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Melt-processable molecular composites via ion–dipole interactions: poly(*p*-phenylene terephthalamide) (PPTA) anion and poly(vinylpyridine)s

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PPTA anion shows polyelectrolyte behaviour in solution and birefringence in film specimens, reflecting rigid conformation of backbone chains. The PPTA anion was blended with a flexible-coil polymer, poly(vinylpyridine) to make molecular composites. Optical clarity, polarizing optical microscopy, and dynamic mechanical thermal analysis all indicate the formation of homogeneous molecular composites for the PPTA anion/poly(4-vinylpyridine) system having up to 2 wt% of PPTA anion. These molecular composites show no phase separation upon heating, indicating that they are melt-processable. Ion–dipole interactions formed between ionic groups of the PPTA anion and ionic dipoles of vinylpyridine groups are responsible for good miscibility. The change of the matrix polymer to poly(2-vinylpyridine) leads to some phase separation, as a result of decreased miscibility due to steric hindrance. © 1997 Elsevier Science Ltd.

(Keywords: molecular composites; PPTA anion; poly(vinylpyridine)s)

INTRODUCTION

Conventional fibres for advanced composites, such as carbon fibre and Kevlar fibre, are aggregates of fibrils and microfibrils, and therefore they contain many inherent defects that can initiate cracks and lead to premature failure of the composite. The idea of 'molecular (level) composites' is based on the fact that an individual rigid-rod molecule, such as poly(*p*-phenylene terephthalamide) (PPTA) molecule, has no defect; therefore, the theoretical strength due to covalent bonds in the backbone chain may be used for reinforcement of matrix materials[1–6]. Molecular composites are also envisaged to be polymer blends in which rigid-rod molecules are dispersed in a matrix of a flexible coil polymer such that the rods act as reinforcement.

Although the idea of molecular composites is promising, most molecular composites developed to date have a major drawback: i.e. these molecular composites are not in a thermodynamically miscible state, since entropy of mixing is very small as demonstrated for polymer blends[7,8], and since rod molecules have a strong tendency to segregate[9]. One way to circumvent this problem is a rapid coagulation from a ternary solution (rod polymer/flexible polymer/solvent) to 'freeze' the miscible rod/coil state, thereby overcoming the unfavourable thermodynamic driving force to phase separation. However, for many molecular composites made by this method, the homogeneous phase morphology is only temporary; for example, phase separation is found to occur after heating[3]. Another way to overcome the problem is using block or graft copolymers that connect rigid-rod and flexible-coil components by covalent bonds; the covalent bonds can force rod and coil components to be in close proximity. Although mechanical properties of these molecular composites are improved compared with simple blends of component polymers, presumably due to improved dispersion of rod molecules[10–12], this usually leads to microphase separation or microfibril formation of rigid rods, again due to inherent thermodynamic immiscibility of the component polymers, as is well known for block/graft copolymers[13,14]. After reviewing the work on molecular composites, Hwang and Helminiak[15] pointed out that a phase-separated rigid-rod/thermoplastic blend is no better in its physical/chemical properties than a corresponding fibre composite and that *enhanced and desirable properties can only be realized in a true molecular composite*; therefore, the key to the success of a rigid-rod molecular composite technology lies in having good molecular dispersity of the rigid rods in a matrix material.

One promising approach to producing a true molecular composite is to make rod and coil components thermodynamically miscible by introducing attractive interactions, such as hydrogen bonds[16–19], between them. This method has proven useful for enhancing miscibility in flexible–flexible blends. However, the interactions between matrix and reinforcing polymers are rather weak intermolecular bonds; therefore, these forces are easily disrupted by applying thermal energy which induces the composite to phase separate. For example, Chen and Kyu reported that miscible molecular composites were

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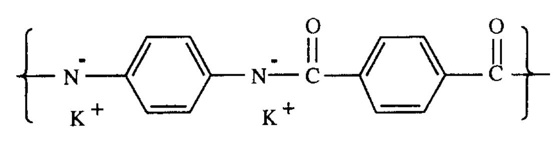

Figure 1 Structure of PPTA anion (K salt)

