Miscibility and immiscibility in functionalized associating polymer systems: polystyrene–poly(phenylene oxide) blends

Dong-Tsai Hseih and Dennis G. Peiffer
Exxon Research and Engineering Company, Corporate Research, Route 22 East, Clinton Township, Annandale, NJ 08801, USA
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The thermal properties of several families of polystyrene–poly(phenylene oxide), sulphonated polystyrene–poly(phenylene oxide), polystyrene–sulphonated poly(phenylene oxide), and sulphonated polystyrene–sulphonated poly(phenylene oxide) blends were studied by differential scanning calorimetry. The appearance of a single glass transition temperature, i.e. blend miscibility, depended on the level of sulphonation of one or both components of the blend. Even though blends formed from the unfunctionalized components were miscible over the complete composition range, miscibility was reduced as the sulphonation level increased in either component. A substantially broader range of miscibility was observed when both blend components were functionalized. Compared with blends containing one sulphonated component, where immiscibility could occur within a relatively modest sulphonation range (typically 2–4 mol%), blends with two sulphonated components retained miscibility over a substantially broader sulphonation range (typically 10 mol%). The results are interpreted in terms of the mean field theory involving interaction parameters for the individual monomer segments.

(Keywords: binary component blends; functionalized components; thermal behaviour; miscibility)

INTRODUCTION

Polymer blends composed of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) are of unusual interest from both a scientific and a technological point of view, since these solid solutions form a homogeneous phase and possess a single glass transition temperature (T_g) over the entire composition range[1,2]. These polymer blends have been characterized by a broad range of techniques, including thermal optical analysis[3], differential scanning calorimetry[4], dynamic mechanical analysis[5], dielectric measurement[6], magic-angle spinning ^{13}C n.m.r.[7], small-angle neutron scattering[8], inverse gas chromatography[9], and infra-red and ultra-violet spectroscopy[10]. The driving force for miscibility of these polymer blends has been investigated by inverse gas chromatography[9] and infra-red and ultra-violet spectroscopy[10] and it was determined that van der Waals interactions between the aromatic rings of PS and PPO, rather than any specific interaction, were primarily responsible for miscibility. In addition, Schneider[11] extensively analysed the T_g data of PS–PPO blends from the literature and concluded that no specific interactions between PS and PPO exist, which is consistent with previous observations[10].

An area of continual interest is the examination of the miscibility of blends containing chemically modified components (one or both) of PS–PPO blends, such as poly(α-methylstyrene)[9], halogenated PS[12], carboxylated PPO[13], sulphonylated PPO[14], and brominated PPO[15]. The primary objective of most of these studies was to explore the limits of miscibility of these scientifically interesting and technological useful blends. Eisenberg and co-workers[16–18] were able to improve miscibility of polystyrene–poly(ethyl acrylate), polystyrene–poly(methyl methacrylate) and polystyrene–polyurethanes by introducing the sulphonic acid group to polystyrene, and 4-vinylpyridine to poly(ethyl acrylate) polymer backbone. The interactions of sulphonic acid–pyridine, and sulphonic acid–urethane were the driving force for improving miscibility. Beretta and Weiss[19] also found that an amine-terminated block copolymer of ethylene oxide and propylene oxide formed a miscible blend with the sulphonated polystyrene.

Alternatively, transition-metal coordination-type interactions can be used to form an interesting family of strongly coherent immiscible blends or even totally miscible polymer mixtures[20]. Peiffer *et al.*[21–23] prepared polymer blends of poly(styrene-co-4-vinylpyridine) and sulpho-ethylene propylene terpolymers (EPDM), and found that the rheological properties were strongly dependent on the transition-metal salt of sulpho-EPDM. Besides the previous approaches, Campbell *et al.*[24] were able to prepare high-impact blends of PPO, PS, and sulphonated EPDM by introducing the zinc salt of sulphonated PS.

It is noteworthy that polystyrene was first fully sulphonated by using a sulphur trioxide–triethyl phosphate complex[25] to prevent crosslinking side-reactions. Makowski *et al.*[26] prepared lightly sulphonated polystyrene in a homogeneous manner by using acetyl sulphate in a dichloroethane solution. The synthesis of sulphonated PPO was reported by Chludzinski *et al.*[27] and by Huang and Kim[28], using chlorosulphonic acid in a halogenated hydrocarbon solvent. Under the reaction conditions, the free acid of sulphonated PPO precipitated during the reaction. Owing to its relatively

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good stability over a wide pH range, sulphonated PPO is useful as a reverse osmosis membrane, but it appears that this material has never been studied as a component of polymer blends.

In this investigation, we explore the phase behaviour of a variety of PS, PPO, sodium sulphonated PS (SPPO) and sodium sulphonated PPO (SPPO) blends and their respective blend components. Both miscibility and immiscibility are observed depending on the specific polymer structure of each blend component and their respective composition. Taking advantage of Makowski's sulphonation method[26], both PPO and PS were sulphonated in a homogeneous manner, and with these functionalized copolymers the miscibility (or immiscibility) of polymer blends using one or both of these ionomeric components was studied.

