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Molecular composites of poly(*p*-phenylene terephthalamide) anion and poly(propylene oxide): mechanical properties

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Abstract

Molecular composites have been prepared by mixing rigid rod molecules of PPTA anion (K-salt) and poly(propylene oxide) in a common solvent and compression molding the precipitated material. As the PPTA anion content of the composites is increased, an upward shift occurs in both the glass transition temperature and the decomposition temperature. The tensile strength, stiffness and resistance to stress relaxation of the composites are significantly increased, even at relatively low concentrations of the rigid rod reinforcement. The enhancement in mechanical properties results from a good dispersion of the rigid PPTA anion molecules and from the presence of ion-dipole interactions between the ionic groups of the PPTA anion and the dipolar units of the poly(propylene oxide) matrix. Additional increases in strength and rigidity may be achieved by changing the counterion from monovalent K^+ to divalent Ca^{2+}. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Molecular composites; Poly(propylene oxide); Poly(*p*-phenylene terephthalamide)

1. Introduction

Molecular composites, in which a relatively small concentration of rigid rod molecules are dispersed in a flexible coil polymer, are interesting new materials [1–4]. To overcome the tendency of the rigid rod molecules to aggregate [5], rather than to be dispersed in the polymer matrix, it is necessary to have, or to induce by suitable modification, some type of attractive interactions between the components. For example, it has been noted that molecular level mixing occurs in blends of poly(glutamates) and poly(vinyl phenol) as a result of favorable hydrogen bond interactions [6].

Acid–base and H-bonding interactions also provide miscibility in melt-processable molecular composites obtained from blending slightly sulfonated polystyrene (SPS) and poly(benzyl-L-glutamate) (PBLG)[7]. One drawback of hydrogen bonds is that they may be dissociated upon heating; as a result phase separation can occur [8].

Ionic interactions have been used to enhance miscibility between the components of various composites [7,9–11]. For example, melt processable molecular composites have been made by using, as the rigid rod molecules, ionically modified ploy(*p*-phenylene terephthalamide) (PPTA) and, as the flexible coil matrix, a polar type polymer such as ploy(4-vinylpyridine) (PVP) or poly(ethylene oxide) (PEO) [12]. In such blends both components can be dissolved in a suitable solvent, such as dimethyl sulfoxide (DMSO), to form a homogeneous molecular dispersion. Ion–dipole interactions then provide the necessary, specific attractive forces between the components to produce good miscibility.

The current investigation involves the preparation and study of molecular composites based on a matrix of an amorphous, rubbery polymer, viz. poly(propylene oxide) (PPrO). This work is a continuation of studies concerning the properties of molecular composites based on use of PPTA anion molecules as a means of reinforcement of various polar, flexible coil polymers. In one previous study [13], the matrix used was the glassy polymer PVP, with a glass transition temperature of 151°C. In this study, miscibility between the rigid rod PPTA anion (K-salt) and the matrix polymer was achieved for all composites containing up to 5 wt% of the rigid rod reinforcement; and, with increasing PPTA anion content, significant increases occurred in tensile strength and in toughness. In another study [14], we investigated the properties of composites in which the polar matrix was a highly crystalline polymer, viz. PEO, with a glass transition of the amorphous phase well below room temperature. In both of these prior studies, the presence of ion–dipole interactions between the components led to an increase in the glass transition temperature,

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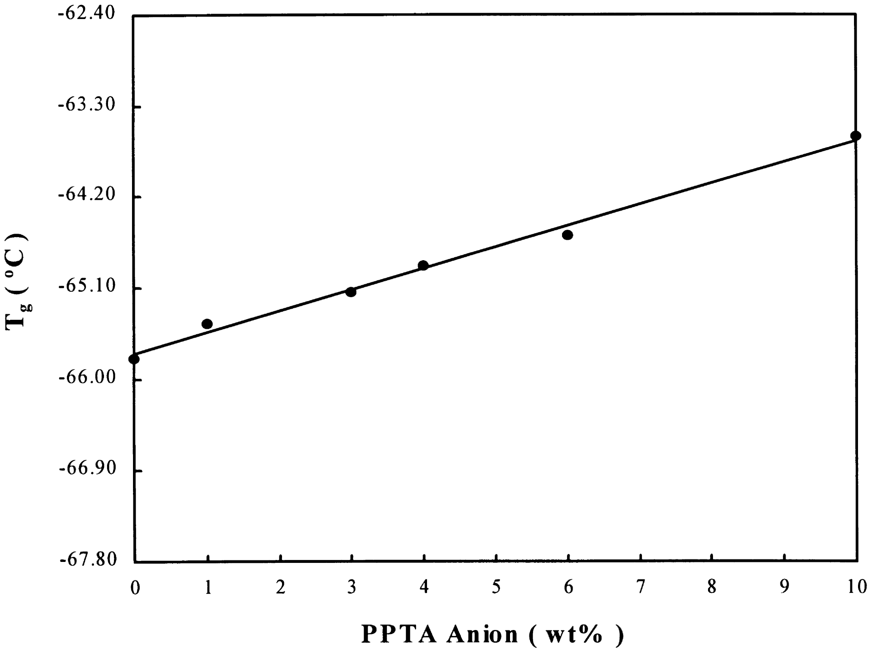

Fig. 1. Glass transition temperature, T_g, vs PPTA anion (K salt) content.