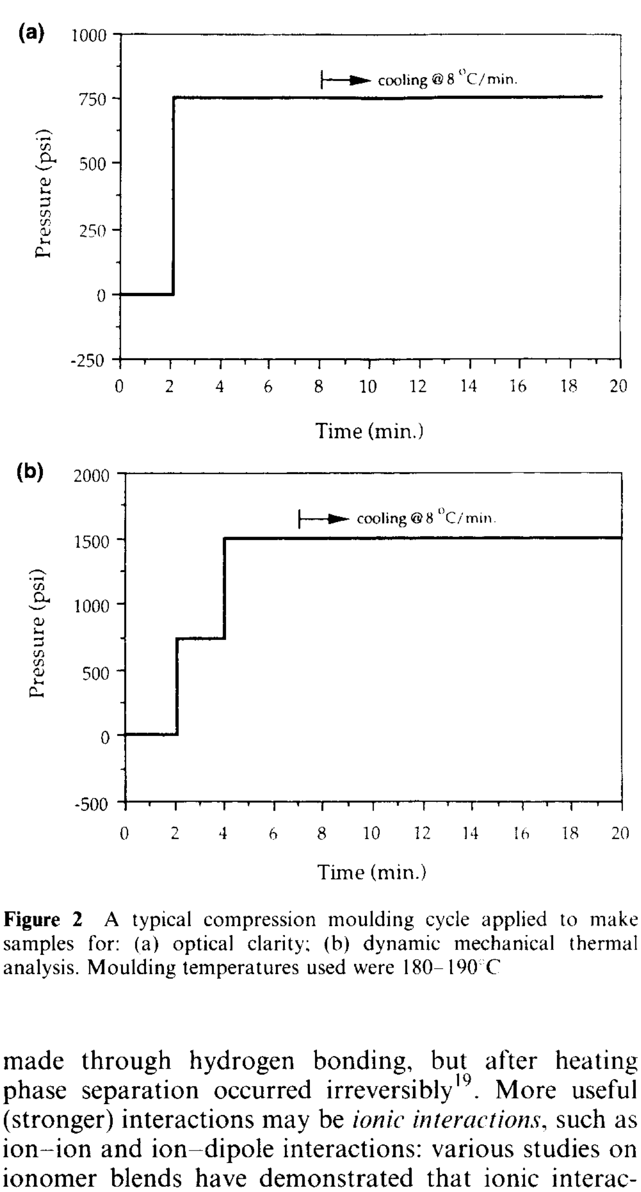

Figure 2 A typical compression moulding cycle applied to make samples for: (a) optical clarity; (b) dynamic mechanical thermal analysis. Moulding temperatures used were 180–190°C

made through hydrogen bonding, but after heating phase separation occurred irreversibly[19]. More useful (stronger) interactions may be *ionic interactions*, such as ion–ion and ion–dipole interactions: various studies on ionomer blends have demonstrated that ionic interactions can enhance the miscibility of otherwise immiscible flexible–flexible polymer pairs[20–23].

Recently, several studies have been reported on molecular composite formation using ionic interactions[24–31]. For example, Tan *et al.*[24] developed a molecular composite that used ion–ion type interactions between rod-like poly(*p*-phenylene benzobisthiazole) (PBZT) and coil-like poly(2-acrylamide-2-methylpropanesulfonic acid) made from methanesulfonic acid solution. Although no phase-separated morphology was detected by scanning electron microscopy with 500 Å resolution, X-ray diffraction studies indicated a small degree of aggregation of rod molecules. The small size of the second phase suggests that with the proper choice of components and processing conditions, a totally miscible molecular composite may be formed due to ionic interactions. These studies are just beginning to appreciate the potential usefulness of ionic bonding in creating homogeneous melt-processable molecular composites. Because of their potential as high-performance polymers, much work needs to be done to fully exploit the effective use of *ionic bonds* in molecular composites.

We have been developing molecular composites based on various ionic PPTAs and polar polymers, such as poly(4-vinylpyridine) (4-PVP) and poly(ethylene oxide) (PEO)[25–29]. In these studies, ion–dipole interactions, which have been proven to be useful in achieving miscibility in flexible–flexible polymer blends, have been applied to a molecular composite system.

In this work, we investigated molecular composites made from PPTA anion and poly(vinylpyridine)s. The amorphous polymer, poly(4-vinylpyridine), was chosen as the coil-like polymer, since it contains ionic dipoles every repeating unit, which can interact with ionic groups of PPTA through ion–dipole interactions. PPTA anion was used as rod-like polymer, since characterization of the PPTA anion by polarized miscroscopy confirmed a retention of the rod-like conformation. It has even been suggested that the polyanion form of PPTA has a more rigid conformation than unmodified PPTA[32]. We previously studied the blend made from 4-PVP and *N*-propyl-poly(*p*-phenylene terephthalamido) (propane-sulfonate) (N-Pr-PPTA-PS), in which all N atoms were substituted by propyl and propanesulfonate groups[33], which showed good miscibility due to ion–dipole interactions. However, the N-Pr-PPTA-PS was not conclusively determined to be in a rod like conformation; therefore, an alternative system was studied for this work, which uses a polyanion form of PPTA as the reinforcing component. Similar to the N-Pr-PPTA-PS/4-PVP system, ion–dipole interactions between the PPTA anion and 4-PVP are formed to achieve good molecular dispersity. In this system, every repeating unit on the reinforcing polymer has two ionic groups (see *Figure 1*), which increases the number of interactions with the ionic dipoles of 4-PVP. It is thought that, by increasing the number of ion–dipole interactions, the enthalpy of mixing of the system can become sufficiently negative to achieve molecular dispersity, which can be maintained after heating. In addition, such conversion leads to dissolution of PPTA in an organic solvent, and thus eliminates the need for an acidic solvent. A strong protic acid, usually necessary to dissolve rod-like polymers, severely limits the choice of coil polymers to be used as a matrix[1].

EXPERIMENTAL

Synthesis of ionic PPTA

The metalation of poly(*p*-phenylene terephthalamide), PPTA, was first described by Takayanagi[34] and later modified by Burch *et al.*[35]. The strong base, potassium methyl sulfinyl carbanion, is generated by the reaction of dimethyl sulfoxide (DMSO) and potassium hydride (KH). The carbanion is capable of deprotonating the slightly acidic amide hydrogens of PPTA, making the PPTA soluble in DMSO.