EXPERIMENTAL

All materials were used as received, without further purification: PPO (Scientific Polymer Products Inc.; $\bar{M}_n = 24\,500$; $\bar{M}_w = 55\,600$); PS (Dow Chemical, Styron 666; $\bar{M}_n = 89\,900$; $\bar{M}_w = 212\,000$); concentrated sulphuric acid (Fisher Scientific); acetic anhydride; anhydrous dichloroethane (DCE); anhydrous methanol; tert-butyl alcohol; 25% sodium methoxide in methanol; and toluene.

Preparation of sodium salts of sulphonated PPO (SPPO) and sulphonated PS (SPS)

A typical run for sodium PPO sulphonate was as follows. A mixture of 20 g (0.167 mole of repeating unit) PPO and 200 ml DCE was charged into a four-neck flask under a nitrogen atmosphere, and kept at 55°C with continual mechanical stirring. A sulphonating agent was prepared by adding 0.82 g (0.0084 mole) concentrated sulphuric acid to 1.67 g (0.0168 mole) acetic anhydride which was kept in an ice bath, and then diluted by 2 ml DCE. The sulphonating agent was kept in an ice bath and added dropwise into PPO solution for 10 min. The reaction mixture was homogeneous and was kept at 55°C for another 2 h. The reaction was subsequently quenched by 5.4 g (0.025 mole sodium methoxide) of a 25% sodium methoxide methanolic solution under constant stirring for 30 min at 55°C. The resulting solution was poured into 4 l methanol, and the precipitate was chopped in an explosion-proof blender with methanol and was further washed with a large excess of methanol until the precipitated polymer was neutral. The sodium PPO sulphonate (SPPO) was dried under vacuum at 100°C for 2 days. The yield was 12.0 g and the sulphur content was 0.95 wt%; 3.7 mol% of repeating unit was sulphonated.

Under these reaction and workup conditions, the efficiency of sulphonation was about 60–80% and the yield was typically 50–80%. It was also observed that the higher the sulphonation level, the lower was the yield. This may indicate that a certain amount of highly sulphonated PPO was soluble in methanol.

Sulphonation of PS was conducted under similar conditions, but the reaction time was 1 h and the SPS was isolated by a steam-stripping method[26]. The detailed sulphonation characteristics of SPPO and SPS are listed in *Table 1*.

Table 1 Characteristics of PPO, PS and their sulphonated derivatives

Sample (sulphonation level, mol%)[a]	Sulphur content (wt%)	T_g (°C)	T_g range, ΔT^b (°C)
PPO	0.0	216	8
SPPO(0.6)	0.17	218	8
SPPO(1.9)	0.50	224	12
SPPO(3.0)	0.77	231	12
SPPO(3.7)	0.95	235	18
SPPO(8.0)	1.99	–[c]	–[c]
SPPO(9.2)	2.28	–[c]	–[c]
SPPO(14.2)	3.37	–[c]	–[c]
SPPO(15.9)	3.74	–[c]	–[c]
PS	0.0	106	6
SPS(1.7)	0.54	108	8
SPS(2.6)	0.83	111	10
SPS(4.2)	1.28	116	12
SPS(6.2)	1.46	124	16

[a] Mole percent of sulphonated repeating unit

[b] As defined in *Figure 1*

[c] T_g of these samples was above 250°C and could not be measured owing to thermal decomposition

Preparation of polymer blends

The various polymer blends were prepared by several different methods since the solubility characteristics of the non-ionic precursors and functionalized polymers were different. PS–PPO blends were prepared by dissolving and thoroughly agitating the two components into DCE (i.e. a common solvent). The solvent was evaporated by introducing a nitrogen stream onto the solution surface (55°C). The solvent residue was removed under vacuum for 2 days at 100°C. Samples of SPS(2.6)–SPPO(1.9) and SPS(4.2)–SPPO(3.7) were prepared under the same conditions as those of PS–PPO blends, using a toluene–methanol solvent pair. For the other polymer blends, DCE–tert-butyl alcohol mixtures were used to dissolve the components. The solvents were removed using a freeze-dry technique. The mixture was rapidly frozen by pouring into liquid nitrogen, and the solvent removed under vacuum at low temperature. Any solvent residue was further removed under vacuum for 2 days at 100°C.

Thermal analysis

The differential scanning calorimetry (d.s.c.) 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, heating was conducted at 20 K min^{-1} under a nitrogen blanket. Calibration was done by a one-point method using indium as the standard. The sample size ranged from 15 to 25 mg. Baseline subtraction was used to improve the quality of the thermograms and facilitated their interpretation. The thermogram from the first heating was discarded and the glass transition behaviour reported was obtained from either the second or the third heating. Between heatings, the samples were quenched at a programmed rate of 320 K min^{-1}. The scheme of d.s.c. data analysis is shown in *Figure 1*.

