Studies of Functionalized Polystyrene–Poly(2, 6-Diphenyl-1,4-Phenylene Oxide) Blends

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SYNOPSIS

The phase behavior of an immiscible binary component blend and its functionalized analogs were studied. The unfunctionalized blends are composed of polystyrene and poly(2,6-diphenyl-1,4-phenylene oxide), whereas the functionalized versions contain a relatively broad range of ionic content, i.e., sodium sulfonate units. Extensive glass transition (T_g) measurements show that these blends are immiscible over a broad ionic content and molecular weight range. This phenomenon, however, does not inhibit these blends from possessing improved mechanical properties since the associating-type ionic interactions can effectively bridge the two phases. These results are in contrast with blends composed of unfunctionalized but miscible components. In this case, miscibility and immiscibility can be tailored through the precise control of the level of functionalization of one or both components of the blend.

INTRODUCTION

Precise control of polymer–polymer compatibility has been an area of intense scientific and technological interest, since compatible or even completely miscible blends possess desirable mechanical properties as compared to the unblended parent materials.[1] This continual attraction of exploring polymeric blends is justifiable for formulating a variety of new and useful materials with tailored physical properties. However, the ability to mix high molecular weight materials is severely limited by the virtually zero contribution of the combinational entropy to the Gibbs free energy of mixing. To overcome this problem, enhanced compatibility or miscibility can occur with the proper selection of interacting groups whereby the enthalpy of mixing becomes exothermic resulting in a favorable free energy of mixing. It should be noted that use of interacting groups chemically bound to a chain backbone is only one out of several methods for enhancing blend properties. A variety of structured compatibilizers, i.e., block and graft copolymers, are quite commonly used.

This work expands on our previous work relating to the ability to precisely control the miscibility and immiscibility of a binary component blend in which the two parent polymers, i.e., polystyrene and poly(phenylene oxide), were originally miscible over the complete composition range.[2] Expanding on this theme, we explore the phase behavior of binary blends containing a variety of polystyrenes (PS) possessing broad and narrow molecular weight distributions and their sulfonated (sodium salts) analogs (SPS), poly(2,6-diphenyl-1,4-phenylene oxide) (DPPPO) and its sulfonated (sodium salt) analog (SDPPPO). As compared to our previous studies, these blends are found to have markedly different phase behavior from somewhat similar blend systems composed of PS (or SPS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and sulfonated PPO (SPPO).

It is also noteworthy that DPPPO is thermally stable ($\geq 300°C$) and can be functionalized through a broad range of synthetic schemes. Functional groups can be placed on both the phenylene ring as well as the phenyl groups, making this polymer quite versatile with regard to modifications in molecular structure.

We should also note that strongly interacting components in a binary blend does not necessarily imply that complete miscibility is ensured.[2] To the

contrary, if the difference in functionality is sufficiently high, immiscibility appears to be the norm. However, these blend types still possess markedly enhanced physical properties due to the "compatibilization" effect on the interfacial region. Recent studies of rubber-toughened polyolefins clearly demonstrate this phenomenon.[3]

EXPERIMENTAL

Polymerization of (2,6-Diphenyl-1, 4-Phenylene Oxide)

The synthetic procedure parallels that described by Hay.[4] In a 250-mL two-neck flask, a mixture of 2,6-diphenyl phenol (48.8 g, 0.2 mol) cuprous bromide (0.28 g, 2 mmol), N,N,N^-,N^- tetramethyl ethylene diamine (0.23 g, 2 mmol), and o-dichlorobenzene (200 mL) was heated to 100°C under N_2 atmosphere. A stream of compressed air at a rate of 500 mL/min was passed through the vigorously stirred solution for 3 h. In a relatively short time period, the solution turned viscous. A 100 mL of chloroform was introduced to the polymer solution, and the resulting polymer was precipitated in 1 L of methanol, which contained 10 mL of concentrated hydrochloric acid and 10 mL hypophosphorous acid. The precipitate was redissolved in 350 mL of chloroform and filtered through Celite. The polymer was again precipitated from the filtered chloroform solution into 2 L of methanol. The essentially colorless product was collected and dried under vacuum at 100°C for 12 h (yield 77.9%). Gel permeation chromatography was used to characterize the polymer ($\bar{M}_w = 127,300$ g/mol; $\bar{M}_n = 78,800$ g/mol). These values are based on polystyrene standards in tetrahydrofuran.