A three-necked reaction flask, equipped with an overhead stirrer, nitrogen inlet and a septum cap, was flushed with N_2 gas. A 35 wt% KH dispersion in mineral oil was added followed by anhydrous DMSO. The solution was mixed for 5 min or until no hydrogen gas was evolved. Dry hexane was then added to scavenge the mineral oil layer, which was removed with a syringe. This

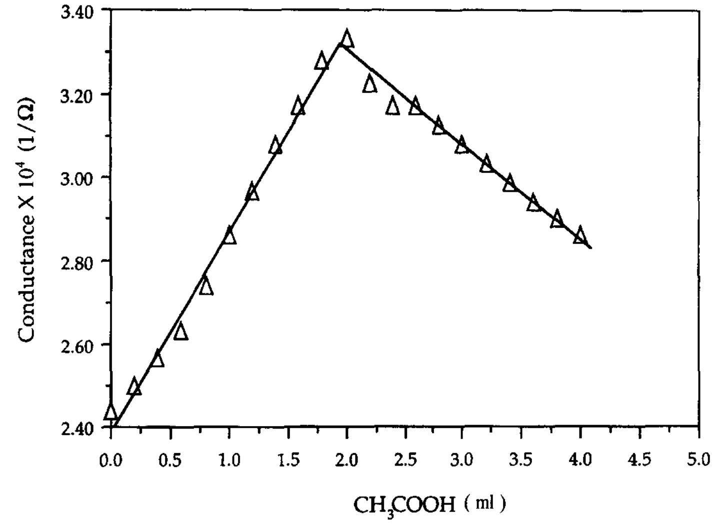

Figure 3 Conductometric titration of PPTA anion with acetic acid in water

Figure 4 A film with crossed polarizers for PPTA anion

was repeated until no mineral oil remained. The resulting potassium methyl sulfinyl carbanion solution was a clear, greenish-yellow, low viscosity liquid. Vacuum dried PPTA pulp (obtained from DuPont), slightly wetted with DMSO to reduce flocking, was added to N_2 gas swept carbanion solution. The solution was mixed for 48 h resulting in a thick, red, moisture-sensitive PPTA anion solution with no unreacted PPTA fibre visible. The PPTA anion structure is shown in *Figure 1*.

Preparation of molecular composites

Molecular composites were made from PPTA anion and poly(4-vinylpyridine) (4-PVP). The 4-PVP polymer, purchased from Scientific Polymer Products, has a weight-average molecular weight of 240 000, as determined by light scattering measurement in DMF. Molecular composite samples were also made with poly(2-vinylpyridine) (2-PVP) (Scientific Polymer Products; molecular weight: 200 000) for comparison. Some molecular composite samples were prepared by vacuum evaporation; others were made by compression moulding. First, samples were prepared by dissolving 3 wt% of PVP in DMSO using a magnetic stirrer for 12 h. The appropriate amount of ionic PPTA solution (a 1.3 wt% solution in DMSO) was then added to yield the desired mixing ratio of rod-like to coil-like polymer. The solution was poured into an aluminium pan and placed under vacuum for 2 h. The temperature was then increased to 100°C and the sample remained under vacuum for 4 weeks to effectively remove residual DMSO. The resulting 200–300 μm thick film was cut into 1 cm × 1 cm squares and stored in a dry box.

Samples used for compression moulding were prepared by two methods. One method used vacuum evaporated samples, which were then freeze milled to a fine powder. The other method consisted of precipitating the composite solution into a nonsolvent, xylene. When the solution was added to xylene, a white solid precipitate formed. The solution was kept for 12 h without stirring, and then replaced with fresh xylene. After allowing to stand another 12 h, the xylene was poured off and the precipitate was collected. The precipitate was dried under vacuum for 48 h at 80°C and then freeze milled to a powder. The powder was then dried at 80°C for 72 h. The dried powder contained no noticeable xylene or DMSO and was then moulded into 17 mm diameter discs having a 400–500 μm thickness. Compression moulding was conducted according to the moulding cycles shown in *Figure 2*.

Measurements

Conductometric titrations were performed in a conductivity cell with conductivity meter (National Instruments Model RC-16B2J). Titrations were performed with 8–12 ml of polyion solution in the conductivity cell, which contained a magnetic stirring bar. The resistance was measured after each addition of reagent. The data were plotted to give two straight lines intersecting at the equivalence point[36]. Details regarding the conductivity measurements are described elsewhere[33].

A Leitz Ergolux Inspection Microscope with a vertical camera unit was used for viewing samples under polarized light. A polarizer was used in the substage condenser and another polarizer above the objective lens—one rotated 90° to the other. Some samples were heated with a Mettler F52 hotstage. Heating began at 54°C with a heating rate of 2°C min^{-1}.

