Studies on Miscibility of Poly(phenylene oxide)-Based Ionomer/Polystyrene-Based Ionomer Blends

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ABSTRACT: The phase behavior of a series of blends obtained from mixing carboxylated poly(phenylene oxide) with sulfonated polystyrene and their respective neutralized ionomers was studied by differential scanning calorimetry. A substantially broader range of miscibility was observed when both blend components were functionalized, compared with blends in which only one of the components contained an acid group or was an ionomer. The properties of metallic cations which were used to neutralize the acid groups in the blends were found to have an effect on the miscibility. The miscibility of the two acid polymers or their ionomers depended on the difference of their functionalization level instead of on the absolute percentage of functional groups on each polymer. It was found that the two acid polymers or their ionomers remained miscible as long as they had a similar percentage of functional groups. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 341–346, 1997

Key words: miscibility; poly(phenylene oxide)-based ionomers; polystyrene-based ionomers

INTRODUCTION

Blends composed of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polystyrene (PS) have attracted wide interest, since they form a well-known homogeneous phase and possess a single glass transition temperature (T_g) over the entire composition range.[1] Recently, interest in the miscibility of PPO/PS blends has been extended to miscibility studies of blends containing a component modified with polar groups, such as PPO/halogenated PS,[2] PPO/sulfonated PS or carboxylated PS,[3] brominated PPO/PS,[4] carboxylated PPO/PS,[5] and sulfonated PPO/PS[6] blends. All

these studies have shown that introducing polar groups on either PPO or PS tends to decrease miscibility and, when enough are carried, will lead to immiscibility, especially when one component was an ionomer. The phenomenon can be easily explained: As we know, attaching a relatively small number of ionic groups to an organic polymer chain can exert profound effects on the physical properties of the material. These effects have been attributed mainly to the aggregation of the ionic groups into physical crosslinking sites due to ion–pair interaction. It was therefore difficult to achieve miscibility when the ionic groups in one of components tended to aggregate into a nanometer-scale phase separation.[7] The situation may become different, however, when the ionic groups were distributed between the two blend components, i.e., blending between two ionomers. There have been only a few studies on ionomer/ionomer blends. Hseih and Peiffer[8] reported on the iono-

mer/ionomer blend system based on PPO/PS; the miscibility was found to have improved when both the PPO and PS were sulfonated compared to only when one of the components was sulfonated. In this article, the phase behavior of a series of blends of carboxylated PPO/sulfonated PS and their ionomers was investigated. The ionomers resulted from the neutralization of the corresponding acid polymer blend with alkali metal salts from Li, Na, and Cs. The objective of the present research was to explore the effects of the amount of acid groups and the types of cations in the two components on their miscibility behavior.

EXPERIMENTAL

Synthesis and Sample Preparation

Sulfonated PS (SPS) was obtained by sulfonating polystyrene with acetyl sulfate in 1,2-dichloro-ethane, following the method described in the literature.[9] The products were represented by x-SPS, where x was the mol % of the sulfonation degree. The sulfonation level was determined by titration of SPS in a toluene/methanol (90/10 v/v) mixing solution to the phenolphthalein end point with $0.1N$ methanolic sodium. The carboxylated PPO (CPPO) was prepared according to the procedure described by Huang et al.[10] The functionalization level of CPPO was determined by titration using $0.1N$ methanolic potassium in dioxane; the products were labeled as y-CPPO, y representing the mol % of the carboxylation degree.

The CPPO/SPS blends were obtained by dissolving a desired amount of CPPO and SPS into a mixed solvent of chloroform/methanol, agitating for over 48 h, then evaporating the solvent. Their corresponding alkali metal neutralized ionomer blends were obtained by an analogous procedure, A stoichiometric amount of a metal salt in methanol was added to a solution containing the CPPO and SPS acid polymers. The alkali metal salts studied were sodium methoxide, lithium, and cesium acetates. The neutralized ionomer blends were represented by alkali metal–(CPPO/SPS).