Sulfonation of Poly(2,6-Diphenyl-1,4-Phenylene Oxide) and Polystyrene

Sulfonation of polystyrene was conducted in dichloroethane as solvent and acetyl sulfate as the sulfonating agent. The detailed procedure has been reported.[2]

Sulfonation of DPPPO

Sulfonation of poly(2,6-diphenyl-1,4-phenyl oxide) was conducted by two methods, i.e., using acetyl sulfate and trimethysilyl chlorosulfate as the sulfonating agents. Sulfonation by acetyl sulfate was as follows: To a 250 mL flask, 12.2 g DPPPO (0.005 mol) in 120 mL dichloroethane was heated to 65°C, and a mixture of 5.1 g acetic anhydride and 4.8 g con-

centrated sulfuric acid was slowly added to the solution in 10 min. The resulting solution was kept at 65°C for 3 h; then 32 g of 25% solution of sodium methoxide in methanol was added and was kept stirring at room temperature for 30 min. The resulting functionalized polymer was isolated by steam stripping. The precipitate was collected and dried under vacuum at 100°C for 24 h. The sulfur content was 0.73%, i.e., the sulfonation level was 6.0 mol %.

Sulfonation of DPPPO by Trimethylsilyl Chlorosulfonate

To a 250 mL flask, 12.2 g DPPPO (0.05 mol) were dissolved in 120 mL dichlorethane, and 2.7 g of chloro trimethyl silane and 2.9 g chlorosulfonic acid were subsequently added. The solution was agitated for approximately 12 h at room temperature. The work-up procedure was identical to the previously detailed acetyl sulfate method. The sulfur content of the copolymer was 3.81%, or a sulfonation level of 34 mol %.

In all instances, trimethylsilyl chlorosulfonate gave higher sulfonation levels. However, both methods gave lower yields than theoretically expected. It is possible that the DPPPO is more resistant to sulfonation due to steric hindrance. In addition, Verdet and Stille[5] pointed out that it was not possible to distinguish the reaction sites in the electrophilic substitution, i.e., halogenation, of DPPPO. However, it is most likely to take place on phenylene rings contained with the chain backbone.

Preparation of the Polymer Blends

Most of the DPPPO and PS blends were prepared from a 5 wt % toluene solution. The appropriate amount of each component was thoroughly mixed and the solvent permitted to evaporate at room temperature. Blends containing DPPPO with a sulfonation level of 6 mol % were prepared from toluene–methanol solutions, and blends containing DPPPO with a sulfonation content of 34 mole percent were prepared by dissolving in N,N-dimethyl formamide with subsequent precipitation in toluene.

Thermal Analysis

The differential scanning calorimetry (DSC) analysis of the blends and their individual components were conducted on a Perkin-Elmer DSC 7 microcalorimeter controlled by a Perkin-Elmer 7500 computer. In all instances, the heating was 20°C/min under a nitrogen blanket. Calibration was done

by a one-point method using indium as standard. Sample size ranged from 15 to 25 mg. Base line subtraction was used to improve the quality of the thermograms and facilitated their interpretation. The thermograms from the first heating was discarded and the glass transition behavior reported was obtained from either the second or third heating. Between heatings, the samples were quenched at a programmed rate of 320°C/min.

It is noteworthy that completely amorphous blends were produced from methylene chloride, while semicrystalline blends were formed from toluene. In either instance, semicrystalline blends were formed upon quenching from elevated temperature.

RESULTS AND DISCUSSION

Characterization of DPPPO and Its Sulfonated Analog

Although DPPPO has a structural similarity to PPO, the physical properties, specifically thermal properties, are quite different. Under a variety of thermal treatments in the DSC, PPO is unable to crystallize to any measureable extent, while DPPPO can rapidly crystallize to a large extent. A salient feature of the as prepared material is its completely amorphous character (T_g = 220°C) (Fig. 1), but it does rapidly crystallize at a crystallization temperature (T_c) of 269°C. These values are consistent with previous measurements.[6] It is interesting to note that the degree of crystallinity as determined by heat of fusion measurements indicates that high values can be obtained ($\geq$ 70%). This behavior is attributable to increased planarity of the DPPPO structure due to the two opposing styrenic units. These latter units also enhance the thermal stability of the chain as compared to PPO. Moreover, this thermal stability enhancement is noted in the blends described here.