T_g, an indication of miscibility, and to enhanced values of the mechanical properties.

It is expected that the molecular composites of the present study, as a result of the interactions between the ionic groups of the salt-form PPTA anion molecules and the dipolar units of the PPrO matrix will also show some enhancement in properties. However, the relative effects of the PPTA anion content may be quite different than for similar composites based on glassy PVP or semi-crystalline PEO. With a rubbery matrix, the molecular chains are less tightly coiled and a larger free volume is present. Factors to be considered in this study include: the effects of PPTA anion content on mechanical and viscoelastic properties and on the glass transition and decomposition temperatures; and the effects of changing the counterion from monovalent K to divalent Ca. In addition, we also study the mechanical properties of some non-ionic PPTA/PPrO blends. From results of these tests, it should be possible to separate the possible reinforcement effects of rigid filler from the effects produced when ion-dipole interactions are present between the components.

2. Experimental

It has been reported by Takyanagi and others [15,16] that rigid rod PPTA molecules can be deprotonated by reacting with a suitable base to convert the Kevlar-like molecules to metal salts of the PPTA anion. In our study, the metal base used was potassium hydride (KH) to yield the polyanion $PPTA^- K^+$, which is soluble in DMSO. One equivalent of base, corresponding to one equivalent of amide bonds in PPTA, was used to insure that no units of the PPTA molecules remained unreacted. Details of the experimental procedure are given elsewhere [17].

The poly(propylene oxide) used as the matrix polymer in this study had a molecular weight of 600,000 and a glass transition temperature of −66°C. The composites were prepared by dissolving, in DMSO for 8 h with stirring, the PPTA anion (K-salt) and the flexible coil PPrO. An excess amount of anhydrous ether was used to precipitate the molecular composites; a typical ratio of the non-solvent to the molecular composite solution was 20:1. The precipitate was dried under vacuum (at 40°C for 48 h) and then freeze milled to a powder. The powder was re-dried and stored in a dessicator until used for thermal characterization or mechanical testing.

Samples for mechanical testing were compression molded at 6.9 MPa for 30 min at temperatures ranging from 65°C for the (2/98) composites to 85°C for the (10/90) composites. A molding temperature of 80°C was used for the preparation of the (4/96) PPTA anion (Ca-salt)/PPrO composite.

Mechanical testing was carried out, under ambient conditions of temperature and humidity, on a Minimat Miniature Materials Tester (Polymer Lab) at a strain rate of 5.5×10^{-3}. Specimen dimensions were 15 mm in length, 6.4 mm in width and 0.50 mm in thickness. Tests were made in accordance with ASTM D-882. At least 5 specimens were tested for each composition; property values quoted herein are average values. Stress relaxation tests were run on the PPrO homopolymer and on two of the composites. All samples were tested in the dry state, as PPTA anion is known to be sensitive to moisture. However,

