Miscibility of carboxylated and sulfonated polystyrene ionomers with polyamides-66, -610 and -11

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Differential scanning calorimetry (d.s.c.) of blends of polystyrene ionomers and polyamide-66 shows that lithium sulfonate groups are more effective than lithium or sodium carboxylate groups in enhancing the miscibility between this polyamide and polystyrene. The miscibility between aliphatic polyamides and the polystyrene ionomer containing 9.8 mol% lithium sulfonate groups decreases as the amide content of the polyamide decreases. Thus, while blends of this ionomer with polyamide-66 and polyamide-610 (PA-610) appear miscible by d.s.c., the blends with polyamide-11 (PA-11) show evidence of some phase separation. Dynamic mechanical measurements of the 50:50 blends of this ionomer with PA-610 and PA-11 confirm the one-phase and two-phase behaviour of these blends, respectively.

(Keywords: miscibility; aliphatic polyamides; polystyrene ionomers; sulfonated; carboxylated)

INTRODUCTION

Miscibility enhancement between otherwise immiscible polymers is a subject of continuing academic and commercial interest[1-3]. Since most polymer pairs are immiscible with each other, miscibility enhancement frequently presents a serious challenge. Aliphatic polyamides constitute an important class of polymers with a wide variety of commercial applications, and the improvement of various mechanical, rheological and other properties of these materials is, therefore, of considerable importance. One way to modify these properties is by blending or alloying with other polymers. Although complete miscibility of the blend components is not always necessary to optimize properties, some favourable interaction between the components is almost always needed.

Polyamides contain amide groups along the polymer backbone, and these offer sites amenable to specific interactions with other polymers through ion–dipole, dipole–dipole or hydrogen bonding interactions. Blends of styrene–acrylic acid copolymers with aliphatic polyamides are examples of blends where hydrogen bonding interactions take place[4], while polyamide/polyamide blends[5] and blends of polyamides with poly(ethylene oxide)[6] are examples of blends where dipole–dipole interactions are operative. Since ion–dipole interactions are usually stronger than either dipole–dipole or hydrogen bonding interactions, the functionalization of polymers with a small amount of ionic groups is a particularly attractive way of compatibilizing various polymers with polar polymers[7-10]. Polymers containing between 0 and about 20 mol% of ionic groups are generally termed 'ionomers'.

A number of patents show that blending polyamides with polyethylene ionomers containing ionic carboxylate groups (e.g. sodium methacrylate) can lead to dramatic improvements in the impact properties of polyamides[11-13]. Numerous studies and patents show that polyethylene ionomers of this type can also be used to compatibilize blends of PA-6 with polyethylene or polypropylene[14-18]. These studies suggest that ionic carboxylate groups interact favourably with polyamides. Recently it has been shown that polyamide-6 (PA-6) can be compatibilized with polystyrene by functionalizing the polystyrene with ionic sulfonate groups[19-27] thus demonstrating that ionic sulfonate groups also interact favourably with polyamides. Polyethylene ionomers containing ionic sulfonate groups are difficult to synthesize and, therefore, a comparison between the miscibility-enhancing effects of carboxylate and sulfonate ionic groups has not been made. However, polystyrene is relatively easily functionalized with both these functional groups; therefore, in this paper, the miscibility enhancement of these two groups is compared in blends of polystyrene ionomers with polyamide-66. Both Li and Na counterions are used for the ionomers since it has been previously shown, in blends of polystyrene ionomer with PA-6, that lithium sulfonate groups can lead to a single glass transition at certain blend compositions; by contrast, a two-phase system results at all compositions when the ionic group is sodium sulfonate (ionic group content 9.8 mol%)[22,26]. It will be shown that the lithium sulfonate groups interact more strongly with polyamide-66 than either the lithium or sodium carboxylate groups.

Since the unfunctionalized polymers (i.e. polystyrene and polyethylene) are immiscible, the functional group

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content of the ionomer and amide content of the polyamide can be expected to play an important role in the miscibility enhancement obtained. A previous study has shown that when the amide content of the polyamide is kept constant (i.e. PA-6), the miscibility of the blend decreases as the lithium sulfonate content of the ionomer is decreased from 9.8 mol% to 5.4 mol%[26]. In this paper the lithium sulfonate content of the ionomer is held constant at 9.8 mol% while the amide content of the polyamide in the blend is decreased. Here it is shown that, not unexpectedly, the miscibility enhancement of polyamides with lithium sulfonated polystyrene ionomers decreases as the amide content of the polyamide decreases. Thus, while blends with polyamide-66 and polyamide-610 show a single composition dependent glass transition temperature (T_g) by differential scanning calorimetry (d.s.c.), the blends with polyamide-11 show strong miscibility enhancement, but evidence of some phase separation. Finally, the miscibility information on blends of lithium sulfonated polystyrene ionomers with polyamides is incorporated into a 'miscibility map' where areas of expected single phase behaviour (on the d.s.c. and dynamic mechanical scale) for 50:50 blends of this ionomer with various aliphatic polyamides is depicted. This is done as a function of the ionic group content of the ionomer and the amide content of the polyamide in the blend.

