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Synergistic enhancement in mechanical properties and microstructure of homoblends made of poly(styrene-*co*-styrenesulfonic acid) and poly(styrene-*co*-4-vinylpyridine)

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Abstract

Bulk mechanical properties and microstructure of a model blend (homoblend), made of poly(styrene-*co*-styrenesulfonic acid) (SPS) and poly(styrene-*co*-4-vinylpyridine) (SVP), were investigated by tensile measurements and modulated differential scanning calorimetry (MDSC). The mechanical properties exhibited synergism: tensile strength and toughness values of the blends were higher than those expected based on the rule of mixtures. The results were attributed to the formation of ionic cross-links due to intermolecular ion–ion interactions between pyridinium cations and sulfonate anions, which arose from proton transfer from sulfonic acid groups to pyridine groups upon blending. MDSC detected only one T_g for the SPS/SVP blends, indicating that the blends were unclustered. However, after annealing the blends at 150 °C for 24 h, two T_g's were detected, reflecting microphase separation (formation of a cluster phase and a matrix phase) due to aggregation of ionic groups during annealing.

Keywords: Synergism; Homoblends; Ionic polymer blends

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1. Introduction

Polymer blends have been developed to enhance physical properties [1,2], including mechanical properties [3–5], of polymeric materials. Typical examples of enhanced mechanical properties through blending can be seen in high impact polystyrene (HIPS) or acrylonitrile-butadiene-styrene (ABS) resins, in which toughness and fracture resistance of glassy polymers have been enhanced through the incorporation of a second, rubbery phase into a matrix glassy polymer [4]. A wide range of mechanical properties can be achieved in polymer blends, depending on various factors, such as the molecular structure of the components, miscibility and compatibility between the components, blend composition, morphology, and processing conditions. In general, changes in mechanical properties upon blending polymers may occur in three different ways: the system may follow the rule of mixtures (mechanical property values follow linear additivity of the respective properties of the two components), it may positively deviate from the rule of mixtures, or it may negatively deviate from the rule. For application of polymer/polymer blending, synergistic effects, i.e. mechanical properties that positively deviate from the values anticipated based on the rule of mixtures, are most valuable and desirable.

Synergistic effects have been achieved in some immiscible and miscible polymer blends. A review of these studies, including possible causes for the synergistic effects, is available [5]. Examples of miscible polymer blends showing synergistic effects are blends of poly(phenylene oxide)(PPO) and polystyrene (PS) [6]. Modulus values of these blends are higher than those anticipated according to the rule of mixtures at all compositions, and the maximum value of the modulus appears to occur at a PPO content of 20–25 wt% [6]. Synergistic effects have also been noted in the tensile strength of the PPO/PS blends, and the synergism is suggested to arise from the presence of favorable molecular interactions between the segments of the component polymers [7]. Examples of immiscible polymer/polymer blends showing synergistic effects in mechanical properties are blends of polycarbonate (PC) and

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poly(styrene-*co*-acrylonitrile)(SAN) [8]. The yield strength values of these blends lie slightly above the additivity line for most of the blend compositions, the strain to fracture reaches a maximum value at 10–30 wt% of SAN and then falls below additivity for the blends containing 40 wt% or more of SAN. The synergistic enhancement in mechanical properties of the PC/SAN blends may result from the presence of partial miscibility between the components and better adhesion between the phases: these effects may be due to hydrogen bonding, ester exchange reactions, and physical entanglements.

Recently, we have made polymeric materials more fracture resistant and tougher by creating rigid–rigid polymer blends that contain ionic interactions [9,10]. The rigid–rigid blends are made of an ionomer and an ionomer precursor polymer, such as those made of sulfonated polystyrene (SPS) ionomer and PS, or those made of poly(methyl methacrylate)(PMMA)-based ionomer and PMMA. In such a combination of (amorphous) ionomer/ionomer-precursor, the degrees of polymerization of both the component polymers can be kept close and no crystalline phase exits. Because of the difference in polarity between the two component polymers in the blend, there is a tendency to phase separation, leading to the creation of rigid–rigid blends. At low ionomer composition, the ionomer second phase particles are dispersed in the matrix polymer (precursor polymer), and ionic aggregates are formed within the ionomer phase. In addition, athermal interactions between identical repeat units of the component polymers may insure compatibility at the interface through interpenetration of polymer chains, and development of some molecular entanglements. It is well known that entanglements are a prerequisite for strength in polymeric systems, and also for good interfacial adhesion [11,12]. Synergistic enhancement in both tensile strength and fracture energy has been achieved in these blends [9,10].

In a recent study [13], involving an extension of our efforts to elucidate the deformation/fracture behavior of ionomers [14–17], we have investigated the deformation behavior of a model blend (homoblend) made of poly(styrene-*co*-styrenesulfonic acid)(SPS) and poly(styrene-*co*-4-vinylpyridine)(SVP), in which sulfonic acid groups and 4-vinylpyridine groups were introduced separately into PS. In this homoblend, proton transfer occurs from sulfonic acid groups to pyridine groups, and as a result intermolecular ionic bonds are formed between sulfonate anions and pyridinium cations (see Fig. 1). We have shown, from transmission electron microscopy (TEM) studies of strained thin films, that, as the content of intermolecularly interacting groups in the SPS/SVP blends rises, there is a change in deformation mode from crazing only to a combination of crazing and shear deformation. Such change can be understood as arising from an increased ‘effective’ (network) strand density due to formation of ionic cross-links upon blending [13]. The development of this multiple deformation mode suggests that the material is more fracture resistant than the component polymers [18]. Hence, it is of interest to see whether bulk mechanical properties of the SPS/SVP blends will develop synergism via introduction of ionic cross-links. In this paper, we report the results of tensile mechanical tests of these blends.