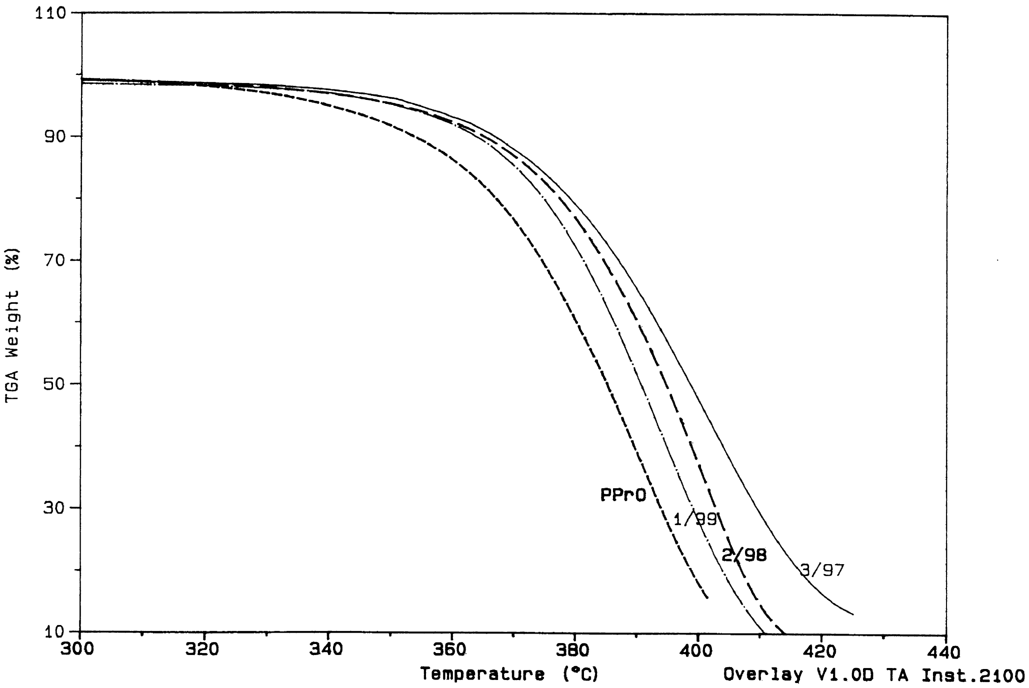

Fig. 2. Thermogravimetric analysis (TGA) weight retained vs temperature for various PPTA anion/PPrO composites.

the PPTA anion/PPrO composites, like the composites of PPTA anion/PVP discussed in a previous publication [13], are more resistant to attack by moisture as the ionic groups of the PPTA anion are surrounded by molecules of PPrO.

Thermal characterization of the composites included DSC measurements, to evaluate miscibility and to ascertain the effects of the rigid rod reinforcement on T_g, and thermal gravimetric analysis (TGA), to obtain a measure of thermal stability of the samples and to determine the possible effects of the counterion on the decomposition temperature. The DSC results, obtained on 5 mg of powder at a scan rate of 10°C/min, are based on recordings of both the second and third DSC scans. Measurements were carried out on a TA Instrument 2100 Thermal Analyst, equipped with a 910 Differential Scanning Calorimeter. For the TGA measurements, the Thermal Analyst was equipped with a 951 Thermogravimetric Analyser. Tests were carried out at a heating rate of 10°C/min on 15–20 mg of powder sample. In both the DSC and TGA studies, the sample pans were continuously flushed with nitrogen at a flow rate of 25 and 50 ml/min, respectively. A scanning electron microscope (SEM) (AMRAY 1200) was used to examine the fracture surface and the side surfaces of some deformed samples.

3. Results and discussion

3.1. Thermal characterization

The glass transition temperature, determined from two separate scans for each composite sample, was taken as the mid-point of the step transition in a typical DSC scan. T_g values are shown as a function of the PPTA anion (K-salt) content in Fig. 1. Over the range of compositions studied, T_g increases steadily with PPTA anion content. This effect is attributed to enhanced intermolecular forces arising from the presence of ion–dipole interactions between the components. These ionic interactions act somewhat like cross-links and increase constraints to molecular motion. A similar situation occurs in molecular composites of PPTA anion and PVP [13]. There too, T_g values, though much higher in absolute terms because of the rigid nature of glassy PVP, increased steadily with increasing concentration, up to about 5 wt%, of the PPTA anion reinforcement.

The PPTA anion/PPrO molecular composites are thermally stable. This is evident from the DSC studies, which give essentially the same value of T_g on both the 2nd and 3rd scans, and from the TGA studies. TGA scans are shown in Fig. 2 for the homopolymer and for three of the composites. With increasing PPTA anion content, the TGA scans shift to higher temperatures. At 300°C there is essentially no weight loss in any of the composites; and the 50% weight loss temperature shifts from 390°C for the PPrO homopolymer to 406°C for the (3/97) composite. There is, however, some loss in heat stability at high PPTA anion contents. For example, for the (10/90) composition the 50% weight loss temperature falls to 371°C. This may reflect a somewhat less uniform dispersion of the reinforcement in the matrix polymer at high PPTA anion content, although the T_g result indicates miscibility between components extends to at least 10 wt% of reinforcement.