EXPERIMENTAL

Materials

Polyamide-66 (PA-66) and polyamide-610 (PA-610) were obtained from Aldrich and purified by dissolving in 88% formic acid and precipitating into an excess of water. The polyamide-11 (PA-11) was purchased from Polysciences Inc. and purified by dissolving into trifluoroacetic acid and precipitating into an excess of water. The polyamides were dried under vacuum at 90°C for 4 days prior to use. Molecular weight information on these polymers is not available and thus the entropic effect on the miscibility of the blends could not be estimated. However, the strong interactions in the blends are expected to dominate, and the effects of the molecular weights on the miscibility of these polyamides with the ionomers are not considered important. The poly(styrene-*co*-methacrylic acid) was produced by free radical random copolymerization of styrene and methacrylic acid in conjunction with another project in this laboratory[28]. This material contained 7.6 mol% methacrylic acid groups and is designated as either LiMAPS8 or NaMAPS8, depending on whether the counterion is Li or Na. Polystyrene (viscosity average molecular weight, $M_v = 280\,\text{kg mol}^{-1}$) was purchased from Aldrich and, after purification, was sulfonated to 5.4 and 9.8 mol% according to the method of Makowski *et al.*[29]. The sulfonated polystyrenes were neutralized with methanolic LiOH or NaOH, freeze dried, and dried under vacuum at 90°C for 1 week prior to use. The polystyrene ionomers containing 5.4 and 9.8 mol% lithium sulfonate groups will be referred to as LiSPS5 and LiSPS10, respectively. The ionomer containing 9.8 mol% sodium sulfonate groups will be referred to as NaSPS10.

Blend preparation

Solutions (5% (w/v)) of the pure materials were prepared by dissolving them in a volumetric flask using the following solvents: *m*-cresol/methanol (80:20) for all the ionomers and PA-66; *m*-cresol/methanol (88:12) for PA-610; *m*-cresol for PA-11. Volumetric amounts of the blend components were mixed under constant agitation, by the dropwise addition of the ionomer to the polyamide solutions. All the blend solutions were clear, and were precipitated into an excess of hexanes. After thorough washing with fresh hexanes to remove the residual solvent, the precipitated blends were allowed to air dry, and then dried under vacuum at 140°C for 1 week. This drying procedure adequately removes residual solvent[25].

Differential scanning calorimetry

A Perkin–Elmer DSC-7 was used for the thermal analysis and was calibrated with indium. The sample cells were kept under a constant purge of dry nitrogen during the runs. The blend samples were first scanned at 100°C min^{-1} to the annealing temperature (see below), held there for 5 min, then cooled at 40°C min^{-1} to −10°C, held there for 2 min, and then scanned at 20°C min^{-1} to above the melting temperature of the blends. The annealing temperatures were chosen to be 20–35°C above the melting temperature (T_m) of the polyamide component, i.e. 280°C for the blends containing PA-66 ($T_m \approx 260$°C), 250°C for the blends containing PA-610 ($T_m \approx 220$°C), and 225°C for blends containing PA-11 ($T_m \approx 190$°C). The crystallization temperatures (T_c) were recorded during cooling, while the T_g and melting temperatures were recorded during the second heating scans. The T_g values were taken at the midpoint of the specific heat change, while T_m and T_c were recorded at the maximum of the endo/exotherms.

The amorphous phase composition of some of the semicrystalline blends was estimated by correcting the total blend composition for the polyamide tied up in the crystalline phase. The weight fraction of crystalline material was estimated by dividing the normalized melting enthalpy of the blend, as obtained by d.s.c., by the heat of fusion for the 100% crystalline polyamide; the latter were taken as 196 J g^{-1} for PA-66, 200 J g^{-1} for PA-610, and 226 J g^{-1} for PA-11[30].