Thermal Analysis

Differential scanning calorimetry (DSC) analysis of the blends was conducted on a Perkin-Elmer DSC-2C under a nitrogen atmosphere. The glass
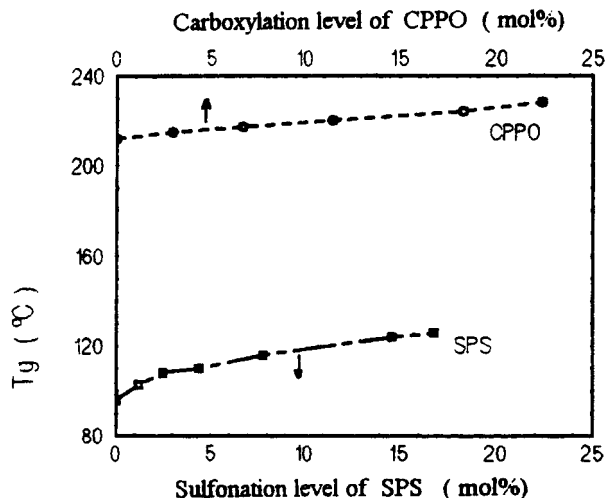

Figure 1 The T_g of SPS or CPPO with different functionalization levels.

transition temperature (T_g) is defined as the temperature at the midpoint of the heat-capacity change, and the transition breadth (ΔT_g) is the temperature range defined by the separation of the points where a line tangent to the midpoint intersects the pre- and posttransition base lines. All the samples were heated at heating rate 40 K/min from 300 to 523 K, then quenched at a programmed rate of 320 K/min to room temperature; the second scanning was from 323 to 623 K at heating rate 20 K/min. The T_g reported was obtained from the second scanning.

RESULTS AND DISCUSSION

Characterization of CPPO and SPS

The T_g's of CPPO and SPS with different functionalization levels are shown in Figure 1. With an increasing functionalization level, the T_g's of both CPPO and SPS were shown to increase.

Effect of the Acid-group Contents of Blend Components on Miscibility

As reported previously, CPPO/PS (50/50) blends[5] are no longer miscible when the carboxylation degree is above 9.0 mol %. This is due to the carboxylic groups' aggregation which hinders the thorough mixing of the remaining PPO and PS. For the same reason, PPO/SPS (50/50) blends[8] are also immiscible with a sulfonation level up to 4.2
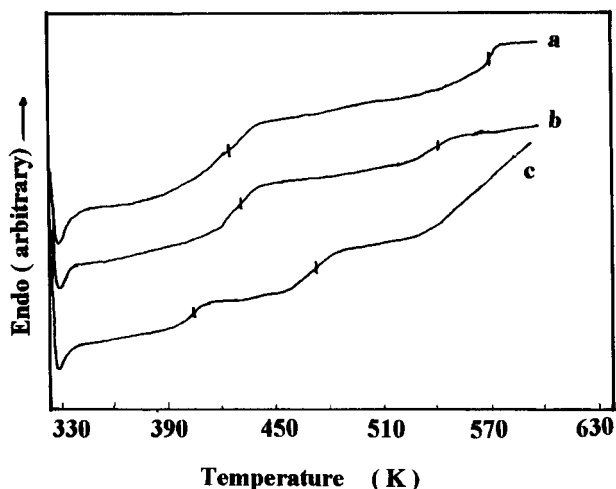
Figure 2 DSC thermograms for SPS/CPPO (50/50) blends: (a) 1.3-SPS/11-CPPO; (b) 2.5-SPS/11-CPPO; (c) 7.8-SPS/11-CPPO.

mol %. But what will happen to the miscibility if both components contain acid groups such as CPPO/SPS, carboxylic groups on PPO chains, and sulfonic groups on PS chains. Whether the two different acid polymers remain aggregated together or individually will affect the overall miscibility and this is explored in the following: First, 11.5-CPPO was blended with a series of SPS with different sulfonation levels and 7.8-SPS was blended with a series of CPPO with different carboxylation levels. The phase behavior of the two series of blends was investigated by DSC (Fig. 2); the results are listed in Tables I and II, respectively.