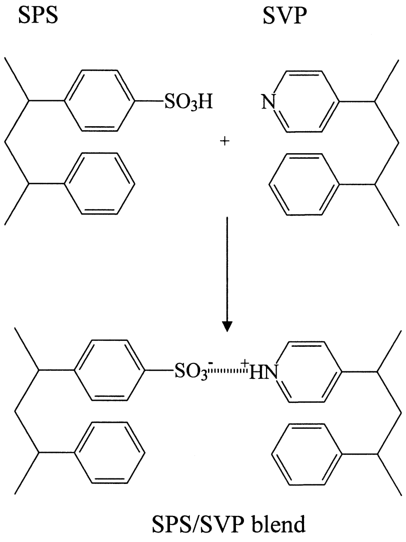

Fig. 1. Schematic illustration indicating chemical structures of polymers and the formation of intermolecular ion–ion interaction (ionic cross-links).

Another purpose of this work is to study the microstructure of SPS/SVP blends. Extensive studies have been conducted on the microphase separation of ionomers (due to ionic aggregation) with metal counterions, e.g. sodium salt ionomers of SPS (SPS-Na) or of poly(ethylene-*co*-methacrylic acid) (P(E-*co*-MANa)) [19–24]. By contrast, few studies have been reported on the potential microphase separation in the homoblend due to aggregation of ionic groups, e.g. sulfonate anions and pyridinium cations [25]. For ionomers with metal counterions, it is now generally accepted that ionic groups tend to aggregate due to the difference in polarity between the ionic groups and the hydrocarbon chains. As proposed by Eisenberg and coworkers [19], two types of aggregates exist in ionomers: multiplets and clusters. A multiplet is defined as an aggregate in which ions (and ion pairs) are in contact with each other with no intervening hydrocarbon chains. A cluster is an aggregate of multiplets, which contain some hydrocarbon chains. In a recent model proposed by Eisenberg et al. the cluster is considered to consist of regions of hydrocarbon chains whose mobility is restricted due to the cross-linking effect of the multiplets [20,24]. In ionomers with metal counterions, only anionic groups are covalently bonded to the polymer backbone chains and metal counterions are attached to anionic groups via ionic bonds. By contrast, both cations and anions are covalently bonded to polymer backbone chains in the SPS/SVP blends. In the SPS/SVP blend, counterions cannot move independently from the backbone molecules to which ions are connected, thus, steric hindrance and requirements of the cooperativity of polymer chains to become part of a cluster may increase. Therefore, it may become more difficult to form multiplets or clusters as compared with the case of metal counterion ionomers. Whether the cluster structure can still be formed in the SPS/SVP blends is in question [25].

In this study, the microstructure of the SPS/SVP blends was investigated by using modulated differential scanning calorimetry (MDSC) [26]. In this new thermal analysis technique, a calorimeter block is subject to a temperature ramp that is linear when averaged over time, but a sinusoidal temperature oscillation (modulation) is overlaid on this conventional linear temperature ramp. MDSC can achieve high sensitivity for detecting weak glass transitions, because it can readily and accurately determine the real changes of the heat capacity over the glass transition region rather than just the absolute value of the heat flow, which is usually obtained by conventional DSC. Other advantages of MDSC include the separation of a complex transition into more easily interpretable components, the measurement of heat capacity under quasi-isothermal conditions, and an increased resolution without loss of sensitivity. Hence, MDSC can provide useful information on the morphological and microstructural features of the SPS/SVP blends.

2. Experimental

2.1. Materials

SPS was prepared by sulfonation of polystyrene with a sulfonating agent, acetyl sulfate, according to the procedure described by Makowski et al. [27]. The starting polymer was PS having a molecular weight of 4.0×10^5 g/mol. After the sulfonation reaction was terminated by the addition of methanol, polymer (acid form) was recovered by steam stripping in boiling water. After being dried in air for at least 3 days, polymer was redissolved in a solvent mixture, benzene/methanol (90/10, v/v) and freeze-dried, followed by vacuum drying at room temperature for at least a week. The acid contents of the SPS samples were determined by conductometric titration of the sulfonic acid groups in DMF solution using a standard methanolic sodium hydroxide solution [28].

SVP was made by radical bulk copolymerization of styrene (S) with 4-vinylpyridine (VP) using benzoyl peroxide as an initiator [29]. The concentration of the initiator was 1.56×10^{-3} mol/l. Polymerization was carried out at 60 °C for 16 h to achieve about 10% conversion. Polymer was recovered by precipitating the 5 wt% polymer solution (in toluene) into 10 volumes of methanol under rapid stirring. Precipitated white polymer strands were broken into fine pieces by using a blender, and the polymer was filtered and vacuum dried at 70 °C for 4 days. The degree of polymerization of the polymer was estimated to be about 1.8×10^3 (or molecular weight of 2.0×10^5 g/mol) by calculation using the concentration of the initiator. The content of VP in the copolymer was determined by Fourier transform infrared (FTIR) spectroscopy; details about the measurements and analysis are described elsewhere [13].