Dynamic mechanical thermal analysis

Samples for dynamic mechanical thermal analysis (d.m.t.a.) were compression moulded at 240°C (PA-610 blend) or 210°C (PA-11 blend) under low pressure. The sample dimensions were approximately 2 mm × 6 mm × 27 mm. A Polymer Laboratories DMTA instrument was used for the analysis, employing a small frame in dual cantilever mode. The samples were scanned at 1 Hz and 1°C min^{-1} from 0°C up to the sample melting points.

RESULTS

Figure 1 shows the d.s.c. data for the blends of the poly(styrene-*co*-methacrylate) ionomers with polyamide-66 (PA-66). The presence of two composition-independent T_gs and the negligible effect on the blend T_ms indicate that these ionomers are not miscible with PA-66. However, the slight decrease of T_c with increasing ionomer content in the LiMAPS8 blends, compared with a relatively composition-independent variation of T_c for the NaMAPS8 blends, does suggest that the LiMAPS8 ionomer may hinder the crystallization process marginally more than the NaMAPS8 ionomer. The slight shift of T_{g1} and T_{g2} towards each other for the LiMAPS8 ionomer

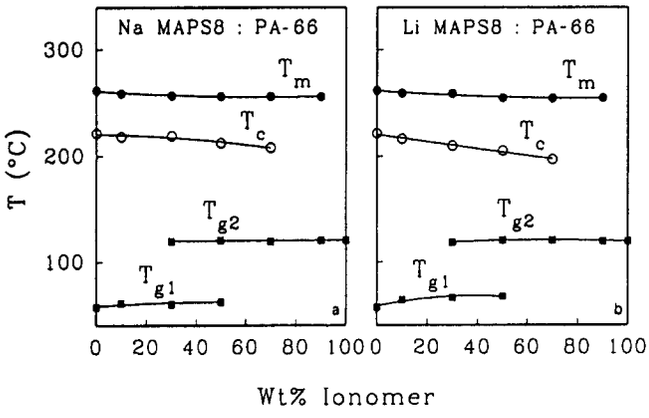

Figure 1 D.s.c. data for blends of polyamide-66 with (a) poly(styrene-*co*-sodium methacrylate) and (b) poly(styrene-*co*-lithium methacrylate) ionomers. The ionomers contain 7.6 mol% ionic groups

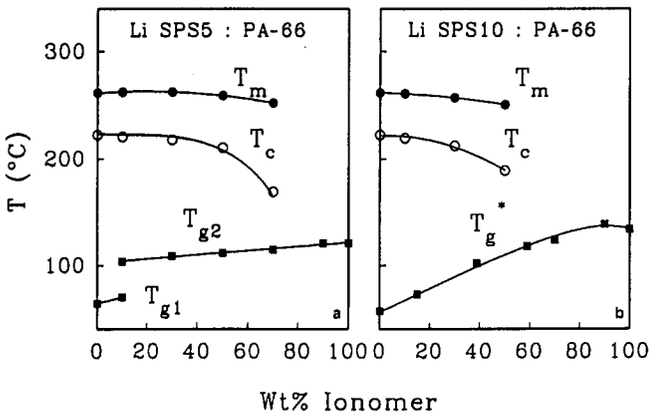

Figure 2 D.s.c. data for blends of polyamide-66 with lithium sulfonated polystyrene ionomers containing (a) 5.4 mol% and (b) 9.8 mol% lithium styrene sulfonate groups. T_g^*, the blend T_g has been corrected for crystallinity (where necessary) and is plotted against the calculated amorphous phase compositions of the blend

blends also suggests that the Li-neutralized MAPS8 ionomer may be marginally more miscible with the PA-66 than the Na-neutralized ionomer. It is worth noting that the T_c values for both the ionomer blends at 90% ionomer content were difficult to locate from the d.s.c. runs. This is probably due to a broadening of the crystallization exotherms and the low amount of crystallizable PA-6 in the blend at these compositions, which results in a weak signal.

The behaviour of the blends of PA-66 with the lithium sulfonated polystyrene ionomers are shown in *Figure 2*. For the LiSPS5 ionomer blends (5.4 mol% lithium sulfonate group content), (*Figure 2a*), the variation of T_m, T_c, T_{g1} and T_{g2} are markedly different from those of the MAPS8 ionomers: T_m and T_c both decrease with increasing LiSPS5 ionomer content until, at 90% ionomer content, the blend is amorphous (no T_m or T_c); T_{g1} and T_{g2} also shift significantly towards each other. The depression of T_m with ionomer content could be due to a less perfect crystalline structure of the PA-6 crystals[31] or to some miscibility of the blend components[31], or both. In either case, some interaction of the blend components would be needed. The shifting of the blend component glass transition temperatures towards each other also implies some miscibility enhancement. Thus, the LiSPS5 ionomer shows considerably greater miscibility enhancement with PA-66 than either the NaMAPS8 or LiMAPS8 ionomer, despite its lower ionic group content (5.4 *versus* 7.6 mol% for the MAPS8 ionomers). Increasing the ionic group content of the LiSPS ionomer to 9.8 mol% (*Figure 2b*), results in a single composition-dependent T_g. Furthermore, there is no crystallinity when the ionomer content is greater than 50%.