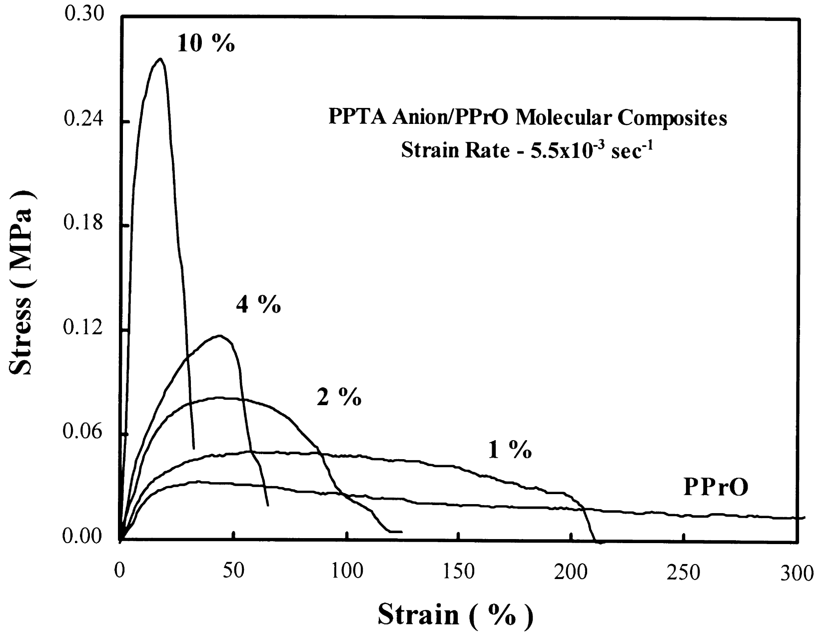

Fig. 3. Stress–strain curves for PPTA anion/PPrO composites.

3.2. Mechanical properties

The influence of PPTA anion content on the stress–strain characteristics of the composites are shown in Fig. 3. Although absolute values of the tensile strength are low, as all of these reinforced elastomers are unvulcanized, there is a marked increase in both strength and stiffness of these molecular composites with increasing amounts of the rigid rod reinforcement. Over the blend ratios studied, the tensile strength increases monotonically with increasing PPTA anion content, as Fig. 4 demonstrates. The increase is dramatic. For example, at only 4 wt% reinforcement, it is over 300%; and for 10 wt% reinforcement, the increase in strength is about 750%. The stiffness also increases appreciably upon addition of the PPTA anion reinforcement. For the composite containing 6 wt% of PPTA

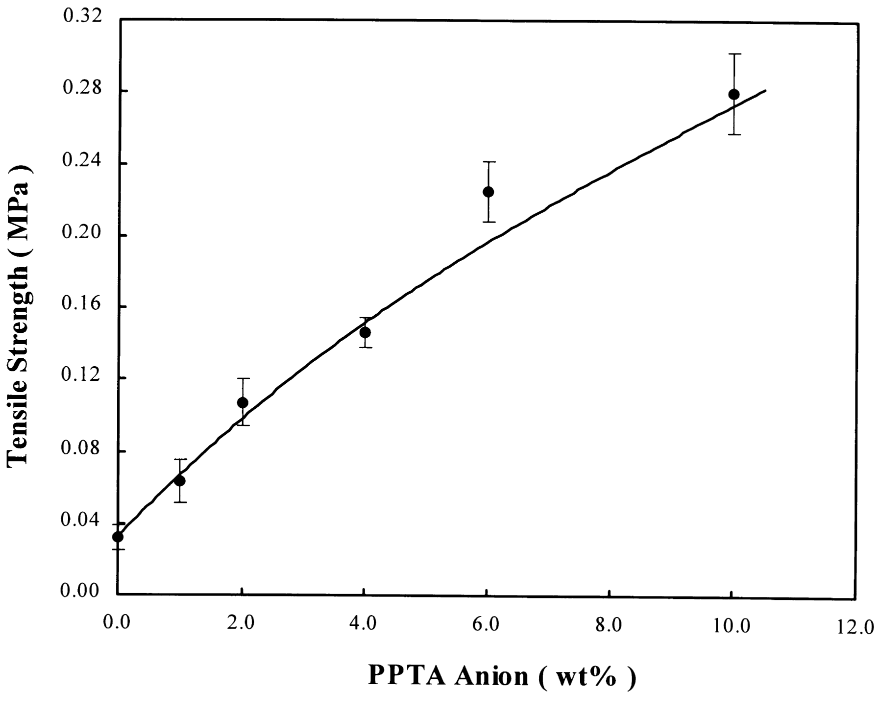

Fig. 4. Tensile strength vs PPTA anion content for PPTA anion/PPrO composites.

