Communications to the Editor

Melt-Processable Polypeptide/Ionomer Molecular Composites

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Introduction. Since Helminiak et al.[1] and Takayanagi[2] first proposed the concept of a molecular composite, considerable research has been directed at developing these materials.[3] Conceptually, molecular composites are mixtures of a rigid rod polymer homogeneously dispersed in a flexible coil polymer matrix, thus providing fiber reinforcement at a molecular level. In practice, however, miscible blends are not obtained due to the tendency for rigid rod polymers to pack excluding the flexible coil molecules.[4] The majority of the published research involved attempts to prepare molecular composites from dilute ternary solutions by rapid coagulation or coprecipitation to overcome the tendency of phase separation. This method has serious limitations as a viable fabrication technique because of the large quantities of harsh solvents required and the fact that the materials phase separate when heated or if melt processed. An alternative approach for making thermally stable, melt-processable molecular composites is by block copolymerization of rigid rod and flexible coil segments.[5-7] The covalent bonds between blocks prevent macroscopic phase separation and intimately connect the reinforcement and matrix.

This paper reports the preparation of melt-processable molecular composites of a rigid rod polymer, poly(benzyl L-glutamate) (PBLG) and a flexible coil ionomer, lightly sulfonated polystyrene (SPS). Specific acid–base and/or hydrogen-bonding interactions between SPS and PBLG were sufficient to overcome the tendency for the rigid and coil polymer to phase separate, and melt-processable miscible blends were obtained.

Experimental Section. Lightly sulfonated polystyrenes were prepared from a commercial polystyrene (Styron 666, Dow Chemical Co.) with M_n = 106 000 and M_w = 280 000 using the procedure described by Makowski et al.[8] Polymers with sulfonation levels of 1.9 and 5.2 mol % were prepared; hereafter these are referred to as 1HSPS and 5HSPS, respectively. PBLG with M_v = 20 100 was purchased from Sigma Chemical Co., and PBLG of M_n = 3000 was synthesized by the method described by Daly and Poché.[9] These are referred to as HPBLG and LPBLG, respectively. Separate solutions of 5% (w/v) of SPS and PBLG were first prepared using a common solvent, chloroform, and the PBLG solution was then added dropwise to the SPS solution with constant stirring. Films of the blends were prepared by solution casting, followed by evaporation of the solvent in air and vacuum drying the solid film at 100 °C for at least 24 h.

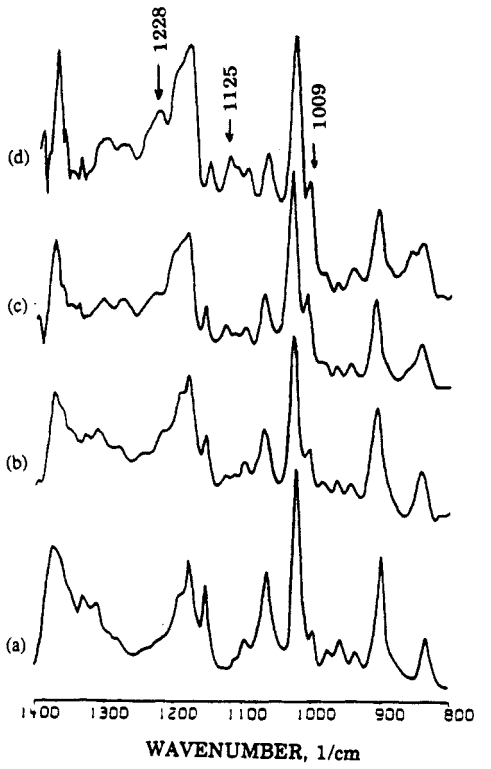

Figure 1. FTIR spectra (800–1400 cm^{-1}) of (a) 5HSPS, (b) 5HSPS/LPBLG (87.5/12.5 w/w), (c) 5HSPS/LPBLG (72/28 w/w), and (d) 5HSPS/LPBLG (60/40 in w/w).