The blends of the sodium-neutralized ionomer (NaSPS10) with the PA-66 (data not presented here) show a series of transitions by d.s.c. similar to those for the NaMAPS8 ionomer blends (*Figure 1a*), indicating that this ionomer is immiscible with PA-66.

To test the effect of decreasing the amide content of the polyamide on the miscibility of the LiSPS10 with the polyamides, d.s.c. was used to analyse the blends of LiSPS10 ionomer with PA-610 and PA-11. The miscibility of the Li and NaMAPS8 ionomers with these polyamides was not tested, since it can be inferred, from the immiscibility of these ionomers with PA-66, that they would also be immiscible with polyamides having an even lower amide content than PA-66. *Figure 3a* shows the d.s.c. data for the blends of LiSPS10 with PA-610. The presence of a single composition-dependent T_g, as well as the decrease of both T_m and T_c with increasing ionomer content in the blend, reflects the strong miscibility enhancement of the ionomer with this polyamide. The T_m and T_c also decrease with increasing ionomer content in the PA-11 blends (*Figure 3b*). On the other hand, the PA-11 blends indicate the possible presence of two composition-dependent glass transition temperatures: the lower T_g increases with ionomer content until, at the 50 and 70% compositions, two transitions are detectable, and only the higher T_g then persists to higher ionomer contents.

The precise position of the glass transition temperatures is difficult to determine from the straight d.s.c. scans, and a clearer picture can be obtained of the position and breadth of these transitions from the first derivative of the d.s.c. traces. A series of such curves for the LiSPS10 blends with PA-11 are depicted in *Figure 4*. It is worth noting that a glass transition appears as a peak in these plots. It can be seen that the broad peak on the PA-11 curve (ranging from about 25°C to 75°C), which is associated with the T_g of the PA-11, moves to higher temperatures as the ionomer content is increased from 0 to 70%. At the same time, the transition width also narrows, until it measures about 30°C for the blend

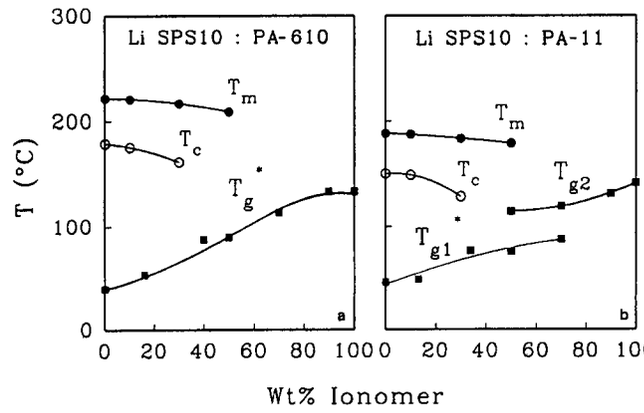

Figure 3 D.s.c. data for blends of LiSPS10 with (a) polyamide-610 and (b) polyamide-11. *, compositions refer to the amorphous phase only, as in *Figure 2*

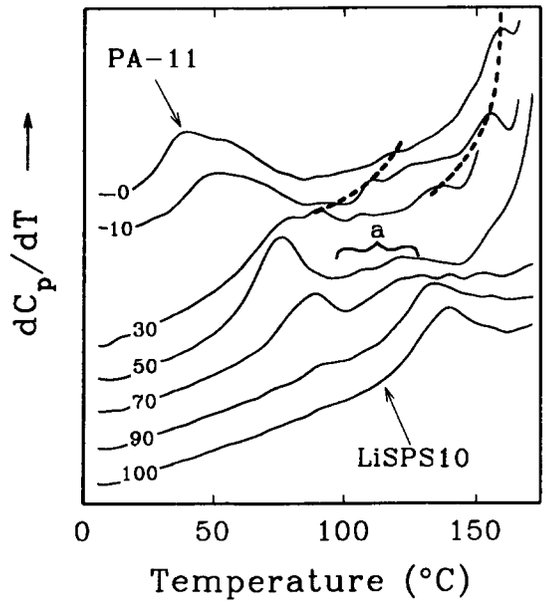

Figure 4 First derivative curves of the d.s.c. scans for the LiSPS10 blends with PA-11. Numbers refer to the wt% LiSPS10 ionomer in the blend; the dashed lines show the position of features that are most probably due to melting of crystallites. 'a', the position of a possible second glass transition