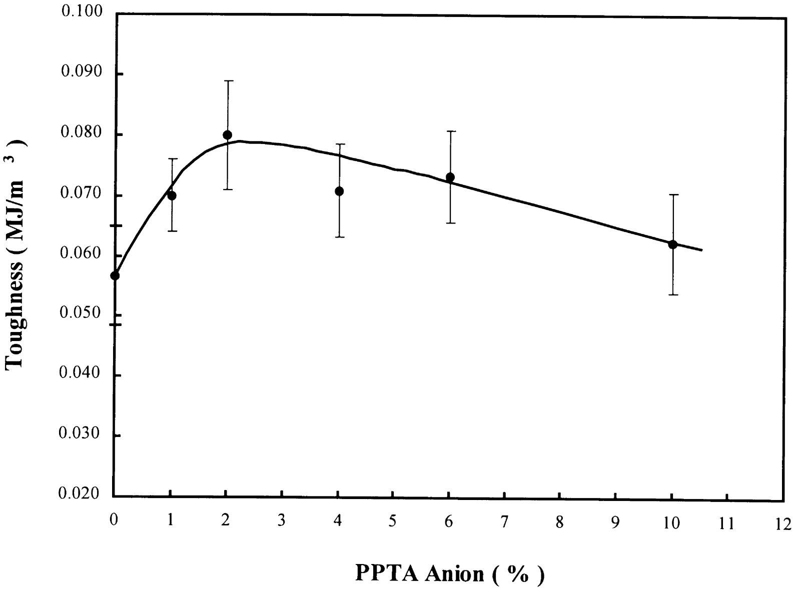

Fig. 5. Toughness vs PPTA anion content for PPTA anion/PPrO composites.

anion, the modulus has increased over 800% compared to that of the homopolymer matrix. The increased strength and modulus of these composites are attributed to both a good dispersion of the reinforcing molecules and an enhancement of the intermolecular interactions.

Relatively small concentrations of PPTA anion (K-salt) are also known to increase the tensile strength and modulus of glassy PVP [13] and semi-crystalline PEO [14]. For example, for 2 wt% PPTA anion content, the average tensile strength for composites made with PVP is increased by 38% and for composites made with PEO by 72%. However, for a comparable concentration of reinforcement, the tensile strength of PPTA anion/PPrO composites is increased by over 240%.

Other differences in performance between these various molecular composites also exist. For example, in molecular composites made with either amorphous PVP or partially crystalline PEO, the tensile strength reaches a maximum value at a PPTA anion content of 5–6 wt% and, at these concentrations, the glass transition temperatures either cease to rise or to drop slightly. These changes were attributed to some loss of miscibility as the PPTA anion content reached about 5 wt% or higher, thereby leading to some aggregation of the PPTA anion molecules and to the

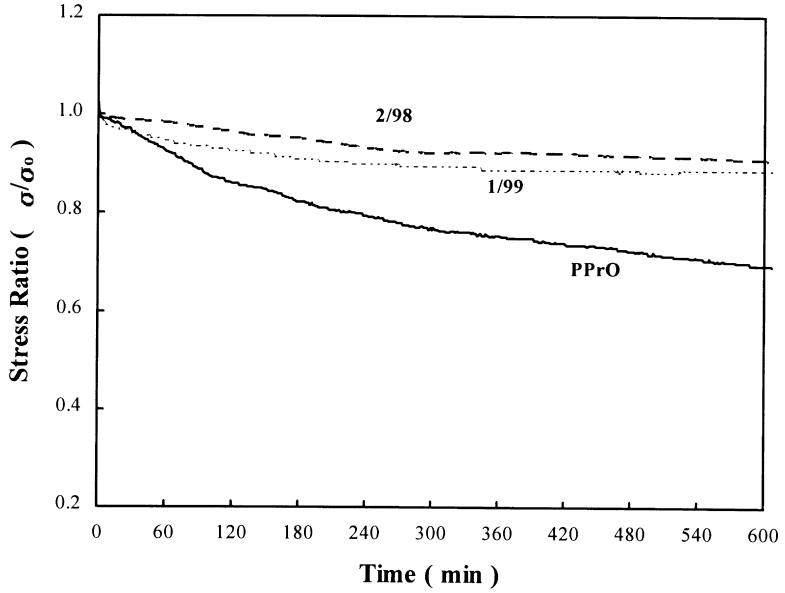

Fig. 6. Stress relaxation behavior of several PPTA anion/PPrO composites.