The sulfonic acid contents of the SPS and the pyridine contents of the SVP are summarized in Table 1 along with the nomenclatures used in this study.

2.2. Blend samples

Blend samples were obtained by solution blending. The SPS and SVP copolymers, having close sulfonic acid and pyridine contents, were dissolved separately in tetrahydrofuran (THF) (4 wt%), and the solutions were mixed by dropwise addition of one to the other under vigorous stirring. Blends were prepared so as to contain stoichiometric amounts of functional groups. Mixing was accompanied by the formation of gel, which would hinder the stirring with a magnetic bar. Hence, stirring was conducted by manually swirling the solution for 30 min after addition. The mixture was then stirred overnight with a magnetic bar. The solution blending products were recovered by casting the solution into a Petri dish: solvent was allowed to evaporate slowly at room temperature for one week, then vacuum dried at 80 °C for 3 days, and vacuum dried further at 140 °C for another 3 days.

The ion contents in the blends, determined by FTIR as described in the recent paper [13], are also included in Table 1.

2.3. Tensile testing

Tensile specimens were dog-bone shaped samples, machined from the compression-molded bars. Compression molding was carried out by pressing the solution blending products under 14 MPa at 170–190 °C for 3 min. The gauge section of the specimen, with a 8 mm length, a 3.5 mm width, and a 0.5 mm thickness, was connected to wider (10 mm) end sections by two long (10 mm) tapered sections. Tensile testing was carried out at room temperature using a displacement rate of 0.1 mm/min (or at a nominal strain rate of $2.08 \times 10^{-4}\ \mathrm{s}^{-1}$ based on the actual gauge length) on a Minimat materials tester (Polymer Laboratory). The average values of at least three specimens were used for analysis.

2.4. MDSC measurement

MDSC measurements were conducted on small specimens that were made by cutting compression molded products. Measurements were performed with MDSC 2910 (TA Instruments Inc.) at a heating rate of 2 °C/min and a temperature oscillation of ± 1.5 °C/40 s. Highly purified nitrogen gas was used for purging at a flow rate of 60 ml/min. The sample weight was about 10 mg. After the first MDSC scan, the SPS/SVP blend samples were annealed at 150 °C for 24 h and reexamined with MDSC

Table 1
Nomenclatures and characteristics of the blends and their component polymers

Blend	Poly(styrene-*co*-styrenesulfonic acid) Sulfonic acid content (mol%)[a]		Poly(styrene-*co*-4-vinylpyridine) Pyridine content (mol%)[b]		Ion content in the blend (mol%)[a]
SPS3/SVP3	SPS3	2.4	SVP3	3.0	2.0
SPS4/SVP5	SPS4	3.6	SVP5	4.7	3.1
SPS6/SVP7	SPS6	5.3	SVP7	6.7	5.8

[a] Determined by conductometric titration.
[b] Determined by IR.

using the same scanning condition. The glass transition was defined as the inflection point of the transition.

3. Results and discussion

3.1. Mechanical properties

Typical nominal stress–strain curves of the SPS/SVP blends with different functional group contents are shown in Fig. 2 along with similar data on PS for comparison. PS exhibits brittle behavior with essentially a linear relationship between the stress and the strain. All SPS/SVP blends show brittle behavior as well; however, it can be seen that both the fracture stress and the fracture strain are increased as the content of functional groups is increased. Moreover, the curves become non-linear before fracture, which indicates that the blends exhibit some plastic deformation and a limited degree of 'ductility'.

The tensile strength and the tensile toughness (defined as the energy absorbed per unit volume, and determined by the area under the stress–strain curve) for the SPS/SVP blends, obtained as the average values for at least three samples, are plotted in Figs. 3 and 4, respectively. The values for the component polymers are also shown for comparison. The SPS and SVP polymers have nearly the same properties. In addition, the SPS and SVP polymers with different functional group contents show little difference in both tensile strength and toughness, with values close to those of PS. Thus, the presence of a relatively low number of either sulfonic acid groups or pyridine groups in PS has little effect on mechanical properties, although there is a potential for the SPS to form hydrogen bonds. By contrast, all the blends show synergism in tensile strength and toughness: values are higher than those expected from a simple additivity based on the rule of mixtures (dashed lines). The tensile strength has increased by about 20% for the SPS3/SVP3 blends, and by more than 30% for the SPS4/SVP5 and the SPS6/SVP7 blends, as shown in Fig. 3. Also, the tensile toughness has increased by about 40% for the SPS3/SVP3 blends, and the value is increased by more than 60% for the

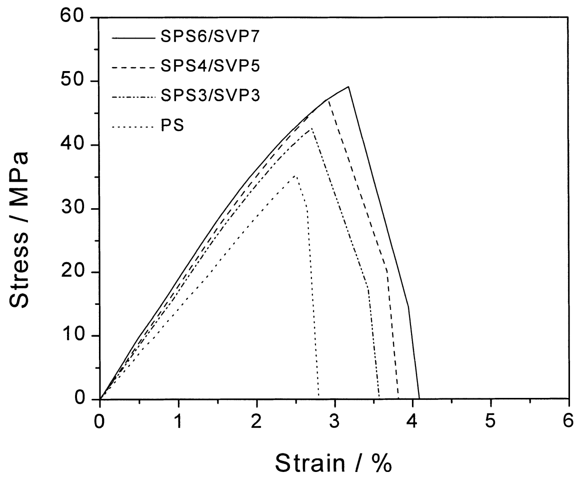

Fig. 2. Typical stress–strain curves for SPS/SVP blends and PS.