As expected sulfonation enhances T_g and T_c. For example, at the 6 mol % level the T_g and T_c are 231 and 300°C, respectively. Moreover, DPPPO with a 34 mol % sulfonate content showed no thermal transitions below 300°C. These observations confirm that sulfonate groups served as crosslink sites, causing an increase in the T_g of DPPPO and strongly inhibiting crystallization even at elevated temperatures.

Characterization of PS-DPPPO Blends

One of the most utilized criterion of polymer miscibility is the detection of a single glass transition
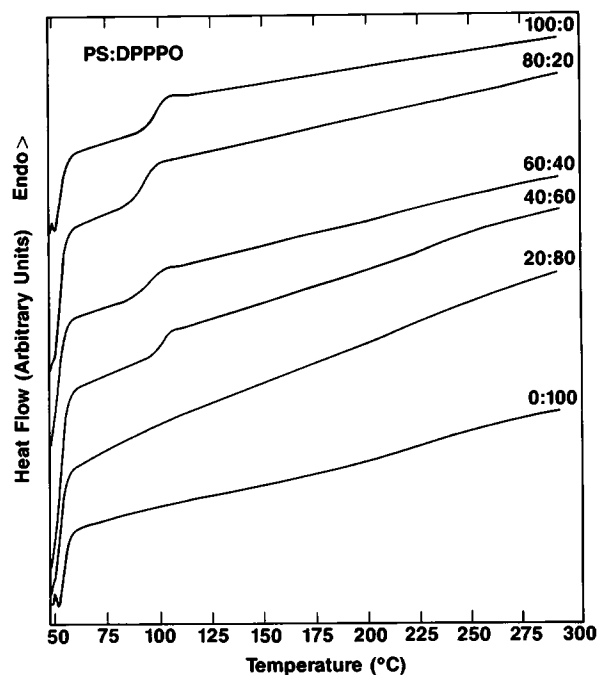

Figure 1 DSC thermograms of a series of blends composed of varying weight ratios of polystyrene (PS) and poly (2,6-diphenyl-1,4-phenylene oxide) (DPPPO).

whose temperature is intermediate, i.e., composition-dependent, between those corresponding to the two component polymers. The PS–PPO blend is one of the most well-documented miscible polymer blends, and was reported to follow the above criteria in many articles.[7-13] Two compositionally independent T_g's is the usual criterion for immiscibility. Extensive measurements of PS and DPPPO clearly confirms that immiscibility is the norm over the entire composition range. Compositionally independent T_g's are observed for PS and DPPPO at 102 and 212°C, respectively.

The above blends of DPPPO and PS prepared from toluene solutions were opaque and have distinct T_g's around 102°C and a very broad and weak T_g transition around 212°C (Fig. 1). The blends prepared from methylene chloride were transparent; however, two distinct T_g's at 102 and 220°C were observed. These measurements have to be performed with care since crystallization began to appear at 269°C. The second scan gave similar results to blends obtained from toluene solution. These data indicate that DPPPO and PS are immiscible under a variety of blend preparations. The first T_g corresponds to PS, and the second broad and weak T_g is due to partially crystallized DPPPO.

Since the Gibbs free energy is composed of enthalpy and entropy terms,[1] the entropy terms be-

come less favorable when the molecular weights of the blend components become higher. Therefore, in order to examine whether molecular weights can influence miscibility, a series of blends prepared from DPPPO and a variety of monodiperse PS with different molecular weights were investigated. The weight ratio for both components was held constant at 50 : 50. These results are presented in Figure 2. All of the samples were prepared from toluene solutions and each blend shows a distinct T_g corresponding to essentially pure PS. The expected variations with molecular weight is noted. These observations indicate that DPPPO is completely immiscible, regardless of the molecular weight of PS.