Thermal analysis of the blends was performed with a Perkin-Elmer DSC-7 using a heating rate of 20 °C/min. Samples were held at 150 °C for 5 min following the first heating scan, quenched to −40 °C, and reheated. Infrared spectra were measured with a Nicolet 60 SX FTIR spectrometer with 100 scans at a resolution of 2 cm^{-1}. Micrographs of fracture surfaces were obtained with an Amray Model 1200B scanning electron microscope using 15 keV and a magnification of 5000×.

Results and Discussion. PBLG adopts an α-helical conformation in chloroform solution.[10] Because of the terminal amine groups, there is a distinct possibility of forming strong acid–base interactions with the sulfonic acid groups of SPS, as has been reported in the case of other polymers containing basic functional groups,[11] including amine-terminated polymers.[12,13] Figure 1 shows the FTIR spectra of blends of 5HSPS with LPBLG containing 12.5%, 28%, and 40% LPBLG. For the blends, the absorptions at 1009, 1125, and 1228 cm^{-1} are characteristic of a sulfonate salt.[14] More specifically, the absorptions at 1009 and 1125 cm^{-1} are the in-plane vibration and the in-plane skeleton vibration for the phenyl ring with a neutralized sulfonate group attached. The absorption at 1225 cm^{-1} is due to the asymmetric stretch of the sulfonate anion. In addition to showing the formation of an amine salt, FTIR also provided evidence for hydrogen bonding between the ester carbonyl group of PBLG and the sulfonic acid group of SPS. Figure 2

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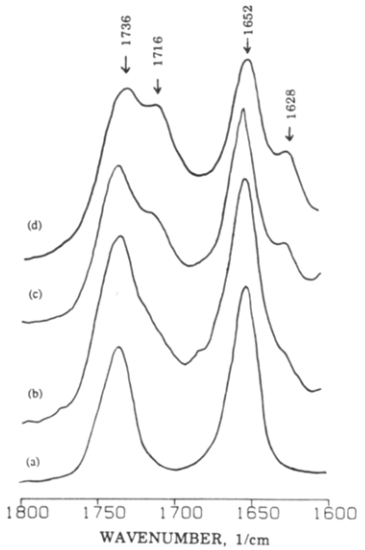


Figure 2. FTIR spectra (1600–1800 cm^{-1}) of (a) LPBLG, (b) 5HSPS/LPBLG (80/20 w/w), (c) 5HSPS/LPBLG (60/40 w/w), and (d) 5HSPS/LPBLG (46/54 w/w).

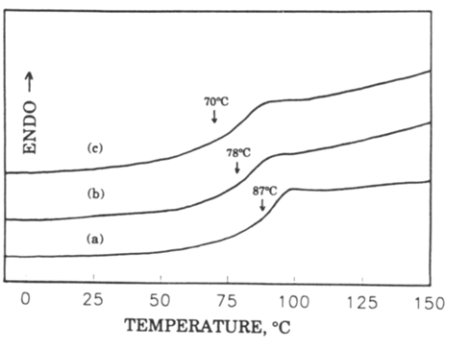
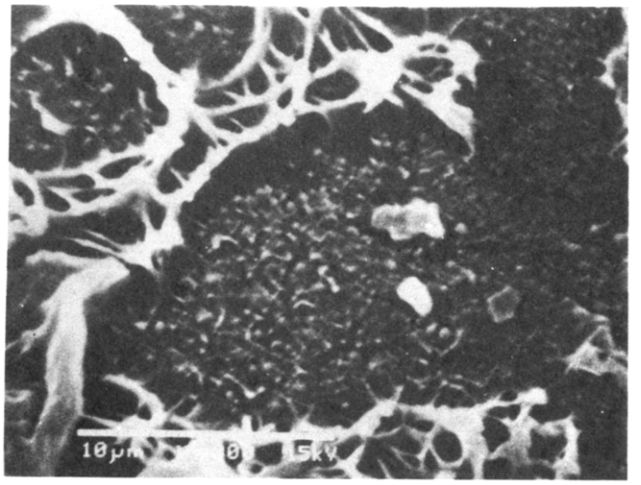
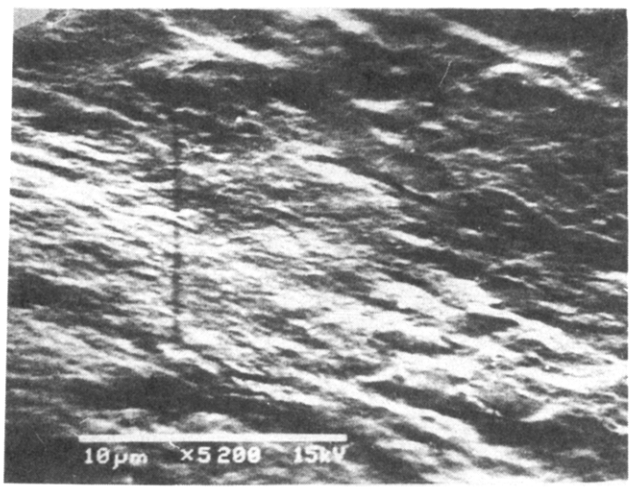