D.m.t.a. measurements were made with a piezotron (Rheolograph Solid made by Toyoseiki, Japan). The heating rate was 4°C min^{-1} and the frequency was 1 Hz. Molecular composite specimens were compression moulded from freeze milled samples. PVP samples were

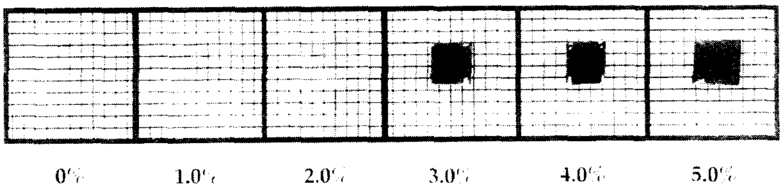

Figure 5 Films of PPTA anion/4-PVP molecular composites with varying weight per cent of PPTA anion

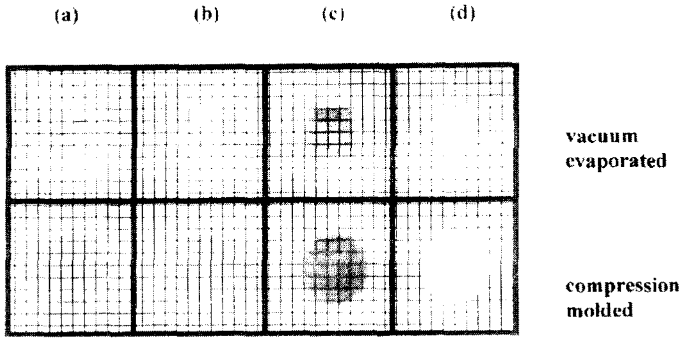

Figure 6 Molecular composite samples as well as 4-PVP, showing the effect of changes in components: (a) 4-PVP; (b) PPTA anion/4-PVP (2/98); (c) PPTA anion/2-PVP (2/98); (d) PPTA/4-PVP (2/98). Samples were made either by vacuum evaporation or compression moulding (according to the thermal profile of *Figure 2a*)

moulded from powder as supplied. The specimens were cut to the dimensions of 0.25 mm × 3.0 mm × 12 mm and polished with 600 emery paper. Details of the d.m.t.a. measurements are described elsewhere[37].

RESULTS AND DISCUSSION

Ionic PPTA (PPTA anion)

Burch *et al.* reported that PPTA anion solutions (K salt) showed polyelectrolyte behaviour by viscosity measurements: i.e. the reduced viscosity of the PPTA anion in DMSO increases significantly with decreasing the polymer concentration. They speculated from these results that PPTA anion chains became stiffer and more expanded than the parent PPTA polymer chains[35].

Since PPTA anion is a polyelectrolyte, conductometric titration was used to determine the ion content of the PPTA anion. The polyanion as synthesized was titrated with dilute acetic acid[38]. The typical titration data are shown in *Figure 3*; the plot shows the conductance initially rising, due to increasing salt formation (i.e. potassium acetate), and decreasing after the equivalence point, which gives an ion content of 97.5 mol%, since salt is no longer produced and the concentration of ions decreases due to dilution. Ion contents of all PPTA anions ranged between 95 and 98 mol%, indicating that most amide nitrogens were converted to their ionic form.

Molecular conformation of a reinforcing polymer is critical in its ability to improve mechanical properties of a molecular composite. To be effective reinforcement, the reinforcing polymer in a molecular composite should be rigid-rod like, having both high aspect ratio and inherently high strength. It was reported that PPTA anion solutions formed liquid crystalline structure (i.e. lyotropic) in DMSO. For example, the Na salt of PPTA anion became birefringent at 5.3 wt% polymer concentration, and the K salt at 13 wt%[35]. Significant liquid crystalline behaviour was also observed with the PPTA anion solid films. *Figure 4* shows the birefringence pattern of the PPTA film, suggesting that rod-like conformation is basically retained when PPTA is converted to the polyanion form.

Molecular composite (PPTA anion/poly(4-vinylpyridine))

Maintaining the molecular dispersity of a molecular composite during all processing steps is essential in preserving their advantageous properties. Thermodynamically, the molecular dispersity of a rod-like molecule in a flexible coil polymer matrix is difficult, since the entropy gain in a polymer blend is nearly zero[7,8]. This makes the enthalpy of mixing most important in causing polymer–polymer miscibility. The tendency of reinforcing rod molecules to aggregate makes the enthalpy of mixing even more important with molecular composites[9]. We intend to overcome this problem by creating strong ion–dipole bonds between the component polymers in molecular composites, which leads to negative enthalpy of mixing.

Transparency in polymer blend films is used to check miscibility on a scale down to 0.1 μm[7]. *Figure 5* shows PPTA anion/4-PVP molecular composite films with varying weight per cent of PPTA anion. The best miscibility was observed with composites having 1.0–2.0 wt% of PPTA anion. This is in contrast to the N-Pr-PPTA-PS system studied before, which was miscible up to 20 wt%[33]. Such difference in the amount of reinforcing polymer between the two systems is believed to be due to the structural modification of PPTA molecules: when side chains are added to form N-Pr-PPTA-PS, the modification is thought to decrease PPTA's ability to form an anisotropic phase, and therefore more ionic PPTA molecules can be added. The possible conformational change of N-Pr-PPTA-PS was the motivation behind the development of the PPTA anion system; the polyanion exhibited a rod-like conformation. The PPTA anion/PVP (2/98) system was chosen for further characterization, since it contained the highest polyanion content while maintaining miscibility.