RESULTS AND DISCUSSION

Characterization of the sodium salt of sulphonated PPO (SPPO)

As noted previously, sulphonation of PPO was conducted in a homogeneous manner by a modified

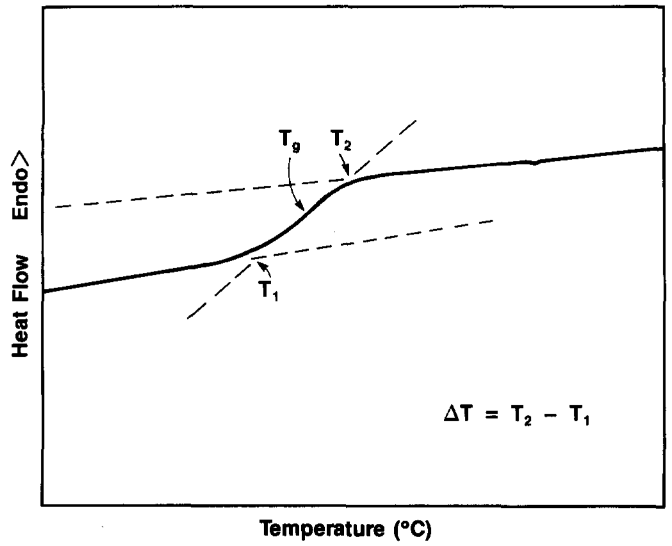

Figure 1 Schematic d.s.c. curve defining the glass transition temperature T_g and the breadth ΔT ($= T_2 - T_1$) of the transition

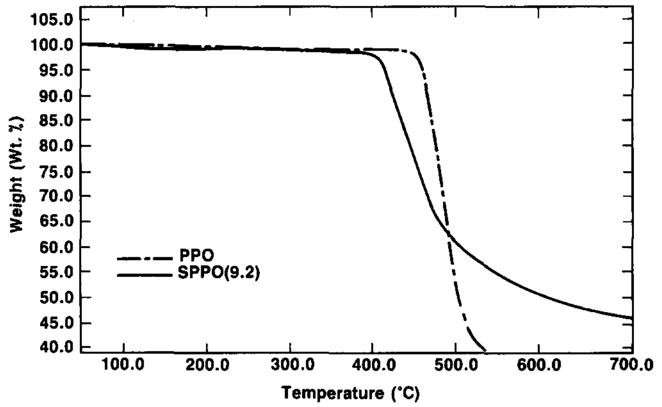

Figure 2 Thermogravimetric analysis of unsulphonated and sulphonated (9.2 mol%) PPO

Makowski method. The elemental analyses and T_g results are listed in *Table 1*. As expected, the T_g of SPPO increases with increasing sulphonate content, owing to the strong inter-chain interactions. When the sulphonation level approaches 8 mol%, the SPPO copolymer possesses a T_g well above 250°C. The exact value cannot be obtained, since the material decomposes slightly, even under a nitrogen atmosphere. In order to examine this phenomenon in more detail, thermogravimetric analysis was conducted on SPPO(9.2) and PPO under a nitrogen atmosphere (*Figure 2*). The t.g.a. showed that SPPO(9.2) decomposed negligibly at 250°C but degraded rapidly at $\geqslant$405°C. However, the d.s.c. scans from 50 to 300°C gave a T_g of 259°C for the first run and 234°C for the second, and the sample turned slightly brown. From *Figure 2* it appears that PPO is initially more stable than SPPO(9.2) but degrades much more rapidly at temperatures exceeding 450°C. Perhaps owing to different sulphonation levels or experimental conditions, Huang and Kim[28] reported that SPPO began to degrade in the vicinity of 250°C, which is much lower than observed here.

Characterization of sodium salt of PS (SPS)

SPS is one of the most well-documented ionomeric polymers, and the literature has been reviewed recently by Fitzgerald and Weiss[29]. Weiss *et al.*[30] observed that for the same sulphonation level but different synthetic methods, i.e. either copolymerization of styrene–sodium styrene sulphonate or sulphonation of the preformed polystyrene, different T_g relationships were found. The SPS used in the present work was obtained by the latter method. Upon increasing the sulphonation level, the T_g of SPS increases, as shown in *Table 1*. The T_g values reported here are somewhat higher than previous results[30]. This can most likely be attributed to differences in the unfunctionalized PS. The T_g of PS for the present work was 106°C, but was about 98°C in Weiss *et al.*'s study.

There are two common features in both SPS and SPPO thermal measurements: (1) T_g increases with increasing sulphonation level; (2) the T_g range becomes broader with increasing sulphonation level. These observations can be attributed to formation of strong, physically associating ionic crosslinks.

