrix Type	Processing Time (min)	Matrix	LCP/Matrix 20/80	LCP/SPS ^a /Matrix				
				19.6/2/78.4	19.2/4/76.8	18.8/6/75.2	18.4/8/73.6	18/10/72
PSF	2	15.3	4.2	3.8	4.6	5.2	4.7	4.5
	7	14.0	5.3	5.6	9.0	8.4	7.0	7.6
PEI	2	12.2	3.8	5.2	4.7	5.8	6.3	4.7
	7	11.9	3.4	4.2	5.8	5.6	5.4	6.3
PC	2	8.3	2.9	3.3	3.5	3.2	3.3	3.6
	7	8.0	2.1	3.2	4.9	3.9	4.1	4.0

^a In cases of PSF and PEI, SPS is 3.4SPS; in case of PC, SPS is 2.7SPS.

Table VI T_g s of PC and Its Blends from DSC and DMA Measurements (in °C)

	T_g (°C)	PC/LCP		LCP/SPS/PC						PC/SPS				LCP/SPS	
		PC	80/20	LCP	19.6/2/78.4	19.2/4/76.8	18.8/6/75.2	18.4/8/73.6	18/10/72	SPS	80/20	60/40	20/80	60/40	60/40
DSC	High	150	150	—	144	142	141	138	136	—	146	144	139	—	—
	Low	—	—	—	—	—	—	—	—	107	114	116	111	—	—
DMA	High	152	152	—	144	140	139	136	134	—	—	—	—	—	96
	Low	—	—	103	—	—	—	—	—	—	—	—	—	—	—

to higher wave numbers in PC/2.7 SPS blends, i.e., 1232 cm^{-1} in PC/2.7 SPS 20/80, 1234 cm^{-1} in PC/2.7 SPS 40/60, 1241 cm^{-1} in PC/2.7 SPS 60/40, and 1245 cm^{-1} in PC/2.7 SPS 80/20, although it was difficult to distinguish the C—O absorption peak and —SO₃ absorption peak, which was weak due to quite a small amount of 2.7 SPS added. The origin of miscibility of PC and SPS comes from ion–dipole interaction between the sulfonic ion in SPS and the polar group of —C=O and C—O bond in PC.

The compatibilization in LCP/PC blends by the addition of SPS was confirmed by DSC and DMA measurements (Table VI). Only one T_g was detected in DSC and DMA thermograms of LCP/2.7 SPS/PC blends, and that was decreased by adding increasing amounts of SPS. The T_g shifts were only 6–8°C when the concentration of SPS in a ternary blend was 10%. The compatibilization in these ternary blends was also confirmed by SEM observation of fractured blend surfaces. The size of the dispersed LCP phase decreased with the addition of SPS.

The compatibilization in ternary blends resulted in improved mechanical properties. Table IV lists tensile strengths and moduli of LCP/2.7 SPS/PC blends, with corresponding values of LCP/PS/PC as references. It is clear that SPS compatibilizes LCP/PC blends. In comparison with mechanical properties of LCP/3.4 SPS/PSF blends, the amount of added SPS for a better effect is different. This can be understood from the different extent of compatibilization caused by SPSs with different sulfonation levels in LCP/PSF and LCP/PC blends.

Together with the compatibilization in LCP/PC blends, the ionomer of proper sulfonation level with proper amount added did not worsen the processability of LCP/2.7 SPS/PC blends. This can be found in Table V, which shows torque values of PC blends processed in a mixer. The processing torques were in the range of 3 to 5 Nm, which are a little larger than that of LCP/PC blend but smaller than that of pure PC. From both the processability and the mechanical performances of compatibilized blends, it is clear that the ionomer is a practically acceptable compatibilizer for polyblends with LCPs.

Polyetherimide Blend Systems

The DSC measurement shows that PEI and the LCP used in this study are immiscible (Table VII). After the addition of SPS, the only T_g in the

Table VII T_g s of PEI and Its Blends from DSC and DMA Measurements (in °C)

	PEI	PEI/LCP 80/20	LCP	LCP/SPS/PEI			SPS	LCP/SPS 60/40
				19.6/2/78.4	18.8/6/75.2	18/10/72		
DSC	214	212	—	208	203	198	107	96
DMA	221	217	103	210	204	201	—	—

DSC thermograms of LCP/3.4 SPS/PEI shifted from 214°C of PEI to 198°C of LCP/3.4 SPS/PEI 18/10/72. DMA results also show this trend. The T_g shifts from DSC and DMA tests show the compatibilization in LCP/3.4 SPS/PEI ternary blends. The size of the dispersed LCP phase decreased by the addition of SPS also confirms this effect.

Similar to PSF and PC blend systems, the PEI blend system also gained an improvement in the mechanical properties (Table IV). At a 2% concentration of 3.4 SPS, the tensile strength of a ternary blend was 85.8 MPa, 13% higher than that of a LCP/PS/PEI ternary blend. When the 3.4 SPS concentration reached 6%, the strength increased 26% and the modulus 25%, compared with LCP/PS/PEI. The effect of compatibilization and interfacial adhesion is significant. However, as previously discussed, a 10% addition of SPS did not result in a better effect, although the strength and modulus remained higher than those of a LCP/PS/PEI blend; so the concentration of SPS added should be optimized for different matrix resins at least, if a much better performance is needed.

As for the processability of LCP/3.4 SPS/PEI ternary blends, the results of torque measurement (Table V) were the same as PSF and PC blend systems. The torque value remained in the range of 4.2 to 6.3 Nm, only half of the value for PEI and about 50% higher than that of LCP/PEI blends.

CONCLUSIONS

Lightly sulfonated polystyrene is partially miscible with PSF, PC, and LCP. The miscibility of SPS with PSF, and SPS with PC, comes from the ion-dipole interaction between the ionic groups of SPS and the polar groups in PSF and PC. Unveiled by the T_g shift in DSC and DMA thermograms, the specific interaction leads to the compatibilization of SPS in LCP/PSF, LCP/PC, and LCP/PEI

blends, which results in a much finer dispersion of the minor LCP phase in PSF, PC, and PEI matrices and a stronger interfacial adhesion between LCP and these matrix phases. As a result, ternary blends of LCP/SPS/PSF, LCP/SPS/PC, and LCP/SPS/PEI have enhanced mechanical properties with lower processing torque values of melts, i.e., acceptable processabilities. It is clear that the ionomer is a practically acceptable compatibilizer for polyblends with LCPs, in both the processability and the mechanical performances of the compatibilized blends.

This research was supported by the National Natural Science Foundation of China, 59373137.

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