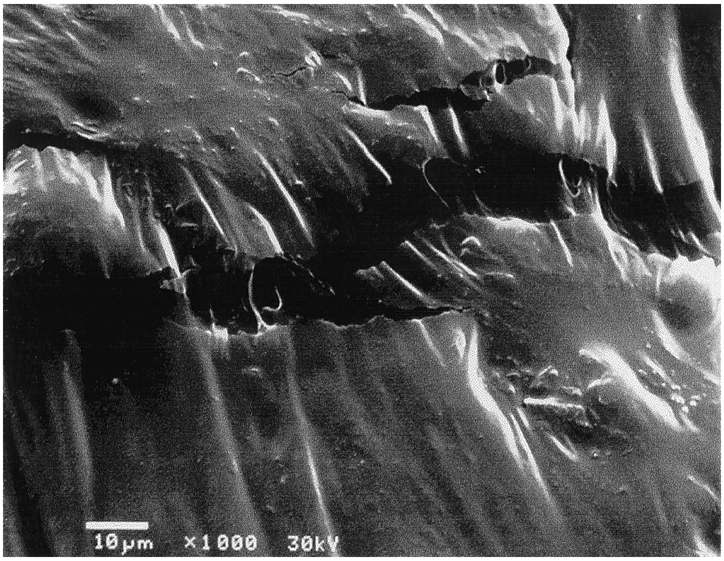

Fig. 7. SEM scan of a portion of the deformed surface of a PPTA anion/PPrO (6/94) sample.

presence of a second phase, as confirmed for the composites based on PVP by transparency tests [13]. However, in molecular composites where the matrix is rubbery PPrO, both the tensile strength and the glass transition temperature contribute to rise with increased PPTA anion content to 10 wt%. Hence, we conclude that miscibility extends to higher concentrations of the reinforcement when the matrix is a rubbery one, like PPrO, rather than a rigid amorphous one, like PVP, or a highly crystalline one, like PEO.

It has been reported that ionic interactions between the components of a blend act rather like covalent cross-links [12,18]. Although greater rigidity and strength may result from enhanced intermolecular interactions, chain mobility will be restricted [19]. One result is, as Fig. 3 indicate, that the strain to fracture decreases with increasing PPTA anion content. However, the toughness, or energy to fracture, of the composites reflects the combined effects of an increasing tensile strength and a decreasing ductility. As Fig. 5 shows, these combined effects lead to a toughness of the PPTA anion/PPrO composites, which initially increases with rising PPTA content, reaches a maximum value (about 40% higher than that of the homopolymer) near 2 wt% reinforcement and then slowly declines. Nevertheless, the toughness of all of the composites remains above that of the PPrO homopolymer.

The influence of the rigid rod reinforcement on stress relaxation behavior of several PPTA anion/PPrO molecular composites is shown in Fig. 6. The amount of stress relaxation, after any given time period, is considerably reduced for the composite samples. For example, the stress acting on a homopolymer sample, after a time period of 600 min has decreased by 39%. The relaxation rates for the two composites shown in Fig. 6 are significantly slower than that of the homopolymer, even though these composites possess only 1 or 2 wt% of the rigid rod reinforcement. This effect is attributed to the presence of ion-dipole interactions between the two components. These interactions provide greater resistance to chain slipping.

Deformation and fracture modes of the composites are also affected by the presence of small concentrations of the PPTA anion molecules. In the rubbery homopolymer, deformation is entirely by shear and there is a considerable reduction in crosssectional area prior to fracture. However, for the composites, especially those containing 6 or 10 wt% of the PPTA anion reinforcement, fracture occurs at smaller axial strains and with less area reduction, by development of a transverse craze-like crack. Fig. 7 is an SEM scan of such a craze-crack that developed in a (6/94) composite sample that was examined prior to final fracture. Fibrillar-like elements, some fractured, and some still spanning the craze-crack, are visible. These drawn fibrils, which have an enhanced strength due to presence of the ion–dipole interactions between the blend components, contribute to the resistance of the composite to fracture and to the enhanced mechanical properties.

3.3. Ionic vs non-ionic PPTA anion/PPrO blends

It is well known that the tensile strength and stiffness of many polymers can be enhanced by the presence of rigid rod molecules and by other types of reinforcement, such as Kevlar, carbon and glass fibers [19–24]. Hence, the question arises to what extent are the enhanced property values noted herein for the PPTA anion/PPrO composites due simply to the presence of the rigid rod reinforcement? To answer this question, some composite samples were prepared based on non-ionic PPTA molecules dispersed in the polar PPrO rubbery matrix. In these samples, which were prepared by converting the PPTA anion back to non-ionic PPTA as previously described [13], there is a poor dispersion of the reinforcing molecules in the matrix polymer as the components are immiscible and form distinct phases.