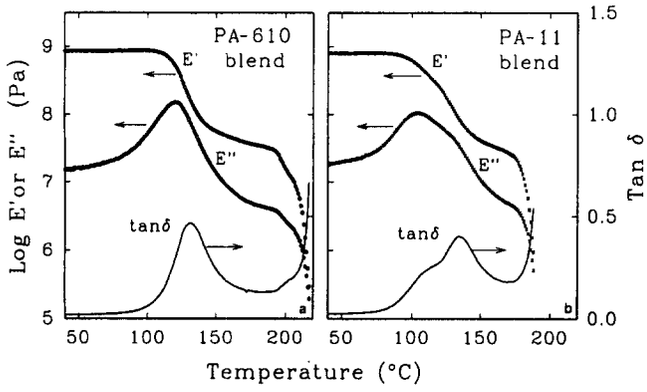

Figure 5 Dynamic mechanical data (1 Hz) for the 50:50 blends of LiSPS10 with (a) PA-610 and (b) PA-11

containing 70% ionomer. The transition widths are taken as T_g(completion) − T_g(onset). In the samples containing 0, 10 and 30% ionomer, some features can be seen occurring at temperatures above the glass transition temperatures. These are most probably associated with multiple melting endotherms of different crystalline phases, as is often seen in aliphatic polyamides. This is supported by the progressive shifting of these features to lower temperatures with increasing ionomer content in the blend (dashed lines in *Figure 4*, connecting peak positions), following the trend of the principal melting endotherm (T_m in *Figure 3b*). The upturns of the first derivative curves occurring between 150 and 170°C, for the blends containing 0, 10, 30 and 50% ionomer, are due to the principal crystalline melting endotherms in these blends. While a second glass transition is not detectable in the blends containing 10 and 30% ionomer, the first hint of a possible second glass transition temperature is shown for the blend containing 50% ionomer and is seen as a low but broad hump centred around 115°C (shown by 'a' in *Figure 4*). This second glass transition appears more pronounced for the blend containing 70% ionomer, and becomes dominant for the blend containing 90% ionomer. Note that the glass transition of the 30% blend occurs at a temperature higher than might be expected from the general trend, and this is also seen for the LiSPS10 blend with PA-610 (*Figure 3a*). The reason for this is not clear, but is possibly a result of the influence of crystallinity in these blends.

Dynamic mechanical thermal analysis can often resolve the presence of one or two phases in a much less ambiguous way than d.s.c. Therefore, it can be used to confirm the single-phase behaviour of the 50:50 blend of LiSPS10 with PA-610, and the apparent two-phase behaviour of the 50:50 blend with PA-11, as seen by d.s.c. The results of d.m.t.a. for 50:50 blends of LiSPS10 ionomer with PA-610 and PA-11 are depicted in *Figure 5*. The PA-610 blend (*Figure 5a*) is clearly a one-phase system (on the scale accessible to d.m.t.a.), and this is shown by the single drop of the storage modulus (E') and the single peaks of both loss modulus (E'') and tan δ. The drop of E' at about 200°C is caused by the melting of the PA-610 crystalline phase, and is not associated with a glass transition, as is confirmed by the simultaneous drop in the E'' at this temperature. The single glass transition temperature of this blend suggests that the blend components are miscible on the 50–100 Å level, reflecting the resolution limit of the dynamic mechanical technique. On the other hand, the PA-11 blend (*Figure 5b*) shows evidence of two glass transitions. This is seen as a two-sloped decrease of E' with temperature at around 125°C, and the presence of humps on the E'' and tan δ curves. These humps are a result of two overlapping glass transitions and this is especially evident in the tan δ profile. Again, the simultaneous drop of E' and E'' at around 180°C is due to the melting of the PA-11 crystalline phase.