Characterization of PS–PPO blends

One of the most unambiguous criteria of polymer miscibility is the detection of a single glass transition whose temperature is intermediate between those corresponding to the two-component polymers, i.e. composition-dependent. The PS–PPO blend is one of the most well-documented miscible polymer blends, and in many articles is reported to follow the above criterion. The d.s.c. results are shown in *Figure 3* and the data are listed in *Table 2*. The results show the same trend as reported in the literature.

The existence of a single glass transition does not

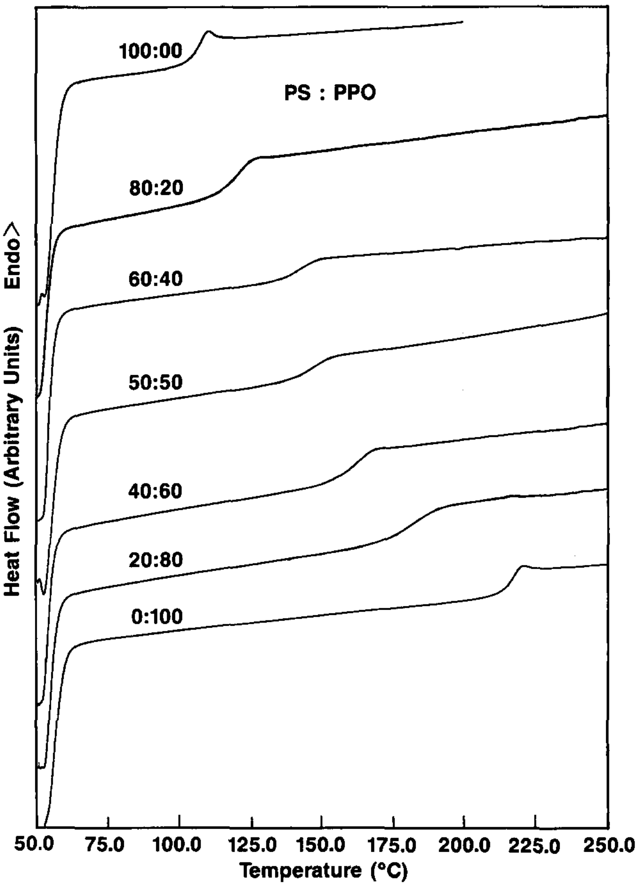

Figure 3 D.s.c. curves of unsulphonated PS–PPO blends

Table 2 Characteristics of PS–PPO blends

PS:PPO (wt ratio)	T_g (°C)	ΔT (°C)
100:0	106	6
80:20	119	21
60:40	140	14
50:50	145	13
40:60	160	16
20:80	180	20
0:100	216	7

necessarily imply that the blends have segmental homogeneity. Utilizing T_g data (alone or in combination with other physical probes), one can explore the molecular interactions between two-component polymers and thus gain a better understanding of a blend system. For example, Kwei and Frisch[31] were able to determine the χ parameter by using T_g data. Very recently, however, Schneider and co-workers[11,32,33] were able to determine the existence of specific interactions between blend components through the so-called third-power equation:

$$(T_g - T_{g1})/(T_{g2} - T_{g1})W_{2c} = (1 + K_1) - (K_1 + K_2)W_{2c} + K_2W_{2c}^2 \quad (1)$$

where

$$W_{2c} = KW_2/(W_1 + KW_2)$$

$$K = \rho_1 T_{g1}/\rho_2 T_{g2} = K'(T_{g1}/T_{g2})$$

Here, W_1 and W_2 are the weight fractions of the blend components, T_{g1} and T_{g2} are their glass transition temperatures, ρ_1 and ρ_2 are their densities, and $K' = \rho_1/\rho_2$. Considering the similar densities of most polymers, the K' parameter can be assumed to be equal to unity. W_{2c} represents the corrected weight fraction of component 2 which possesses the higher glass transition temperature, assuming volume additivity for the blend components. K_1 is related to the differences between the interaction energies of hetero- and homo-contacts required to be overcome at T_g to allow for the characteristic conformational mobilities in the polymer melt. This term includes the energetic perturbations in the molecular surroundings of the binary contacts. Both K_1 and K_2 are related to the orientation effect of the hetero-interactions in the blend, and also depend on molecular weight. For the case of volume additivity, both K_1 and K_2 are zero and the result should be a straight horizontal line around unity in the plot of $(T_g - T_{g1})/(T_{g2} - T_{g1})W_{2c}$ vs. W_{2c}; otherwise straight lines of slope K_1 ($K_2 = 0$) or curves ($K_2 \neq 0$) are found.

Through the third-power equation, Schneider[11] found that in many cases PS–PPO blends follow the volume additivity assumption and exhibit no or very little specific interaction between the two components, except for low-molecular-weight PPO. This conclusion is consistent with *FT*i.r. and u.v. spectroscopy studies[10].