Blends of SDPPPO and SPS

As noted, previously interactions between the components in a blend is one method to achieve miscibility between polymers. Therefore, in these blends, sulfonate groups were introduced onto both PS and
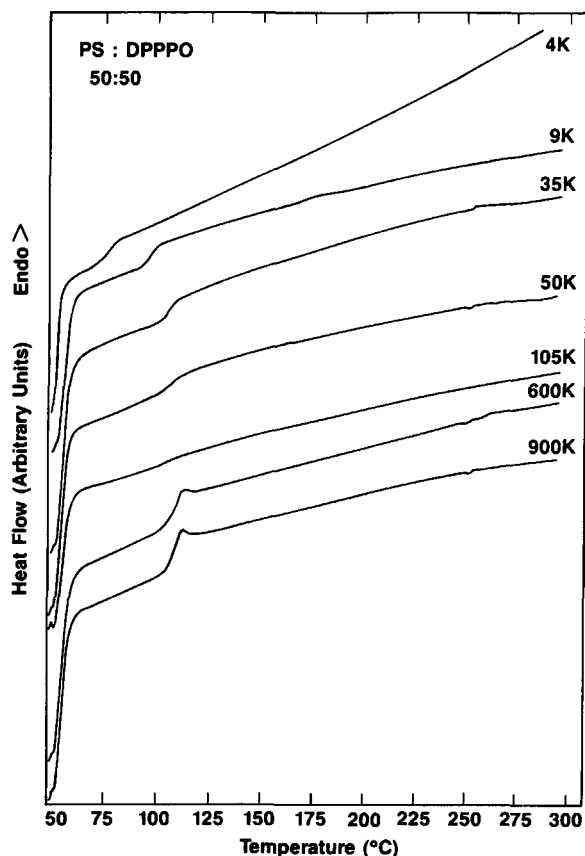

Figure 2 DSC thermograms of a series of blends composed of DPPPO and monodispense polystyrenes spanning a wide range of molecular weights. The weight ratio of the blend components in 50 : 50.
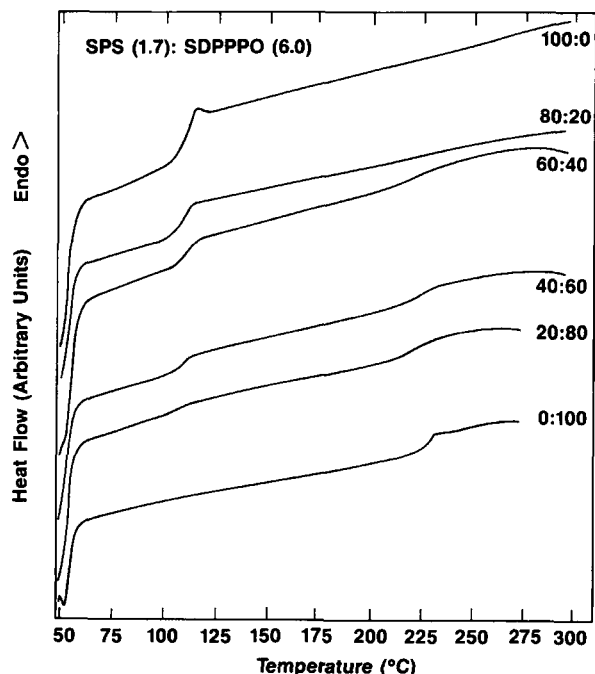

Figure 3 DSC thermograms of a family of blends composed of sulfonated polystyrene (SPS) and sulfonated poly(2,6-diphenyl-1,4-phenylene oxide) (SPPPO). The number in parenthesis denotes the sulfonation level (mol %).

DPPPO. Improved mechanical properties can result due to the microphase separation of the ionic groups into domains containing ion pairs from both types of chains. Compatibility is certainly enhanced, and if the level of sulfonation is sufficiently high, miscibility is achieved.

In the case of blends of DPPPO and PS containing low sulfonation levels, two T_g's are observed, i.e., the T_g of SPS (1.7) and SDPPPO (6.0) are about 108 and 225°C, respectively (Fig. 3). A T_c is noted at above 300°C. These results again conclusively show these interacting blend components are immiscible. These results were also confirmed through extensive light microscopy examination spanning the identical temperature range.