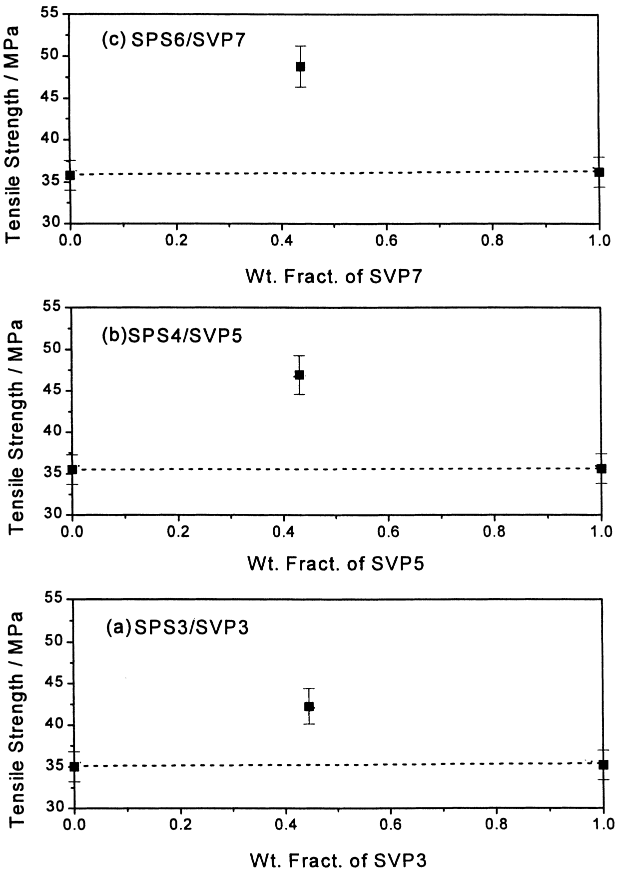

Fig. 3. Composition dependence of the tensile strength for SPS/SVP blends. The dashed lines represent the rule of mixtures.

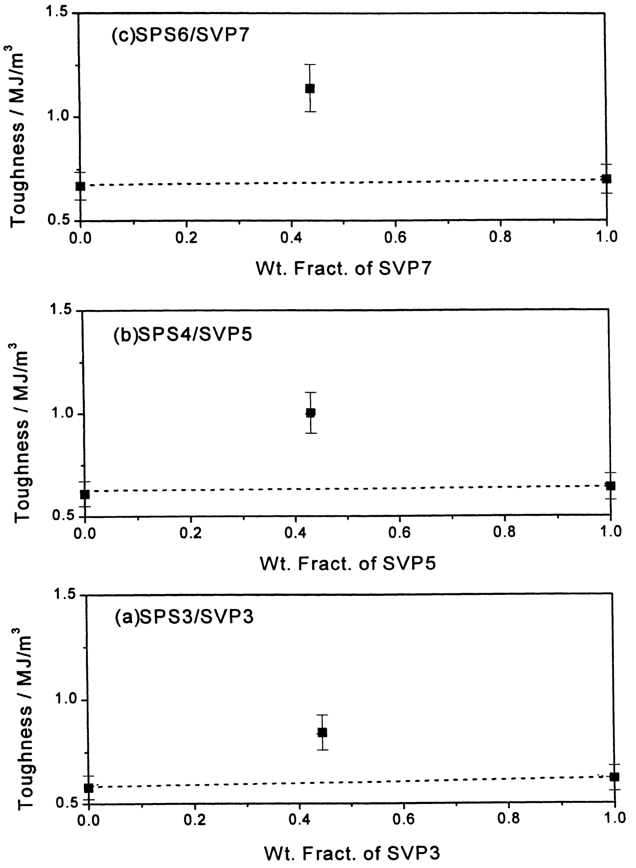

Fig. 4. Composition dependence of the tensile toughness for SPS/SVP blends. The dashed lines represent the rule of mixtures.