PS–PPO blends composed of relatively high-molecular-weight components were also examined in the present work, and the validity of the third-power equation was tested by using T_g data from the available literature and this work. The results of this analysis are shown in *Figure 4* and *Table 3*. The first six series of PS–PPO blends show reasonable agreement, with little or no specific interaction based on the third-power equation analysis. However, series 7 and 8 deviate significantly from the ideal of volume additivity. Schneider has previously suggested that this type of deviation may be attributed to the method of sample preparation. A detailed analysis in relation to sample preparation of a variety of blends is presently being conducted and will be the subject of a future publication.

Characterization of SPS–PPO blends

As noted previously, the introduction of low levels of ionic functionality onto wholly hydrocarbon chains

Table 3 Analysis of T_g data of PS–PPO blends using the third-power equation

Blend series	Intercept	Slope	Ref.
1	0.8794	0.0794	34
2	0.7940	0.0056	35
3	0.9246	−0.0158	11
4	0.9582	−0.1279	5
5	1.0944	−0.0352	3
6	0.8432	0.0113	this work
7	0.6072	0.5892	31
8	0.6298	0.5044	31
1–6[a]	0.9561	−0.0041	–

[a]Average of blend series 1 to 6

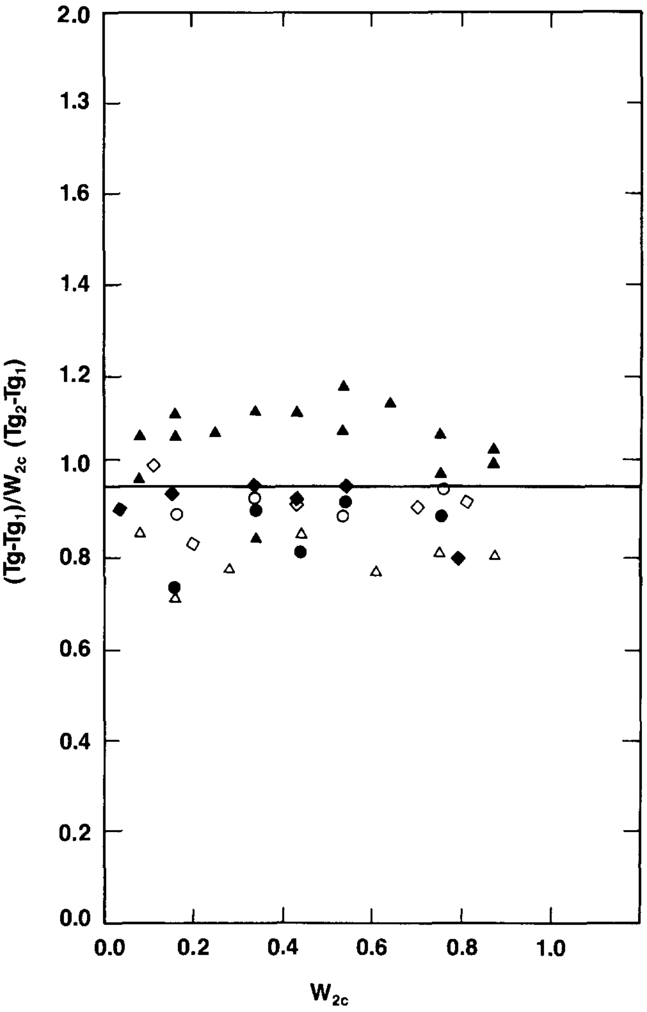

Figure 4 Third-power analysis of PS–PPO blends: (○) ref. 36; (△) ref. 37; (◇) ref. 11; (◆) ref. 5; (▲) ref. 3; (●) this work. The straight line shows the average relationship (see *Table 3*)

results in substantial modification of the physical properties of the polymer. These groups have subsequently been used to create new polymer blend systems, since they are capable of specifically interacting with various groups chemically bound to the other polymer chains. A different approach would be to explore the change in properties of a initially miscible blend, i.e. PS–PPO, when one or both of the components is functionalized. In this case, the specific functionality is the sodium sulphonate moiety. It is also of further interest to examine whether the sulphonate units on different blend components are still able to undergo microphase separation with each other. If this occurs, blends can be formed with improved properties by simply copolymerizing the appropriate ionic functionality onto the polymer chains and mixing. Strong bonding of the individual components should occur, owing to the microphase separation phenomenon known in these systems. Miscibility or immiscibility may be found, depending on the level of functionality on the individual blend components and their compatibility characteristics in their unfunctionalized state. In order to explore these phenomena, a series of blends was formulated. The first series of measurements pertains to the compatibility characteristics of SPS with unfunctionalized PPO.