DISCUSSION

The d.s.c. results on the blends of LiSPS and MAPS8 ionomers with PA-66 show unambiguously that lithium styrene sulfonate groups are more effective in enhancing the miscibility between polystyrene and PA-66 than either lithium or sodium methacrylate groups. Some basis for this difference in interaction strength can be obtained by considering the way that the ionic groups interact with the amide groups. In one study it has been suggested that ion–dipole interactions between the Li cation and the amide nitrogen may take place[23,24]. Based upon earlier studies on mixtures of LiCl salts with model amides[32–37] and polyamides[38–41] it has also been suggested that the Li cations may rather interact with the carbonyl oxygens of the amides, with the resulting sulfonate anions interacting with the amide hydrogens[26]. Assuming that the latter interaction mechanism is the correct one, it is reasonable to expect that a similar mode of interaction also occurs in the blends of LiMAPS with polyamides. Thus, the interactions of the Li sulfonate and Li carboxylate groups with amides could be written as:

$$-SO_3^-Li^+ + HN + CO \rightarrow -SO_3^-HN + COLi^+ \quad (1)$$

$$-COO^-Li^+ + HN + CO \rightarrow -COO^-HN + COLi^+ \quad (2)$$

The NH and CO are indicated as independent of each other because the interactions could be with the same or with different amide units in the blends. Equations (1) and (2) essentially represent the dissociation of the $-SO_3Li$ and $-COOLi$ salts by the polar amide groups, which is akin to the dissociation of acids in water. Since the counterions (H *versus* Li) are the same for the two types of anions in the acid and salt cases, dissociation constants of acids in water can provide some insight into the relative stability of the $-SO_3^-$ and $-COO^-$ anions in polar diluents, such as water or amides. Dissociation constants of acids in water at 25°C are given as follows[42]: benzenesulfonic, 2×10^{-1} ($pK_a = 0.70$); benzoic, 6.46×10^{-5} ($pK_a = 4.19$); acrylic, 5.6×10^{-5} ($pK_a = 4.25$). Thus the higher dissociation constant of sulfonate anions (benzenesulfonic acid) *versus* carboxylates (benzoic and acrylic acid) suggests that the reaction given by equation (1) is more likely to occur than that shown by equation (2). To some extent, this can explain the better miscibility enhancement obtained with lithium styrene sulfonate groups than with lithium methacrylate groups.

It is worth noting that the marginal co-miscibility of the LiMAPS8 ionomer with PA-66 (as compared to none with NaMAPS8 ionomer), is not entirely unexpected: several studies have shown that ionomers having Li counterions are more effective in enhancing the miscibility with polar polymers than ionomers with Na counterions[10,21,26,37]. This is generally attributed to counterion size and surface charge density differences.

The miscibility behaviour of the blends of LiSPS10 and LiSPS5 ionomers with PA-66 parallel the results obtained for the blends of these ionomers with PA-6. In both cases the blends with LiSPS10 ionomer show strong miscibility enhancement (a single composition-dependent T_g by d.s.c., and a maximum T_g at 90% LiSPS10 content[26]), while the blends with LiSPS5 ionomer are only partially miscible. A notable difference is the absence of crystallinity at 70% LiSPS5 content for the blend with PA-6 as opposed to the presence of some crystallinity for the blend with PA-66, as shown by the measured T_m and T_c in *Figure 2a*. The glass transition temperatures of PA-6 and PA-66 are about the same ($T_g \approx 50$°C), but the melting temperature of PA-66 (260°C) is considerably higher than that of PA-6 (220°C). Since crystallization must take place between T_m and T_g, the higher melting temperature of the PA-66 affords a larger temperature interval ($T_m - T_g$) for the crystallization of the PA-66 during the d.s.c. experiment than for the PA-6. Indeed, during the slow heating run (1°C min^{-1}) of the dynamic mechanical analysis of the PA-6 blend, crystallization is also found to occur[26]. Thus, the presence or absence of crystallinity in the 70% ionomer blends is most probably a kinetic rather than a miscibility effect, and, from the similarity of the glass transition behaviour, it can be concluded that the extent of miscibility of the LiSPS ionomer with PA-6 or PA-66 is about the same. Furthermore, the immiscibility of the NaSPS10 ionomer with PA-66 also parallels the result found for the blend of this ionomer with PA-6. Since PA-6 and PA-66 both have the same amide content and only differ in the way that these amide groups are arranged along the polymer backbone, the results show that the miscibility is not affected by minor structural differences and is mainly dependent on the concentration of amide and lithium styrene sulfonate groups in the blend.

As the concentration of either the lithium styrene sulfonate or amide groups decreases in the blend, the driving force for miscibility also decreases, as is seen when the lithium styrene sulfonate content is decreased from 9.4 to 5.4 mol% in the blends with PA-66. One way of describing the amide content of aliphatic polyamides is by considering one polymer 'unit' to consist of two backbone atoms. Using this definition, the aliphatic polyamides then consist of regular sequences of ethylene and amide units. Thus PA-66 (or PA-6) contains 28.6 mol% amide units while PA-610, PA-11 and polyethylene contain 22.2, 16.7 and 0 mol% amide units, respectively. The d.s.c. and d.m.t.a. results show that while the blends of LiSPS10 with PA-610 are single phase, the blends with PA-11 are two phase. This trend is as expected since the number of favourable interactions between the amide and the lithium sulfonate groups decreases as the amide content in the blend decreases, with a simultaneous increase in the number of unfavourable interactions between the styrene and the ethylene units.