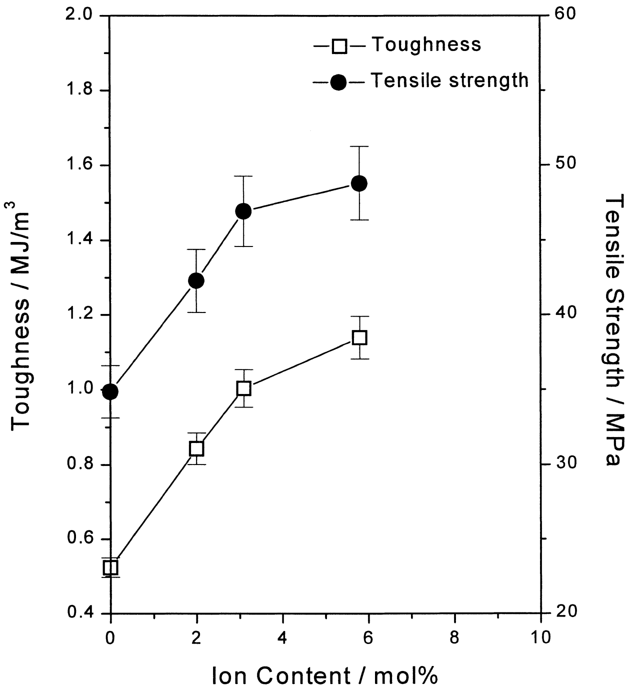

Fig. 5. Effect of ion content on the tensile strength and the tensile toughness of SPS/SVP blends.

SPS4/SVP5 and SPS6/SVP7 blends, as shown in Fig. 4. The changes of the tensile strength and toughness as a function of ion content in the SPS/SVP blends are shown in Fig. 5. Values for the blends are higher than those of unmodified PS, and the values of both properties increase with ion content. For the SPS6/SVP7 blend (5.8 mol% ion content), a 35% increase in the tensile strength and a 70% increase in the toughness have been achieved as compared with unmodified PS. The change in modulus value is smaller than that in strength and toughness, although the trend seen in Fig. 5 is same. For example, at 5.8 mol% level, an increase in modulus is less than 20% as compared with those in strength and toughness, 35 and 70%, respectively. Similar trend has been noted for ionomers, such as SPS-Na ionomers. This is because modulus is related to small-scale (local) deformation of the polymer chains, whereas strength and toughness are related to large-scale deformation of the polymer molecules, thus the effect of morphological changes (i.e. formation of ionic aggregates) is more significant in stress and toughness values.

The synergistic enhancements observed in both the tensile strength and toughness upon blending SPS with SVP can be attributed to the presence of intermolecular ion–ion interactions. In this model homoblend, the basic polymer backbone is styrene for both components. The only difference between the SPS/SVP blends and PS is the presence of ion–ion interactions between sulfonate anions and pyridinium cations in the blends, which arise from proton transfer from sulfonic acid groups to pyridine groups upon blending [30–32]. The ion–ion interaction between the pyridinum cation and the sulfonate anion provides cross-linking. We have previously observed that the introduction of ionic cross-links will change the deformation mode of thin films of SPS/SVP blend subject to simple tension [13]. PS, SPS, and SVP all deform only by crazing; however, the deformation mode of the SPS/SVP blends was changed from crazing only to crazing plus shear deformation, and the degree of shear deformation increased when the ion content was increased. The ionic cross-links are believed to be responsible for this change. The effective (network) strand density of the system is increased upon introduction of ionic cross-links, thereby increasing the crazing stress, whereas the yield stress is little influenced by cross-links. This allows shear deformation to compete with crazing [18]. Shear deformation can suppress craze growth, inhibit or delay crack formation due to craze fibril breakdown, and prevent early fracture. This in turn increases the strain to fracture, dissipates more mechanical energy, and enhances the toughness [18].

It is worthwhile to note that the enhancement of toughness in our system is achieved without reducing the tensile strength and modulus, unlike the situation in rubber toughened polymers, where the enhancement in toughness is more significant but is achieved at the expense of appreciable reductions in the modulus and the strength. Moreover, ionic cross-links are thermolabile and thus their introduction will not lead to the loss of melt processability of the polymeric materials. Thus, introduction of ionic cross-links provides a more practical way than the incorporation of covalent cross-links to enhance mechanical properties of glassy polymers.

3.2. MDSC studies

Although extensive studies have been conducted on the structure of ionic aggregates for ionomers with metal counterions [19–23], little information is available about the aggregation of ionic groups (e.g. sulfonate anion and pyridinium cation) in homoblends [25]. One of the most widely used techniques to study ionomer morphology is dynamic mechanical thermal analysis (DMTA) [23,33–38]. For ionomers with metal counterions, DMTA has revealed a high-temperature loss peak in addition to a low-temperature T_g peak. As the ion content increases, the low-temperature peak reduces in intensity, while the intensity of the high-temperature peak increases and eventually dominates the entire relaxation behavior. The high temperature transition is considered to be the glass transition of the ionic cluster 'phase' [24]. This interpretation, however, has not received universal acceptance. This is due, in part, to the fact that the detection of both T_g's by conventional DSC frequently fails, although it has been successful in some cases, e.g. poly(styrene-*co*-sodium methacrylate) (P(S-*co*-MANa)) and poly(ethylacrylate-*co*-sodium acrylate) ionomers [35].

In this study, a new thermal analysis tool, MDSC, was used to study ionic aggregates. Unlike conventional DSC, which operates with a single, linear heating (or cooling) rate, MDSC adds a sinusoidal oscillation to the controlled temperature, leading to a change of heating rates [26]. This modifies the heat flow result obtained from a single DSC experiment. The total DSC heat flow is comprised of two components: one is a heat capacity component, which directly follows the modulated heating rate, and the other is a kinetic component, which is a function of time and temperature, governing the kinetic response of any physical or chemical transitions observed in conventional DSC. MDSC can separate the total heat flow into these two components. The deconvoluted heat capacity component obtained by MDSC, named as reversing heat flow, is very sensitive to the glass transition process. In this paper, the glass transition behavior of the SPS/SVP blends and their parent polymers is analyzed by using this reversing heat flow signal.