The phase behaviour as a function of composition of three series of SPS–PPO blends was investigated using d.s.c. The results are listed in *Table 4* and a specific example, SPS(4.2)–PPO, is presented in *Figure 5*. Polymer blends of the series SPS(1.7)–PPO and SPS(2.6)–PPO gave a single glass transition which increased with increasing PPO content. The trend of increasing T_g is similar to that of the PS–PPO series. However, the transition temperature range (ΔT, *Figure 1*) of these two series of blends is markedly broadened upon increasing the PPO content. It is important to note that for the series SPS(4.2)–PPO, the blend became immiscible when the PPO content approached 60% or more.

Table 4 Characteristics of SPS–PPO polymer blends

SPS sulphonation level (mol%)	SPS:PPO weight ratio	T_g[a] (°C)	ΔT (°C)
1.7	100:0	108	8
	80:20	126	13
	60:40	143	6
	40:60	163	28
	20:80	184	43
	0:100	216	7
2.6	100:0	111	10
	80:20	127	15
	60:40	139	23
	40:60	157	31
	20:80	186	56
	0:100	216	7
4.2	100:0	116	12
	80:20	125	16
	60:40	138	24
	40:60[a]	147 206	35 20
	20:80[a]	126 212	15 12
	0:100	216	7

[a] Blends have two glass transition temperatures

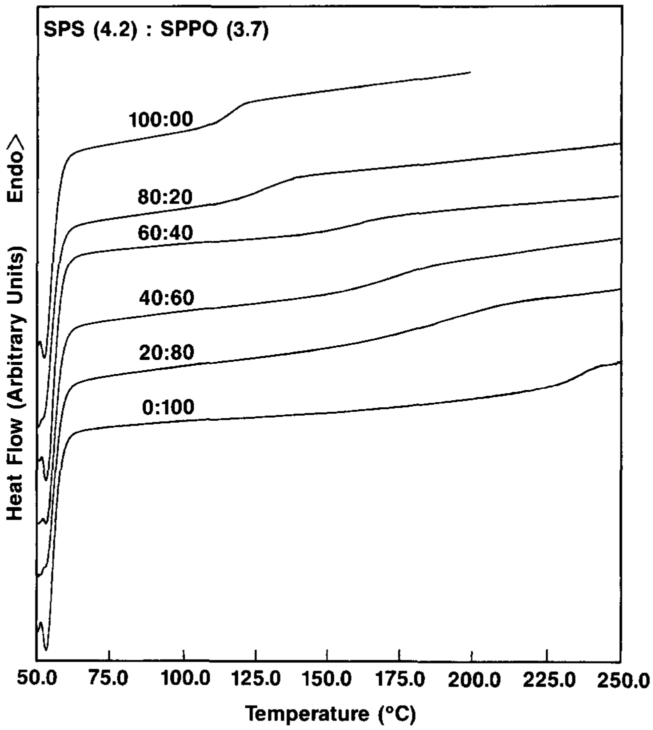

Figure 5 D.s.c. curves of sulphonated (4.2 mol%) PS–unsulphonated PPO blends

A broad temperature range may indicate that the blend is a two-phase system and both phases contain different but finite concentrations of each component. Therefore, when the T_g values of both phases are close to each other, a broad T_g is observed. When the T_g values of the two phases are widely separated, two possibilities arise: a fairly broad T_g or two distinct T_gs that are compositionally dependent. Thermal measurements on the blend series SPS(4.2)–PPO revealed a single T_g at low PPO content, two relatively broad T_gs at 60% PPO, and two relatively narrow T_gs at 80% PPO. These observations suggest that this series is a single phase at low PPO content and then approaches and subsequently becomes two phases at high PPO content. The data show that the two-phase blend must be composed of a PPO-rich component with a high T_g and an SPS(4.2)-rich component with a lower T_g. From these observations, it is apparent that PPO possesses good solubility in SPS(4.2), but is a poor 'solvent' for SPS(4.2).

Finally, in a comparison of these polymer blends at identical PPO content, e.g. 80%, the results reveal that the higher the sulphonation level, the broader is the transition temperature range. Two T_gs may even appear. These observations can be attributed to increasing polarity of SPS and the resulting decreasing miscibility of SPS in the unfunctionalized PPO.

Characterization of PS–SPPO blends

In order to explore whether sulphonate moieties on PPO have the identical (i.e. symmetrical) effect on properties as in the previously described SPS–PPO blends, three PS–SPPO blends were prepared at a 1:1 weight ratio. The thermal measurements are listed in *Table 5*. A close examination of the data reveals that blends of this series show a similar trend to that of the SPS–PPO series. As in the latter blends, increasing ionic content broadens the T_g range and can even result in two

Table 5 Characteristics of 1 : 1 PS–SPPO polymer blends

Sulphonation level of SPPO (mol%)	T_g (°C)	ΔT (°C)
0	145	13
1.9	145	38
3.0[a]	112 221	8 18
3.7[a]	108 224	8 26

[a] Blends have two glass transition temperatures

T_gs. It is noteworthy that the PS–SPPO(3.0) blend gave two T_gs, but the SPS(2.6)–PPO blend had only a single T_g. In other words, to promote phase separation in these blends, increasing the sulphonation content on the PPO chains is more efficient than placing the ionic groups on PS chains.