Miscibility was not only affected by the amount of

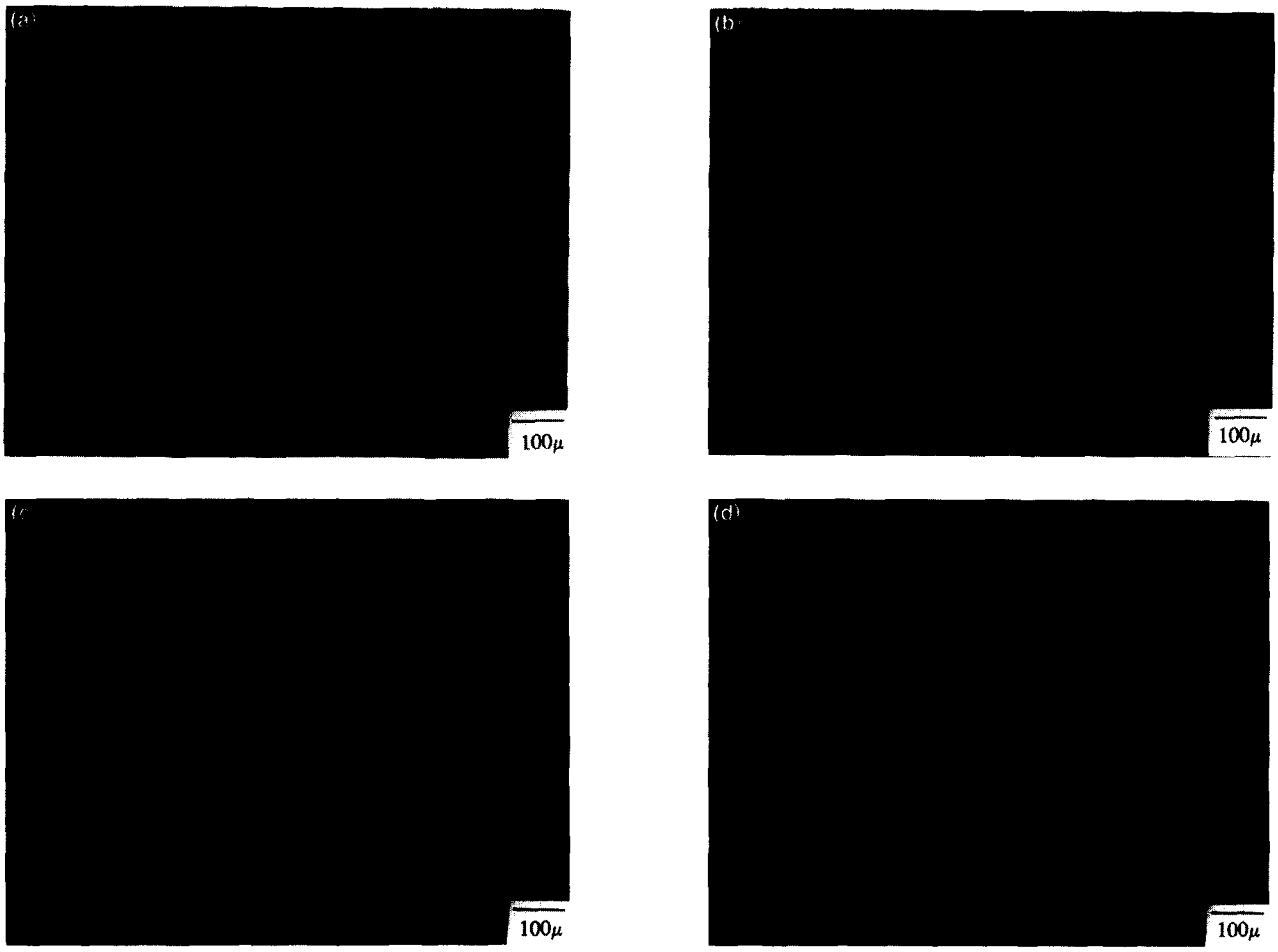

Figure 7 Films under crossed polarizers: (a) PPTA/4-PVP (1/99); (b) PPTA anion/2-PVP (2/98); (c) PPTA anion/4-PVP (2/98); (d) PPTA anion/4-PVP (2/98) heated to 250°C min^{-1}

PPTA in the composite. The PPTA anion is hydroscopic, and residual water present in the solution, atmosphere or precipitating solvent was found to rehydrate the polyanion converting it back to the original PPTA form. The rehydrated PPTA anion invariably led to phase separation, since it could no longer ionically interact with the matrix. In the molecular composite, however, the PPTA anion did not rehydrate, possibly because the polyanion molecules are well dispersed and each anionic group is surrounded and protected by many PVP molecules. Since the diffusion of water through a PVP matrix is difficult and slow, rehydration reactions are largely prevented in the solid composite material.

Figure 6 compares films of the PPTA anion/4-PVP (2/98) system and of the unmodified-PPTA/4-PVP system: disk specimens of *ca* 0.4–0.5 mm thickness were placed on a grid, and were observed from the top. Lines are clearly seen below transparent samples, while lines on opaque samples are not clear. A 4-PVP sample is shown as a reference and a PPTA anion/2-PVP system film is also shown and it will be discussed later. While the PPTA anion-4-PVP (2/98) sample is transparent, which is comparable to 4-PVP, the unmodified PPTA/4-PVP (2/98) sample is opaque. Changing the reinforcing polymer from PPTA anion to unmodified PPTA eliminates the ionic interactions between the components. From their structure, hydrogen bonds may be formed; but, this is not strong enough to overcome phase separation. In contrast, the PPTA anion has lost nearly all its amide hydrogen atoms; thus, no hydrogen bonds can be formed. This strongly suggests that the employment of ion–dipole interactions is capable of overcoming a rod-like polymer's tendency to aggregate when mixed with an amorphous polymer. Both vacuum evaporated samples and compression moulded samples are shown in *Figure 6*. It can be seen that the PPTA anion/4-PVP system remains transparent after thermal consolidation, indicating that the system is melt-processable.