The MDSC results on the specimens taken from the compression-molded products are shown in Figs. 6–8. Fig. 6 shows the plots of reversing heat flow against temperature for the SPS6/SVP7 blend along with its components, SPS6 and SVP7. The main feature for the SPS6 and the SVP7 is the appearance of one transition, located at 114.1 and 108.4 °C, due to the glass transition of pure SPS6 and SVP7, respectively. The SPS6/SVP7 blend without annealing also shows only one transition at 117.9 °C. The higher glass transition of the SPS6/SVP7 blend as compared with its parent polymers can be attributed to the effect of ionic cross-links, formed between the two component polymers, via pyridinium cation and sulfonate anion. This result, somewhat similar to the effect of covalent cross-links on the blend's T_g, is consistent with previous results obtained by conventional DSC [31]. In contrast to the unannealed sample, the SPS6/SVP7 blend annealed at 150 °C for 24 h develops a second high-temperature glass transition at 167.6 °C in addition to a low-temperature transition, located at 112.4 °C. Similar results were obtained for the SPS4/SVP5 and SPS3/SVP3 blends, as shown in Figs. 7 and 8: i.e. two glass transitions were found in the blends after annealing at 150 °C for 24 h, while only one glass transition appeared in the blends without annealing. A single T_g appeared also in their parent polymers. The glass transition temperatures of the blends and their parent polymers obtained with MDSC are summarized in Table 2.

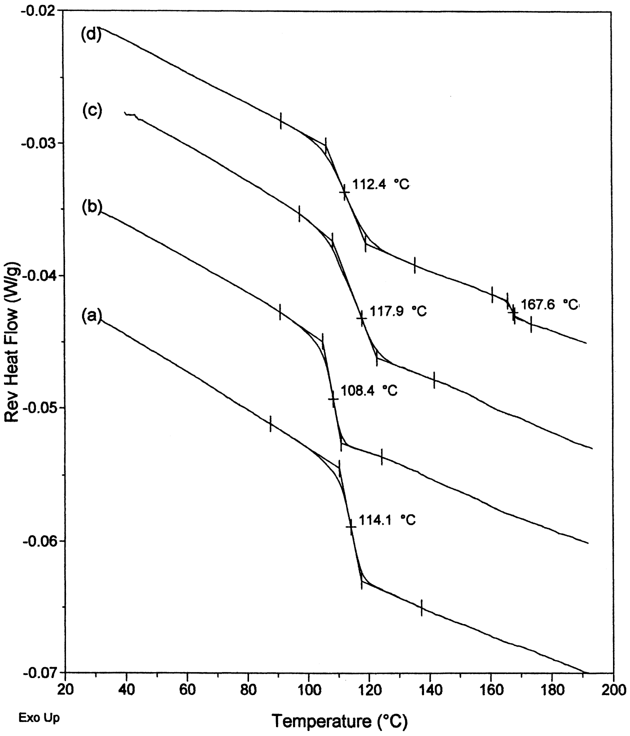

Fig. 6. MDSC curve: (a) SPS6; (b) SVP7; (c) SPS6/SVP7 blend without annealing; (d) SPS6/SVP7 blend annealed at 150 °C for 24 h.

The appearance of two glass transitions in the annealed SPS/SVP blends suggests the presence of two regions (phases) with different chain mobility. One region can be attributed to the matrix phase with the T_g close to that of its parent polymer (PS), and the other region with a higher T_g, can be attributed to an ionic cluster 'phase' arising from the aggregation of sulfonate anions and pyridinium cations.

The second transition in the annealed SPS3/SVP3 blend is not as clearly delineated as in the case of the SPS6/SVP7 and SPS4/SVP5 blends. However, a common characteristic feature is observed for these three blends: the primary glass

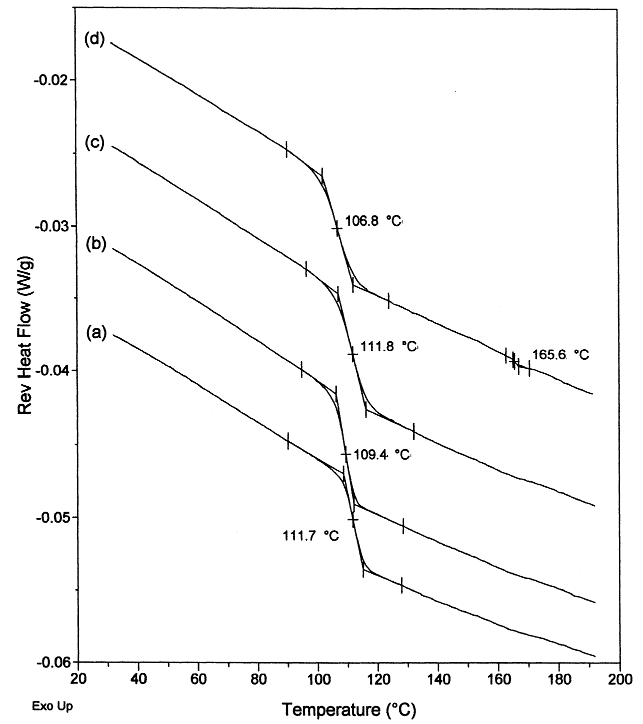

Fig. 7. MDSC curves: (a) SPS4; (b) SVP5; (c) SPS4/SVP5 blend without annealing; (d) SPS4/SVP5 blend annealed at 150 °C for 24 h.