Characterization of SPS–SPPO blends

From the thermal measurements previously described, it is clear that in the blends containing one sulphonated component, the lower the sulphonate content, the more likely is miscibility to be observed. Of course, immiscibility will occur when the sulphonate content exceeds a specific value in either component. This was further elucidated by the examination of three series of SPS–SPPO blends spanning the entire compositional range. The d.s.c. results of a series of SPS(2.6)–SPPO(1.9) and SPS(4.2)–SPPO(3.7) blends are listed in *Table 6*. The thermograms of the SPS(4.2)–SPPO(3.7) blends are shown in *Figure 6*. It is noteworthy that these polymer blend systems possess only a single T_g over the entire composition range and that the value increases with the content of the higher-T_g component. It is apparent that sulphonate–sulphonate interactions are non-specific with regard to the composition of the chain to which they are chemically bound. However, it is noteworthy that the SPS(4.2)–SPPO(3.7) blends are completely miscible and the SPS(4.2)–PPO blends are miscible at low PPO content but immiscible when the PPO content is ⩾60%.

Finally, a series composed of 1 : 1 weight-ratio blends of SPS(6.0) and SPPO spanning a wide sulphonation range was examined in order to probe the phase behaviour with extreme differences in sulphonation content. The results of this study are listed in *Table 7*. The data show again that the closer the sulphonation levels, the better is the miscibility. The extreme cases in this study were the SPS(6.0)–PPO and SPS(6.0)–SPPO(14.2) blends. The SPS(6.0)–PPO blend possessed two T_gs which are close to the T_g of the pure components. Blend SPS(6.0)–SPPO(14.2) had a T_g close to that of pure SPS(6.0), and it is believed that there was another T_g far above 250°C. All of the other sulphonate–sulphonate blends at this composition (1 : 1) possessed a single T_g, indicating complete miscibiity. It is also noteworthy that ΔT was approximately 30°C, relatively independent of the difference in sulphonation level between the two components.

CONCLUSIONS

The glass transition temperature behaviour of a series of PS–PPO, SPS–PPO, PS–SPPO and SPS–SPPO blends shows that even though blends formed from the unfunctionalized polymer are miscible over the entire composition range, sulphonation of one or both components of the blend has a marked effect on compatibility.

Table 6 Characteristics of SPS–SPPO polymer blends

Sulphonation level of SPS–SPPO (mol%)	SPS–SPPO weight ratio	T_g (°C)	ΔT (°C)
2.6–1.9	100:0	111	10
	80:20	127	14
	60:40	146	9
	40:60	162	30
	20:80	182	30
	0:100	224	11
4.2–3.7	100:0	116	12
	80:20	127	22
	60:40	169	29
	40:60	173	31
	20:80	186	49
	0:100	235	18

Table 7 Characteristics of 1 : 1 SPS(6.0)–SPPO polymer blends

Sulphonation level of SPPO (mol%)	T_g (°C)	ΔT (°C)
0[a]	125 205	16 6
1.9	170	36
3.0	171	25
3.7	168	32
9.2	174	49
14.2[b]	133	23

[a] This polymer blend gave two glass transition temperatures

[b] This polymer blend may have another T_g above 250°C, since SPPO(14.2) possessed a T_g well above 250°C

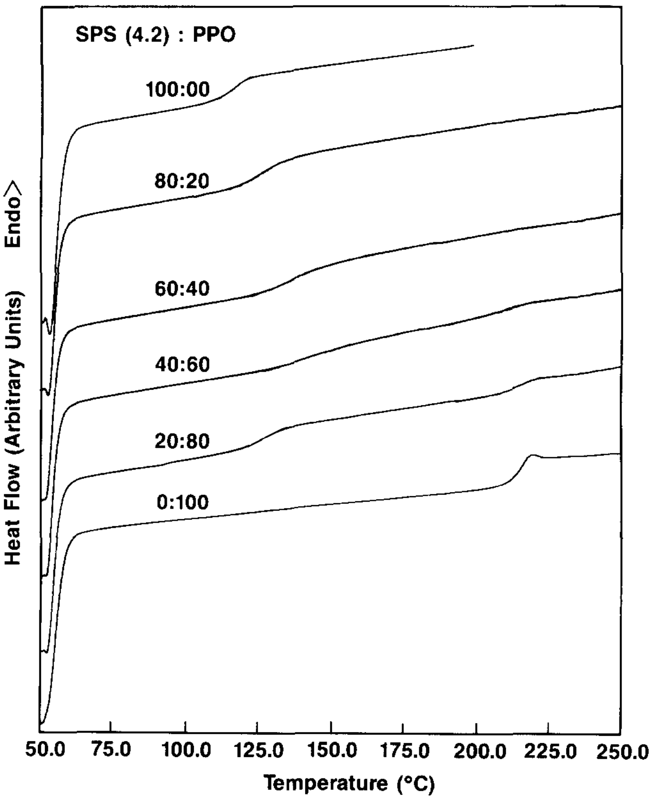

Figure 6 D.s.c. curves of sulphonated (4.2 mol%)PS–sulphonated (3.7 mol%)PPO blends