As expected, the PS/11-CPPO (50/50) blend is

Table I   Characteristics of SPS/11–CPPO (50/50) Blends

Blends	T_g (°C)	ΔT_g (°C)
PS/11–CPPO[a]	113	18
	217	15
1.3–SPS/11–CPPO[a]	149	20
	295	10
2.5–SPS/11–CPPO[a]	156	28
	266	40
4.4–SPS/11–CPPO	160	28
7.8–SPS/11–CPPO	164	28
14–SPS/11–CPPO	188	75
16.8–SPS/11–CPPO	204	85

[a] Blends having two glass transition temperatures.

Table II   Characteristics of CPPO/7.8–SPS (50/50) Blends

Blends	T_g (°C)	ΔT_g (°C)
PPO/7.8–SPS[a]	147	30
	202	22
2.9–CPPO/7.8–SPS	162	20
6.7–CPPO/7.8–SPS	165	23
11.5–CPPO/7.8–SPS	165	28
13.5–CPPO/7.8–SPS	167	28
18.3–CPPO/7.8–SPS[a]	131	15
	198	32

[a] Blends having two glass transition temperatures.

almost completely phase-separated; the lower T_g and upper T_g correspond to the pure PS and CPPO phases, respectively. The miscibility behavior changes drastically, however, when some sulfonic groups are introduced to PS. Even if the sulfonation level of SPS is as low as 1.3 mol %, improvement in miscibility is observed. The 1.3-SPS/11-CPPO blend possesses two distinct T_g's in which the lower T_g corresponds to a mixed SPS/CPPO phase while the higher T_g corresponds to a CPPO-rich phase. The T_g of the miscible mixed phase is 149°C, approximately equal to the value calculated from the Fox equation.[11] Due to the small amount of sulfonic groups on PS compared to carboxylic acid groups on PPO in this blend, it is unlikely that the sulfonic groups can destroy completely the self-aggregated state of carboxylic groups. The T_g located at the higher temperature area may be related to the dissociation of the carboxylic group aggregation. Our previous FTIR study[12] on the CPPO/PS system showed that the blend actually has undergone a thermally induced phase-separation procedure if subjected to a very low heating rate (1°C/min); a new absorption band at 1696 cm^{-1} assigned to the formation of dimers was split out from the carboxylic band at 1710 cm^{-1} at about 230–240°C. Therefore, in the present case, some carboxylic acid dimers may exist in the separated CPPO-rich phase, and because the dimer requires more energy to dissociate than that of simple aggregated chains, the higher T_g observed can be related to the dimer contents in the CPPO-rich phase. The more dimer contents, the higher T_g observed.

This suggestion can be confirmed by the following experimental data: The ratios of [COOH]/[SO$_3$H] in the blends of 1.3-SPS/11-CPPO, 2.5-SPS/11-CPPO (shown in Table I), and 7.8-SPS/
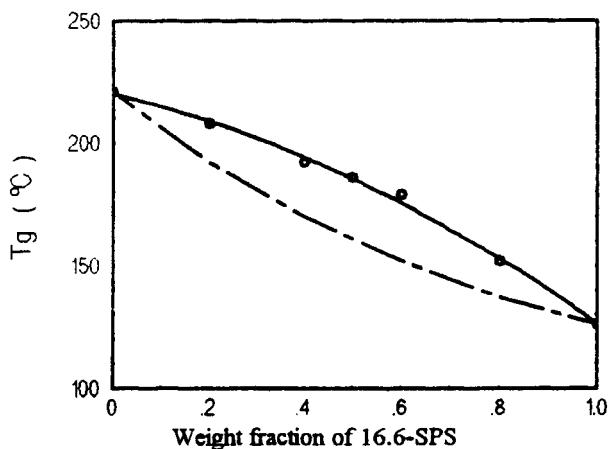
Figure 3 Summary of DSC results for 16.6-SPS/16.8-CPPO blends. (------) Fox equation.