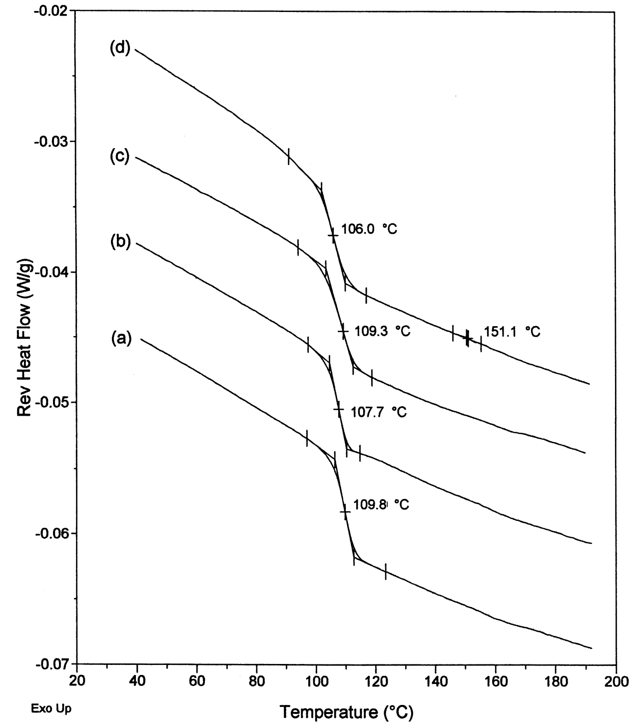

Fig. 8. MDSC curves: (a) SPS3; (b) SVP3; (c) SPS3/SVP3 blend without annealing; (d) SPS3/SVP3 blend annealed at 150 °C for 24 h.

Table 2

Glass transition temperatures of the SPS/SVP blends and their component polymers

Sample	T_g (matrix phase, °C)	T_g (cluster phase, °C)
PS	106.4	–
SPS3	109.8	–
SPS4	111.7	–
SPS6	114.1	–
SVP3	107.7	–
SVP5	109.4	–
SVP7	108.4	–
SPS3/SVP3	109.3 (106.0)[a]	– (151.1)[a]
SPS4/SVP5	111.8 (106.8)[a]	– (165.6)[a]
SPS6/SVP7	117.9 (112.4)[a]	– (167.6)[a]

[a] The temperatures inside parenthesis represent the glass transition temperatures for the samples annealed at 150 °C for 24 h.

transition temperature is decreased to the value close to the T_g of PS after annealing the samples. According to these results, we can conclude that, during annealing, microphase separation occurs between ion pairs and the PS matrix. The ion pairs, which are made of pyridinium cation and sulfonate anion and are initially dispersed in the matrix of the blends, aggregate to form multiplets and then multiplets further coalesce to form a cluster 'phase'. The primary T_g of the blends falls down to a value close to the T_g of PS after annealing; this may indicate that most of the single ion pairs aggregate into the cluster 'phase' and leave the matrix essentially similar to PS.

For the unannealed samples, the glass transition temperature of the blends increased with ion content, as seen in Table 2. This result indicates that single ion pairs made of pyridinium cation and sulfonate anion provide a cross-linking effect even though the system is unclustered.

The glass transition temperatures associated with the cluster 'phase' are plotted as a function of ion content in Fig. 9, along with data obtained for SPS-Na and P(S-*co*-MANa) ionomers. The cluster T_g of the blends obtained in our experiments is in good agreement with that obtained by Douglas et al. [25]. It increases with increasing ion content in the same way as it does for the SPS-Na and P(S-*co*-MANa) systems, but the position of the cluster T_g in the SPS/SVP blends is lower than that in the P(S-*co*-MANa) ionomer, and much lower than that in the SPS-Na ionomer.

The much higher cluster T_g in the SPS-Na system than in the P(S-*co*-MANa) system has been attributed to the stronger electrostatic attractions between $-SO_3^-/Na^+$ ion pairs in a multiplet than those between $-COO^-/Na^+$ ion pairs, based on the assumption that the glass transition in the cluster 'phase' involves ion hopping [35,39,40]. Ion hopping is understood as the removal (or migration) of ion pairs, attached to a particular chain segment, from one ionic aggregate to another [41]. During ion hopping, a migrating ion pair no longer anchors the polymer chain to which it is attached. Thus, the polymer chain segments with restricted mobility experience an increase in mobility. The motions in these chain segments during the ion-hopping period are likely to be consistent with glass transition phenomena. Thus, the T_g of the cluster 'phase' is influenced