Polarizing optical microscopy was useful in characterizing the PPTA anion molecular composites since the polyanion was found to be optically anisotropic. Therefore, phase separation in a molecular composite due to aggregation of PPTA anions can be characterized under crossed polarizers. Polarizing microscopy results shown in *Figure 7* coincide with the conclusions drawn from the optical clarity tests. Evaluation of unmodified PPTA composite films, *Figure 7a*, indicates large-scale phase separation. This behavior is likely since the composite system involves no strong, miscibility-enhancing interactions, and therefore has an insignificant enthalpy of mixing. *Figure 7b*, involving blends with 2-PVP will be discussed later. In a 4-PVP matrix, ion–dipole interactions can be formed between the component polymers, resulting in an isotropic molecular composite as shown in *Figure 7c*. The isotropy is retained after heating the film to 250°C at 2°C min^{-1}, as shown in *Figure 7d*. Maintaining isotropy under polarized light after heating is again an indication of the melt-processability of the composite.

Dynamic mechanical data for the PPTA anion/4-PVP

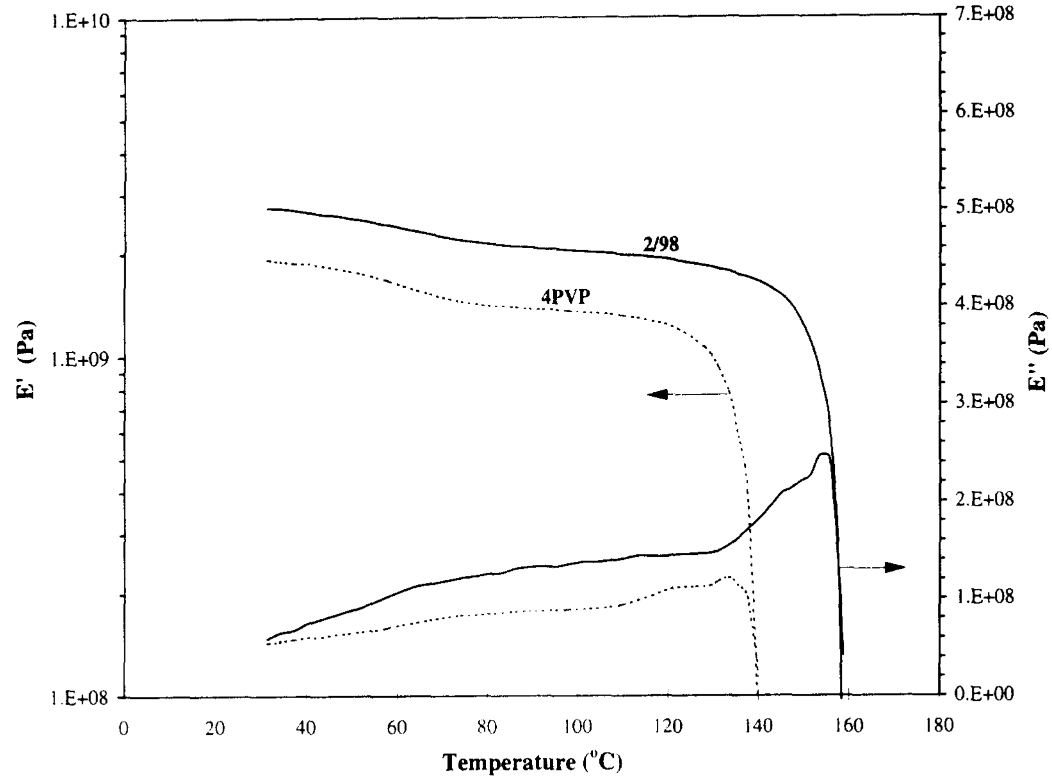

Figure 8 D.m.t.a. data, storage modulus (E') and loss modulus (E'') as a function of temperature, for PPTA anion/4-PVP (2/98) molecular composite (solid lines) and for 4-PVP (dashed lines)

(2/98) composite and a 4-PVP are shown in *Figure 8*. A large increase in glass transition temperature of the composite over 4-PVP is readily apparent. A shift of the T_g to a higher temperature indicates enhanced miscibility[7,8], although the miscibility may be difficult to judge from these data only, as evident for the systems which have two distinct T_gs of component polymers[33,39]. Another indication of enhanced miscibility can be deduced from the modulus vs temperature plot before the respective primary transition. A fairly strong secondary, β-transition peak occurs in 4-PVP around 80°C which is believed to be due to the torsional motion of the pyridine rings[40]. The PPTA anion/4-PVP (2/98) composite also shows a secondary transition at 80°C, but it is slightly suppressed as compared with 4-PVP. Diminution of intensity of the secondary relaxation can be noted in the blends where specific interactions are involved[7]; and, it has been suggested that suppression of a β-transition peak in a polymer blend is an indication of good miscibility[41,42]. For example, the broad low-temperature β-relaxation of 2,6-dimethyl poly(phenylene oxide)(PPO) is suppressed by the addition of small amounts of polystyrene, which is known to be miscible with PPO at the segmental level[41]. Therefore, the slight suppression of the β-transition peak of the molecular composite reflects enhanced miscibility.