18.3-CPPO (shown in Table II) are 8 : 1, 4 : 1, and 2.4 : 1, respectively. Their T_g's measured are 295, 266, and 198°C for the separated CPPO-rich phase, respectively, indicating their relationship with the carboxylic acid dimer concentration. The DSC thermograms for above blends are also shown in Figure 2 for comparison.

A similar phase-separated phenomenon was observed for 2.5-SPS/11-CPPO. Eventually, when the sulfonation level is at 4.4 mol % or above for the SPS, only a singe T_g was detected for the SPS/11-CPPO (50/50) blends, which indicates an extensive degree of phase mixing to complete miscibility. SPS/11-CPPO blends are found to remain miscible even if the sulfonation level is as high as 16.8 mol %. Since a broad glass transition usually reflects some sort of heterogeneity (in molecular scale) within a phase, careful inspection of the ΔT_g of the series of SPS/11-CPPO blends indicates, although miscibility is improved with the sulfonation level increases initially, that the breadth of the T_g becomes broader when the sulfonation level is above 14.6 mol % suggesting the existence of segregation at the molecular scale.

Similar phase behavior was observed for blends of 7.8-SPS with a series of CPPO. When a few carboxylic groups (e.g., as low as 2.95 mol %) are attached to PPO, the miscibility is improved greatly and is even complete. As the carboxylation level is further increased, miscibility remains until it is at 18.3 mol %. Two T_g's were detected in the 18.3-CPPO/7.8-SPS blend; the higher T_g is suggested to be a new CPPO-rich phase.

Obviously, our results show that the CPPO/SPS blends are miscible with a wide range of acid group concentrations. Also, to some extent, the experiments also indicate the SPS/CPPO blends can remain miscible as long as their acid contents are closely matched but independent of the actual acid level in the individual component. This is different from the previous studies on blends containing only a sulfonated or carboxylated component, in which the lower the functionalization level the more likely is the miscibility to be observed. The miscibility of SPS/CPPO also suggests that the carboxylic and sulfonic groups tend to aggregate with each other rather than being limited to aggregate among themselves; namely, there is some carboxylic–sulfonic aggregation or interactions, which acts as one of the driving forces to disperse and mix the two components and eventually to enhance the miscibility. The formation of acid or ion aggregates or clusters, however, need elucidation by further experimental works on X-ray scattering studies in the future.

The specific interaction between the two kinds of acid groups are further elucidated by investigating the phase behavior as a function of composition of the 16.6-CPPO/16.8-SPS blends; the DSC results are shown in Figure 3. Although both components have a relatively high acid group content, the blends are miscible over the entire composition range. In general, the T_g of a nonspecific interacting miscible blend should be in good agreement with the Fox equation, but this blend system shows a relatively large positive deviation from the Fox equation, suggesting intensive acid–acid interactions between the blend components or formation of physical cross-linking sites which hinder the segment movement and result in a relatively higher T_g. This case is similar to what Hseih and Peiffer[8] observed in SPPO/SPS blends despite that the two kinds of acid groups on the two components studied in this article are differ-

Table III Characteristics of Li–(SPS/11–CPPO) (50/50) Blends

Blends	T_g (°C)	ΔT_g (°C)
Li–(PS/11–CPPO)[a]	105	18
	206	15
Li–(2.5–SPS/11–CPPO)	152	32
Li–(4.4–SPS/11–CPPO)	162	30
Li–(7.8–SPS/11–CPPO)	164	18
Li–(14–SPS/11–CPPO)	198	12
Li–(16.8–SPS/11–CPPO)	204	16

[a] Blends having two glass transition temperatures.

ent, which somewhat indicates that the two kinds of acid groups may interact relatively in disregard of the types of acid groups and the polymer chain structure to which they are chemically bonded. The result may be very useful in practical application.