Blends with increased levels of sulfonation were also studied. These results are presented in Figure 4. All the thermal traces show only a single compositionally invariant T_g at about 132°C, which is consistent with the T_g of the unmixed SPS. Even a reduction in the molecular weight of the SPS component does not permit a change in the T_g except again for the anticipated reduction due to molecular weight variations (Fig. 5).

CONCLUSION

A detailed study of the thermal behavior, i.e., glass transition measurements, of a family of binary component blends containing of polystyrene–poly(2,6-diphenyl-1,4-phenylene oxide) and its sulfonated analogs were examined in order to determine phase behavior. The blends formed from the unfunctionalized polymers are immiscible over the entire composition range. In addition, a detailed examination of the molecular weight dependence on miscibility confirms that complete phase separation occurs. Even though it is known that sulfonation on both components of a binary blend markedly improves the mechanical properties of these blends (a subject of a future publication), immiscibility dominants blend structure. Therefore, it appears when the initially unfunctionalized components are immiscible, relatively large increases in ionic content do not produce a miscible blend. These results are in marked contrast to blends composed of initially miscible components, i.e. PS, PPO, and their sulfonated analogs.[2] In this case, immiscibility and miscibility is directly controlled by the ionic content on one or both of the components of the binary blend.[2]

Figure 5   DSC thermograms of blends composed of SPS and SDPPPO at a 50 : 50 weight ratio of blend components. The numbers in parenthesis denotes sulfonation level and molecular weight (K denotes a thousand), respectively.

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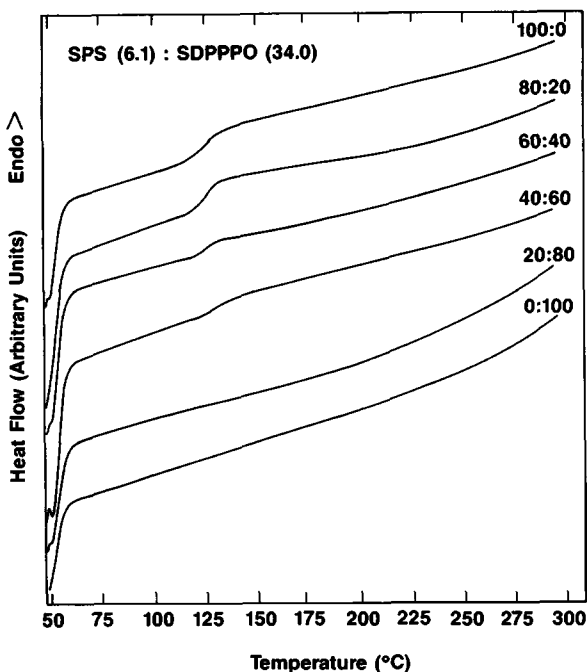
Figure 4   DSC thermograms of a family of blends composed of SPS and SDPPPO spanning the entire composition range. The number in parenthes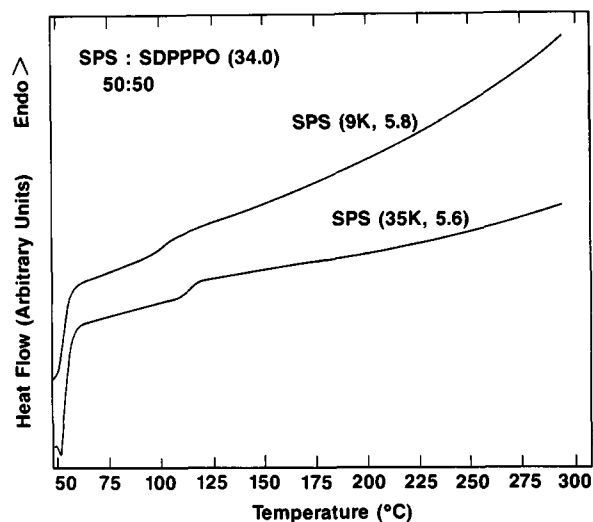is denotes the sulfonation level (mol %).