As the level of sulphonation in either component is increased, the initial miscibility is reduced. It appears that the sulphonate groups on PPO are more effective in promoting immiscibility than those on the polystyrene component. The reason for this effect is not clear. A substantially broader range of miscibility is encountered when both blend components are sulphonated. In contrast to blends containing only one sulphonated component, where immiscibility can occur with a change of approximately 2–4 mol% in sulphonation, the sulphonate copolymer combinations retain their miscibility over an approximately 10 mol% range of sulphonate content. These results have interesting implications for blend formulation, since it is apparent that these sulphonate–sulphonate interactions are relatively non-specific with regard to the chain structure to which they are chemically bound.

Qualitatively, these results can be understood in terms of the recently introduced mean field theory of phase behaviour in homopolymer–copolymer and copolymer–copolymer systems[12,15,34]. These copolymers contain a random arrangement of monomer units but do not necessarily contain a common monomer segment as with the binary component blends of S-PS and S-PPO. The model envisages each copolymer as comprising structural units which are capable of interacting in either an intra- or an intermolecular fashion, regardless of whether these units are covalently bonded together or not. Miscibility occurs when the polymer–polymer interaction parameter χ is negative.

If it is assumed that the homopolymers and copolymers are of sulphonated (S-PO) and unfunctionalized phenylene oxide (PO) and sulphonated (NaS) and unsulphonated styrene segments (S), then it can be shown that for the homopolymer–sulphonated copolymer blend,

$$\chi_{\text{blend}} \sim \chi_{\text{PO–NaS}} + \chi_{\text{PO–S}} - \chi_{\text{NaS–S}} \qquad (2)$$

where the χs are the interaction parameters for the appropriate monomer segments. For reasons of clarity, the composition-dependent coefficients are not shown. It is known that $\chi_{\text{PO–S}}$ is known to be negative, while $\chi_{\text{NaS–S}}$ and $\chi_{\text{PO–NaS}}$ are found to be positive because the homopolymer blends of S-PS and PS (likewise S-PPO and PPO) are immiscible in all proportions. Therefore at low sulphonation levels, χ_{blend} is negative, but it becomes increasingly positive at higher ionic contents. This is due to the increasingly unfavourable contributions of $\chi_{\text{NaS–S}}$ and $\chi_{\text{PO–NaS}}$. Similar results occur in S-PPO–PS blends. The 'miscibility' window occurs between 2 and 4 mol% sulphonation level (sodium salt) in these specific blends.

With regard to the sulphonated binary blends, the blend interaction parameter is given by the following equation:

$$\chi_{\text{blend}} \sim \chi_{\text{PO–S}} + \chi_{\text{PO–NaS}} + \chi_{\text{SPO–S}} + \chi_{\text{SPO–NaS}} - \chi_{\text{PO–SPO}} - \chi_{\text{S–NaS}} \qquad (3)$$

For the reasons given above, all the χs are positive for sulphonated and unsulphonated residues, i.e. two composition-independent T_gs are observed in their respective homopolymer blends. Because of the well-known strong attraction of sulphonate groups towards each other, $\chi_{\text{SPO–NaS}}$ is assumed to be negative. Therefore, when the difference in sulphonation level is less than ≈ 10 mol%, $\chi_{\text{PO–S}}$ and $\chi_{\text{SPO–NaS}}$ ('attraction' force) and $\chi_{\text{PO–SPO}}$ and $\chi_{\text{S–NaS}}$ ('repulsion' forces) determine the overall blend interaction energy, and miscibility occurs. However, blend immiscibility is observed at differences in sulphonation level greater than ≈ 10 mol%. This is due primarily to the increasingly higher positive value contribution of $\chi_{\text{PO–NaS}}$ and $\chi_{\text{SPO–S}}$. That is, 'repulsion' forces between sulphonated and unsulphonated monomer segments dominate interaction energies in these blend systems. These modes of phase separation do not, however, produce blends having poor interfacial properties. In fact, extensive tensile measurements on a series of coulombically associating rubber-toughened polyolefin blends confirm that excellent properties are achieved even when phase separation occurs[35]. In these blends, immiscibility with strong interfacial adhesion is highly desirable.

More detailed studies of this phenomenon are presently being pursued and will be the subject of a number of future publications.

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