By restricting the description of miscibility to the d.m.t.a. level (domain resolution of 50–100 Å[43–45]) and to the 50:50 blends, and by taking the miscibility information into account, it is possible to predict, within limits of uncertainty, 'miscible' and immiscible blends of LiSPS ionomers with various aliphatic polyamides. This can be done as a function of the amide (NHCO) and lithium sulfonate ($-SO_3^-Li^+$) content of the polyamide and LiSPS, respectively. In this way a miscibility map can be drawn. The blend of LiSPS5 (5.4 mol% $-SO_3^-Li^+$) with PA-66 (or PA-6) represents a blend close to the miscibility threshold, while another miscibility threshold exists between the blends of LiSPS10 (9.8 mol% $-SO_3^-Li^+$) with PA-610 and PA-11, i.e. between 22.2 and 16.7 mol% NHCO, as previously discussed. Polyethylene (PE) is not expected to be miscible with LiSPS, regardless of the mol% $-SO_3^-Li^+$, due to the strong self-association of the $-SO_3^-Li^+$ groups and the lack of polarity of PE. Unfunctionalized polystyrene is known to be immiscible with PE, and is not expected to be miscible with any of the polyamides, as has been shown for PA-6[22]. Therefore, both the 0 mol% axes describe the locus of immiscible blends on a miscibility map. Such a miscibility map is shown in *Figure 6*, with the shaded miscibility region drawn to satisfy the miscibility considerations and experimental results, as discussed. Note that the miscible/immiscible boundaries are not well defined at the 15–20 mol% $-SO_3^-Li^+$ range and the 40–50 mol% NHCO range, and some additional experimental points would be helpful in locating the boundaries more precisely. However, the shaded miscible region in *Figure 6* has been estimated rather conservatively, so that the miscibility region at high $-SO_3^-Li^+$ or NHCO contents, as determined by d.m.t.a., may actually be larger than shown.

From this miscibility map, it can be predicted that 50:50 blends of polyamides-4 and -46 (40 and 33.3 mol% NHCO, respectively) should be miscible (on the d.m.t.a. scale) with LiSPS containing >6 mol% $-SO_3^-Li^+$ groups; while 50:50 blends of polyamides-4, -46, -6, -66, -69 and -610 (40, 33.3, 28.6, 28.6, 23.5 and 22.2 mol% NHCO, respectively) can all be expected to be miscible with LiSPS containing $\geqslant 10$ mol% $-SO_3^-Li^+$. Polyamides-11 and -12 (16.7 and 15.4 mol% NHCO, respectively) may only show single-phase behaviour when the LiSPS10 has 15–20 mol% $-SO_3^-Li^+$ groups.

It must be remembered that the miscibility of the LiSPS

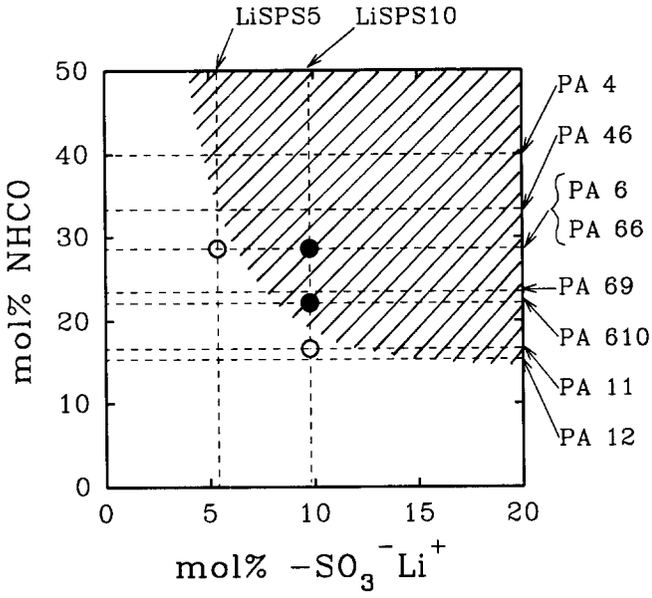

Figure 6 Miscibility map for 50:50 blends of lithium sulfonated polystyrene ionomers (LiSPS10) with polyamides. The shaded region represents expected single-phase behaviour of the blends when analysed by d.m.t.a. or d.s.c.