Effect of the Cation on Miscibility

The properties of the cation used to neutralize the above acid polymer blends and their influence on the miscibility behavior is another question to be addressed. To be compared with the acid polymer blends as described above, a series of alkali metal (Li, Na, Cs) ions has been introduced to the SPS/11-CPPO blend system studied above under the same conditions. Their phase behavior was examined by DSC; the results are listed in Tables III–V, respectively. Comparison of the results for the three different cation groups in relationship to the acid polymer blends is as follows:

The miscibility behavior of SPS/11-CPPO blends neutralized with Li or Cs salts is very similar, and their results also only slightly differ from that of the SPS/11-CPPO blends except when the sulfonation level is low at 2.5 mol %. Both Li (or Cs)–(SPS/11-CPPO) are miscible at this sulfonation range while the SPS/11-CPPO blend is phase-separated, indicating that introducing Li^+ (or Cs^+) into the blend system makes it easier to obtain miscibility. However, the T_g's of Li–(SPS/11-CPPO) are almost equivalent to those of the acid polymer blends (SPS/11-CPPO), while the T_g's of Cs–(SPS/11-CPPO) show some variations.

Similar to SPS/11-CPPO, the miscibility of the Na–(SPS/11-CPPO) ionomer blend series shows gradual improvement with increase of the sulfo-

Table IV   Characteristics of Na–(SPS/11–CPPO) (50/50) Blends

Blends	T_g (°C)	ΔT_g (°C)
Na–(PS/11–CPPO)[a]	106	16
	177	10
Na–(2.5–SPS/11–CPPO)[a]	138	32
	250	20
Na–(4.4–SPS/11–CPPO)	168	30
Na–(7.8–SPS/11–CPPO)	185	60
Na–(14–SPS/11–CPPO)	252	20
Na–(16.8–SPS/11–CPPO)*	137	10
	252	25

[b] Blends having two transition temperatures.

Table V   Characteristics of Cs–(SPS/11–CPPO) (50/50) Blends

Blends	T_g (°C)	ΔT_g (°C)
Cs–(PS/11–CPPO)[a]	110	12
	202	5
Cs–(2.5–SPS/11–CPPO)	132	18
Cs–(4.4–SPS/11–CPPO)	130	20
Cs–(7.8–SPS/11–CPPO)	123	30
Cs–(14–SPS/11–CPPO)	210	20
Cs–(16.8–SPS/11–CPPO)	210	18

[a] Blends having two transition temperatures.

nation level as seen in Table IV. The sodium ions neutralized ionomer blends become miscible when the sulfonation level is increased to 4.4 mol %, but unlike the others, its miscibility reaches a limit and becomes phase-separated when the sulfonation level is at 16.8 mol %. In addition, the T_g for Na–(SPS/11-CPPO) is much higher than is the T_g of the acid polymer blends as well as the T_g for the Li (or Cs)-neutralized ionomer blends. For example, the T_g of 14-SPS/11-CPPO (50/50) is only 188°C, while the T_g of Na–(14-SPS/11-CPPO) (50/50) is as high as 252°C. The differences may result from that the Na^+ has a greater potential to aggregate together and can generate stronger ionic aggregation. Therefore, as the sulfonation level is further increased to 16.8 mol %; there are not so many sodium carboxylate ions to match the sodium sulfonate ions so that the excessive Na–sulfonate ions may be expelled to form a new Na–SPS-rich phase. The very high T_g for the Na-blend series may be due to a stronger ion-pair interaction as well as to the larger number of ion pairs that participated in the aggregation. Since the Li, Na, and Cs all belong to the alkali metal series, the differences of phase behavior among these three series of blends may be attributed to their different ionic radii. More detail studies on how to interpret these phomomena will be reported in the future.

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