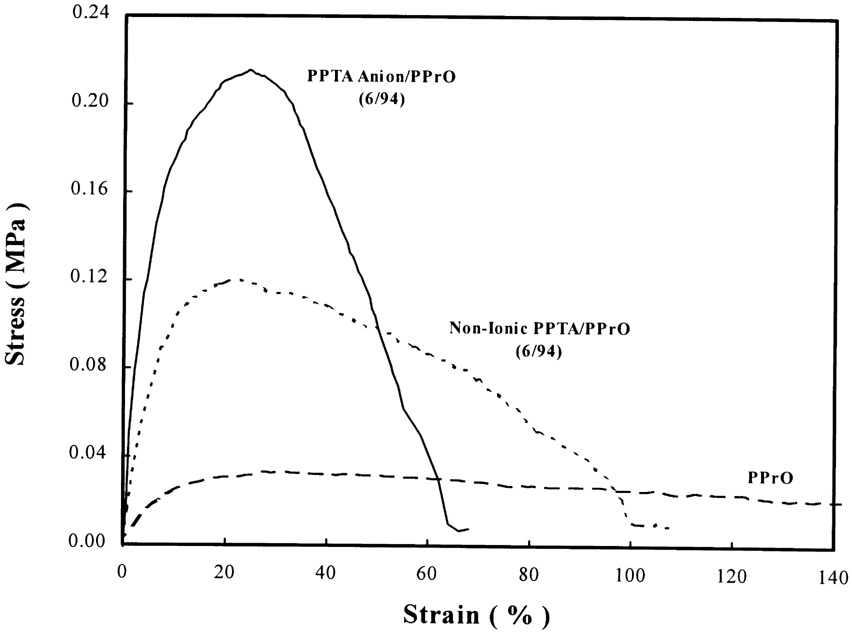

Fig. 8. Comparative stress-strain curves of non-ionic PPTA/PPrO (6/94) composite and PPTA anion/PPrO (6/94) composite.

Stress–strain measurements, carried out on a non-ionic PPTA/PPrO composite, are shown in Fig. 8. For comparison purposes, a stress–strain graph is also shown for a PPTA anion/PPrO molecular composite having the same concentration of reinforcement, viz. 6 wt%. It is evident that the tensile strength and modulus of the two-phase, non-ionic composite are increased significantly as compared to the PPrO homopolymer. However, the enhancement effects are much greater when the reinforcement is ionically modified PPTA. For example, the molecular composite having PPTA anion molecules as the reinforcement, has a tensile strength over 80% higher and a modulus over 135% higher than corresponding values for the non-ionic composite. It may be concluded that the reinforcement effect of the rigid rod molecules is appreciably increased when they are chemically modified so that they become miscible with the matrix polymer as a result of ion–dipole interactions that develop between the reinforcement and the (PPrO) matrix. A somewhat similar conclusion was reached for molecular composites in which PPTA anion molecules were dispersed in a glassy poly(4-vinyl pyridine) matrix [13].

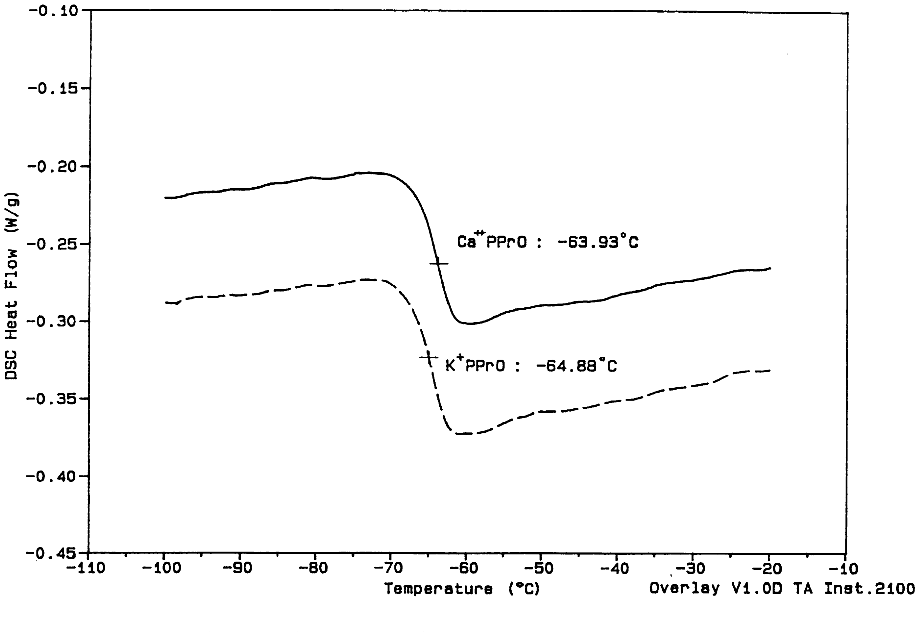

Fig. 9. DSC scans of PPTA anion/PPrO (4/96) composites having either Ca or K as the counterion.