The mechanical behaviour of the PPTA anion/4-PVP (2/98) is also seen in *Figure 8*. The addition of only 2 wt% of PPTA anion to 4-PVP increases its storage modulus by 50%. The rod-like structure of polyanions that are well dispersed due to ionic interactions is thought to be behind the improved modulus. The well dispersed rod-like polymer eliminates the fibre-matrix interface and reduces the number of defects. Moreover, the stiffness of the reinforcing polymer should come from the valence bond strength of the PPTA anion's backbone chain which would be much higher than that of the macroscopic fibre.

Figure 9 shows the d.s.c. scan (third run) of the PPTA anion/4-PVP (2/98) composite. A clear T_g is seen at 154°C, which is consistent with the d.m.t.a. data in *Figure 8*. It should be added that the d.s.c. data (third run) is identical to the data of the second run. This indicates that this composite is stable upon thermal cycling. It is also our observation that no phase separation, as seen in opacity of the composite specimens, has occurred upon heating at high temperature. This also indicates that our molecular composites are thermally stable.

It has been demonstrated that ion–dipole interactions can enhance miscibility of flexible–flexible polymer blends[20]. For example, introducing ionic groups into polystyrene (PS) has been found to significantly enhance the miscibility of PS with poly(ethylene oxide) (PEO) or poly(propylene oxide) (PPrO)[43]. It was shown that only a small percentage of ions (*ca* 10 mol%) on PS was necessary to render an otherwise entirely immiscible system miscible. The miscibility was achieved through the interaction of ionic dipoles associated with PEO or PPrO and the ions attached to PS. Blend films made of poly(styrene-*co*-4-vinylpyridine) and lightly sulfonated polystyrene were also found to be miscible as indicated by transparency and an appearance of a single glass transition temperature, after annealing the cast films that show two T_gs. Miscibility was attributed to attractive interactions between the ionic dipoles of pyridine rings and the sulfonate anion accompanied by cation[44].

Figure 10 schematically illustrates the possible interactions occurring between the conjugated amide bond

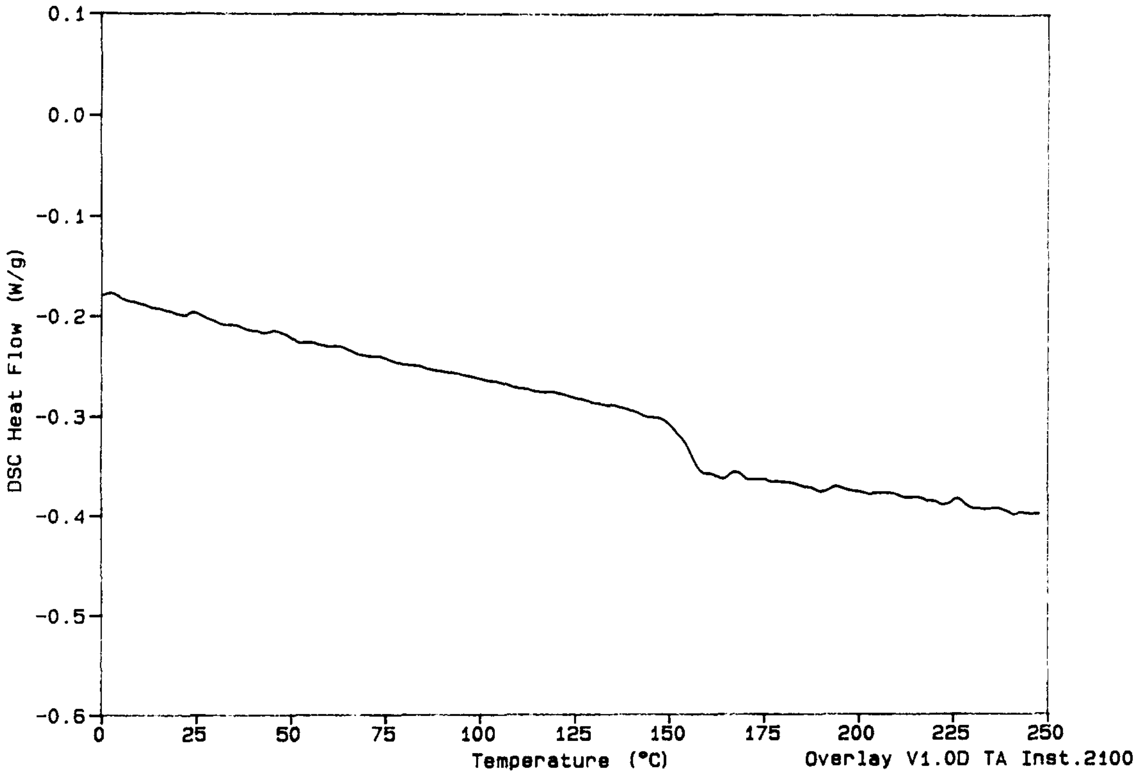

Figure 9 D.s.c. data (third run) for PPTA anion/4-PVP (2/98) molecular composite

and the 4-PVP dipoles. The rod-like conformation of the PPTA anion maximizes the number of matrix polymer molecules it interacts with, and in turn the number of pyridine units per ionic group. The synergistic effect creates a miscible molecular composite with a substantially higher T_g than the matrix.