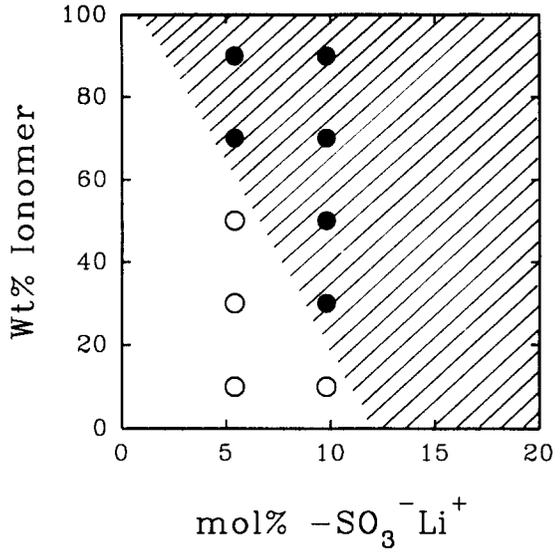

Figure 7 Single-phase blends (filled symbols and shaded region) of the LiSPS ionomer with PA-6 as a function of composition and lithium sulfonate content. Experimental points taken from ref. 26

with polyamides can be expected to be composition-dependent. A detailed study, using dynamic mechanical measurements, of the phase behaviour of LiSPS ionomers with PA-6 has shown that the miscibility of these two polymers is not only dependent on the ionic group content of the ionomer, but also on the blend composition[26]. For example, if the ionomer contains 5.4 mol% lithium sulfonate groups, the blend shows a single glass transition only if the ionomer content is greater than 50 wt%. If the ionomer has 9.8 mol% ionic groups, a single phase occurs only if the ionomer content is greater than 10 wt% in the blend. Calculation has suggested that the polystyrene ionomer containing 12 mol% lithium sulfonate groups can be expected to be miscible throughout the composition range (by d.m.t.a. and d.s.c.). These results are plotted in *Figure 7* which then represents a 'cut' along the PA-6 line of *Figure 6*. In this way the two-dimensional miscibility map of *Figure 6* could be extended into a third dimension, i.e. blend composition. It has also been shown that this composition-dependent miscibility can be related to the specific interaction of the lithium sulfonate groups of the LiSPS with the amides of the polyamide[26]. This can be expected to be a general rule for blends of LiSPS ionomers with aliphatic polyamides, so that miscibility would always improve with ionomer content. Taking this composition-dependent miscibility into account, the shaded region of the miscibility map of *Figure 6*, therefore, defines a lower miscibility limit for blends containing >50 wt% ionomer. Despite the limited experimental data, and the limitations of d.m.t.a. in resolving phases smaller than 50–100 Å in size, this map does provide a useful guide for choosing miscible polymer pairs.

It should be noted that blends in this study were all prepared by solution methods, and as such provide no indication of the melt processability of these blends. In a previous study it has been shown that unneutralized sulfonated polystyrene blends with PA-6 can be quite easily prepared by melt mixing[22,27]. On the other hand, LiSPS ionomers can be expected to be much more difficult to disperse due to strong self-association of the ionic groups. The melt rheology of LiSPS blends with PA-6 is currently being investigated and will be the subject of a future paper.

CONCLUSIONS

It has been shown that polystyrene ionomers containing lithium or sodium methacrylate groups are much less effective in enhancing the miscibility between polystyrene ionomers and polyamide-66 than lithium styrene sulfonate ionic groups. This can be expected to be a general rule for blends of ionomers with aliphatic polyamides.

The miscibility of the lithium sulfonate functionalized polystyrene ionomer (LiSPS) with aliphatic polyamides decreases with a decrease of the functional group content of the ionomer, or a decrease of the amide content of the polyamide, or both. Thus, 50:50 blends of LiSPS (containing 9.8 mol% lithium sulfonate groups) with polyamide-610 show a single glass transition by dynamic mechanical analysis, while the blends with PA-11 show the presence of two phases. However, even in the two-phase PA-11 blends, considerable miscibility enhancement occurs, as can be seen by the significant shifting of the glass transitions of the blend components towards each other.

A miscibility map, defining single-phase regions as a function of ionic group content of the LiSPS and the amide content of the polyamide is drawn as a guide to expected miscibility on the 50–100 Å level for 50:50 blends of LiSPS with aliphatic polyamides.

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