Figure 3. DSC thermograms of (a) 5HSPS/LPBLG (87.5/12.5 w/w) (b) 5HSPS/LPBLG (72/28 w/w) (c) 5HSPS/LPBLG (60/40 w/w).

shows the carbonyl region of the FTIR spectra of 5HSPS/LPBLG blends with varying composition. The peak at 1736 cm^{-1} corresponds to the free ester C=O group of the PBLG side chain, and a new peak at 1716 cm^{-1} observed for the blends represents hydrogen-bonded ester C=O groups.[15] The amide I mode of the polypeptide is sensitive to its conformation. It occurs at 1652 cm^{-1} for the C=O stretching of an α-helix and at 1628 (strong) and 1700 cm^{-1} (weak) for the C=O stretching of a β-sheet form in the solid state.[10] As the PBLG concentration in the blends increased, the ratio of the intensities of the bands at 1628 and 1652 cm^{-1} in Figure 2 also increased, though the absorbance at 1700 cm^{-1} was too weak to be observed. Brumberger and Cheng[16] reported that the amide I band for the random coil PBLG conformation, which usually occurs at 1658 cm^{-1}, shifts to 1628 cm^{-1}, close to that for the β-sheet, when the C=O is involved in hydrogen bonding. This assignment is consistent with the observation of the 1716-cm^{-1} band for hydrogen-bonding ester and with the ^1H NMR spectrum (not shown), which indicated the presence of some random coil PBLG conformation in the blend solutions. Thus, it appears that the 1628-cm^{-1} band is due to the random coil conformation of PBLG and not the β-sheet. This also indicates that the interaction with SPS induced some helix-to-coil transition of the PBLG. The breakup of the helix is presumably due to a competition between intramolecular hydrogen bonding of the amide groups in the PBLG helix and intermolecular hydrogen bonding of PBLG with the sulfonic acid of SPS. The amount of helix-to-coil transition that occurred



4(a) PS/HPBLG (82/18 w/w)



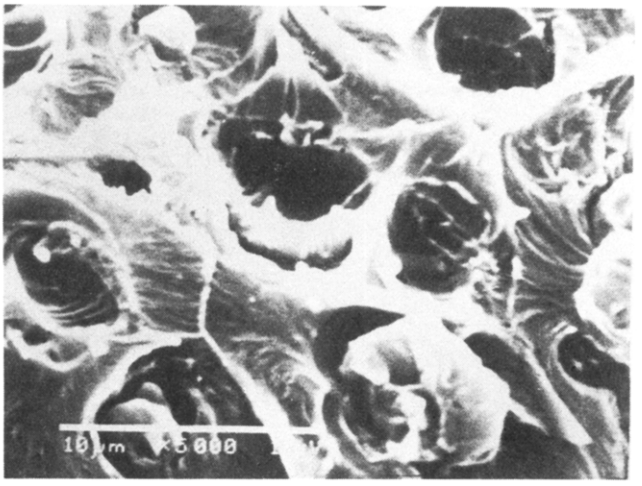
4(b) 1HSPS/HPBLG (82/18 w/w)

Figure 4. 5000× magnification images of PS/HPBLG (82/18 w/w) and 1HSPS/HPBLG (82/18 w/w).