The rod-like structure and ionic nature of polyanions are thought to play an important role in determining the properties of the molecular composites. One effect is through entanglements with the random coil polymer matrix. It has been shown that, for molecular composites to have integrity such that they can be processed into fibre or film forms, they must possess a minimal number of entanglements between the reinforcing and matrix polymers[45]. Ionic crosslinks due to ionic bonds add additional entanglements as shown for ionomers[46]. Another contribution may come from the potentially extended chain conformation of PPTA anion, which allows it to pass through a higher number of matrix polymer molecules than if it were a random coil. Also, the rod-like structure allows ample spacing between each ionic group and eliminates any steric hindrance which a pyridine ring may experience with the polyanion's main chain when trying to interact. Although we do not have direct evidence that PPTA anion retains its rigidity in the molecular composite, it seems reasonable, since the rod-like conformation is retained in solution where there are more factors inducing the flexibility of polymer chains. It should be added that these factors are also contributing to the change in deformation mode of molecular composites: for example, PVP deforms only by crazing, but the molecular composite of PVP with ionic PPTA shows the development of shear deformation. This is due to an increase in 'effective' entanglement (strand) density of the molecular composites[26,27].

Molecular composite (PPTA anion/poly(2-vinylpyridine))

In ion–dipole blends made of flexible polymers, it has been reported that steric hindrance between ionic groups and ionic dipoles hinders effective interactions, reducing the degree of miscibility[47]; for example, polar polymers with no bulky side chains, such as poly(ethylene oxide), poly(ethyleneimine), and polysulfide, show good miscibility with polystyrene ionomer, while polar polymers with bulky side groups, such as poly(vinyl acetate) and poly(dimethyl siloxane), show little miscibility with the same ionomer. This is also noted in our experiments of molecular composites made from PPTA anion and 2-PVP. A comparison was made between the PPTA anion/4-PVP (2/98) system and a system having a different matrix, 2-PVP. *Figure 6* shows that changing the matrix from 4-PVP to 2-PVP can initiate phase separation. *Figure 7* also shows the results of polarizing optical microscopy. While 4-PVP composite films (*Figure 7c*) shows no second phase, 2-PVP composite films (*Figure 7b*) reveal a finely dispersed reinforcing phase, although the size is smaller than that seen in the unmodified PPTA composite films (*Figure 7a*). The only difference accompanying the change in matrix from 4-PVP to 2-PVP is the positioning of the pyridine nitrogen as shown in *Figure 10*. Favourable interactions between the composite components exist, but the steric hindrance of the 2-pyridine nitrogen with its main chain does not allow optimum interaction with the ions in PPTA anion. In a 4-PVP matrix, the nitrogen atom on the pyridine ring is furthest from the main chain. This allows optimum interaction with PPTA anion, resulting in an isotropic molecular composite as shown in *Figures 6* and *7*.

The steric hindrance associated with 2-PVP is thought to explain its ineffectiveness in ionically interacting with the PPTA anion, which results in a phase separated

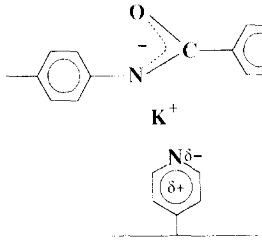

Figure 10 Schematic illustration of possible interactions between the PPTA anion and 4-PVP

composite. Xue *et al.* reported the difference in reactivity between 4-PVP and 2-PVP with epoxy compound (1,4-butanediol diglycidyl ether), studied by *FT*i.r.: the reaction of 2-PVP is much slower than 4-PVP due to the steric effect of 2-PVP[48]. Our conclusion is consistent with these results.

CONCLUSION

Ion–dipole interactions between the rod-like and coil-like polymers in a molecular composite were found to be an effective approach for offsetting the system's favourable thermodynamics and for maintaining molecular dispersity after thermal consolidation. In this work, molecular composites were made from an ionic Kevlar$^{\text{R}}$ (PPTA anion) as a reinforcing polymer and poly(vinylpyridine) as a matrix polymer. The significant rise in T_g and modulus upon addition of only a 2 wt% reinforcing polymer was observed, which could be attributed to the rod-like molecules being molecularly dispersed, allowing each anionic group on the main chain maximum interaction with the dipoles present in the matrix.

PPTA anion was found to be less miscible with 2-PVP than with 4-PVP. This is due to the steric hindrance associated with 2-PVP, which is consistent with results reported on flexible polymer blends via ion–dipole interactions.

The rehydration of the PPTA anion by residual water during processing, thereby converting it back to the original PPTA form, was found to affect its miscibility with 4-PVP. The proper processing conditions should therefore be explored, where the PPTA anion remains in its ionic form. Our results indicate that use of extremely anhydrous reagents and precipitation methods (instead of evaporation methods) lead to formation of more reliable molecular composite samples. Improvements in processing technique may further improve the situation. Since one of the important end uses of molecular composites is for structural applications, their mechanical properties, including deformation and fracture behaviour, should be thoroughly evaluated. Moulding techniques must also be thoroughly studied to allow the molecular composite systems to have wide application. Processes, such as injection moulding, may also create a more anisotropic material by aligning the rod-like molecules. These are the subjects of future studies.

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