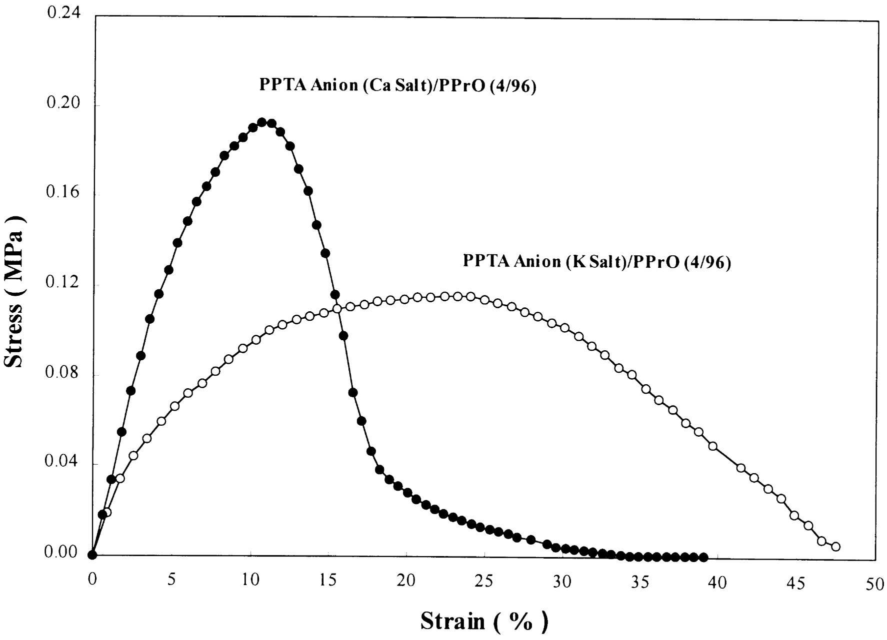

Fig. 10. Comparative stress-strain curves of Ca-salt and K-salt PPTA anion/PPrO (4/96) molecular composites.

3.4. Effect of counterion

In SPS ionomers it is known that the strength and thermal stability of ionic interactions are enhanced if the counterion is changed from singly-ionized K^+ or Na^+ to doubly-ionized Ca^{++} [25]. Also, in PMMA-based ionomers, it has been reported that, upon changing the counterion from Na to Ca, the glass transition shifts to higher temperatures and the principal deformation mode in thin films subject to simple tension changes from crazing to combined crazing and shear [26]. These results imply that Ca-salt ionomers tend to have a greater resistance to fracture than Na-salt ionomers.

To investigate whether a similar enhancement in properties would occur upon changing the nature of the counterion in PPTA anion/PPrO composites, we have carried out both thermal characterization and mechanical property studies on a (4/96) molecular composite of PPTA anion (Ca-salt)/PPrO. Results obtained were then compared with previous results on PPTA anion (K-salt)/PPrO composites of the same PPTA anion content. For both types of composites, DSC scans are shown in Fig. 9. The T_g value is about 1°C higher when the counterion is Ca, and is equivalent to that of K-salt composite of 8–10 wt% PPTA anion content. TGA studies of the composite show that the decomposition temperature is also somewhat higher for the Ca-salt based composites. These results suggest that the intermolecular interactions between the ionic groups of the reinforcement and the dipole units of the matrix polymer are stronger when the counterion is doubly ionized Ca.

The stronger intermolecular interactions when Ca is the counterion also lead to enhanced values of the principal mechanical properties. This is evident from comparison of the two stress–strain curves shown in Fig. 10. In these (4/96) composites, changing the counterion from K to Ca has increased the tensile strength about 50% and the modulus by close to 100%. This enhancement in strength and rigidity is accompanied by a reduction in ductility, as frequently occurs when the attractive forces between components of a blend are increased [27]. However, in so far as strength and rigidity are concerned, presence of a divalent counterion in these composites provides a more effective reinforcement than when the counterion is singly ionized. Also, to obtain a given level of reinforcement, a smaller PPTA anion content can be used when the counterion is Ca.

4. Conclusions

1. The presence of ion-dipole interactions between dispersed PPTA anion molecules and a (PPrO) matrix leads to an increase in the glass transition temperature and to an enhanced miscibility between the components of the composite.
2. With increasing concentration of PPTA anion content in PPTA anion (K-salt)/PPrO molecular composites, tensile strength and modulus are significantly increased, strain to fracture is reduced and toughness reaches a maximum value at about 2 wt% of the reinforcement.
3. In PPTA anion/PPrO composites, changing the counterion from monovalent sodium to divalent calcium enhances intermolecular bonding, increases thermal stability and leads to higher strength and rigidity.
4. Enhanced mechanical properties in PPTA anion/PPrO molecular composites arise from two effects: one is a simple reinforcement effect of adding rigid rod molecules to a rubbery matrix; and the second is the result

of enhanced intermolecular interactions that develop between the ionic groups of the PPTA anion molecules and the dipolar units of the (PPrO) matrix.

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