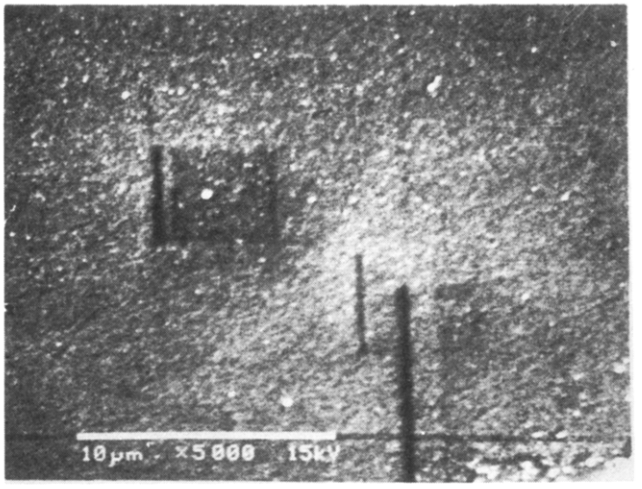
increased with increasing mixing time in solution.

Figure 3 shows the DSC thermograms of annealed (5 min at 150 °C) blends of 5SPS with LPBLG ranging from 10 to 40% (w/w) PBLG. In each case, only one T_g was observed, located between the T_g of pure 5SPS (105 °C) and pure LPBLG (20 °C). As the concentration of LPBLG increased, the T_g of the blend decreased, which indicates that these molecules were miscible, i.e., single phase, within this composition range. When the higher molecular weight HPBLG was blended with the SPS with lower sulfonation level, 1HSPS, a single T_g was observed from 0 to 20% (w/w) PBLG. Above 20% PBLG two T_g's were observed, though they were significantly shifted toward each other, compared with the T_g's of the neat compounds. That result indicates that even when two phases occur, strong intermolecular interactions are prevalent.

Figures 4 and 5 show SEM micrographs (5000×) of fracture surfaces of several blends prepared by solution casting. Figures 4a and 5a are blends of polystyrene with HPBLG and LPBLG, respectively. In both cases, significant phase separation of spherical PBLG-rich domains occurred. In stark contrast to the micrographs of the PS/PBLG blend, the 1HSPS/HPBLG and 5HSPS/LPBLG blends, Figures 4b and 5b, respectively, appeared homogeneous on a size scale of $\ll 0.1$ μm. Melt-pressed films of the SPS/PBLG blends were optically clear, and the mechanical properties of melt-extruded fibers significantly improved compared with those of the neat SPS.



5(a) PS/LPBLG (86/14w/w)



5(b) 5HSPS/LPBLG (86/14 w/w)

Figure 5. 5000× magnification images of PS/LPBLG (86/14 w/w) and 5HSPS/LPBLG (86/14 w/w).

Conclusions. Miscibility of a rigid rod and random coil polymer was achieved by promoting strong intermolecular interactions such as hydrogen bonding and proton transfer. In the case of SPS/PBLG, hydrogen bonding also opened up parts of the α-helix of PBLG. The blends remained optically clear after melt processing. The blends exhibited only a single, composition-dependent glass transition temperature under a certain composition range, and SEM failed to detect any heterogeneities in fracture surfaces. Melt-spun fibers of the blends were golden in appearance, and the addition of 10% HPBLG to 1HSPS resulted in a modulus increase from 2.3 GPa (pure PS fiber) to 3.4 GPa. These materials appear to be melt-processable molecular composites.

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