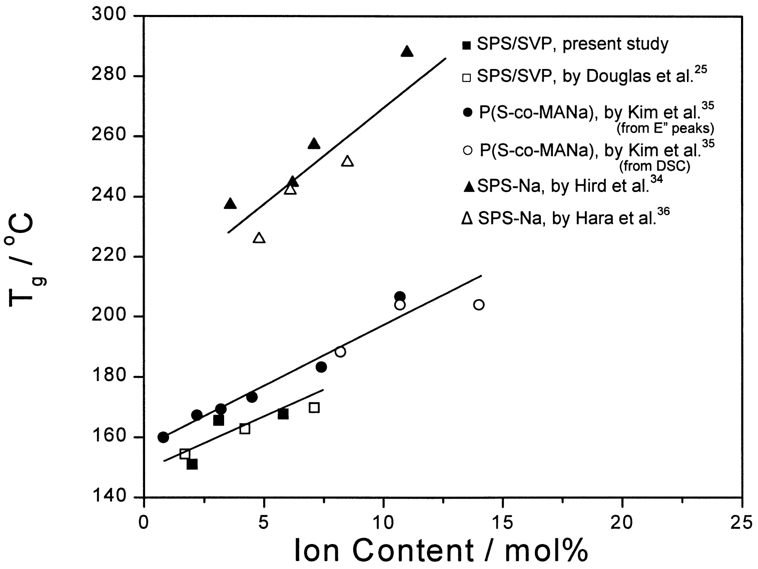

Fig. 9. Ion content dependence of the glass transition temperatures of the cluster 'phase' for SPS/SVP blends annealed at 150 °C for 24 h, along with those for SPS-Na ionomer and for P(S-*co*-MANa) ionomer.

by the strength of electrostatic interaction between the ion pairs and the mobility of the polymer chain [35,39,40].

Since the materials in the cluster region are essentially the same for these three blends (i.e. PS), the mobility of polymer chains in the cluster 'phase' are alike. Thus, the cluster T_g in these three blends is more directly related to the strength of electrostatic interaction between ion pairs. We suggest that the lower T_g of the cluster 'phase' in the SPS/SVP system, as compared with either the P(S-*co*-MANa) system or the SPS-Na system, is because the electrostatic interaction through sulfonate anion/pyridinium cation ion pairs is weaker than that through $-SO_3^-/Na^+$ ion pairs or that through $-COO^-/Na^+$ ion pairs. This seems reasonable, because the pyridinium cation is larger than Na^+.

The absence of a cluster 'phase' T_g for the unannealed SPS/SVP blends can be understood as follows. The formation of multiplets (not cluster) depends on the competition between electrostatic interactions among ion pairs and the elastic forces of the chains to which the ionic groups are attached: low electrostatic interactions between ion pairs and high elastic forces of the chains are against aggregation [19]. The larger pyridinium cation in the SPS/SVP blends results in a weaker attractive electrostatic interaction between ion pairs. Moreover, both pyridinium cation and sulfonate anion in the SPS/SVP blends are attached to polymer chains. This may result in higher energy barriers for the conformational rearrangement of polymer chains so as to allow more ion pairs to come into direct contact with each other and thus form a multiplet. Therefore, it appears that the relatively low electrostatic interactions and higher energy barriers hinder the formation of multiplets. During annealing at the temperature above the T_g of the matrix polymer, energy barriers are overcome and the electrostatic interaction may now be sufficient to form multiplets, and create a significant volume of material of restricted mobility around the multiplets. These restricted mobility regions may then overlap and eventually form fairly large domains (clusters), which exhibit phase-separated behavior and possess their own T_g.

4. Conclusions

A model blend, SPS/SVP, was investigated to study the effects of intermolecular ionic interactions and ionic cross-links on bulk mechanical properties. In this homoblend, two functional groups, 4-vinylpyridine and sulfonic acid, were introduced separately onto polystyrene chains. Upon blending, proton transfer occured from sulfonic acid groups to pyridine groups, and as a result ionic interactions between pyridinium cations and sulfonate anions were formed. Such ionic interactions act as ionic cross-links. The formation of the intermolecular ionic cross-links via pyridinium cation/-sulfonate anion ion pairs resulted in a synergistic enhancement in bulk mechanical properties. The average values of tensile strength and toughness were higher than those expected based on the rule of mixtures, and both properties increased in value with the functional group content. The synergism is believed to arise from a change in deformation mode, from crazing only to crazing plus shear deformation, upon introduction of the ionic cross-links.

The microstructure of the SPS/SVP blends was also studied by MDSC and discussed in terms of the aggregation of ionic groups. For the molded samples, only one glass transition was detected, indicating that the blends were unclustered. However, after annealing at 150 °C for 24 h, two glass transitions were detected, indicating that microphase separation due to the aggregation of ionic groups occurred during annealing. The microphase separation led to the formation of a cluster 'phase' and a matrix phase. The cluster glass transition temperatures of the SPS/SVP blends were lower than those of PS-based sodium salt ionomers, such as SPS-Na or P(S-*co*-MANa). This may be due to the lower electrostatic interactions between ion pairs for the pyridinium cation/sulfonate anion pairs than for $-COO^{-}/Na^{+}$ pairs and $-SO_3^{-}/Na^{+}$ pairs.

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