Molecular composites of ionic Kevlar/poly(4-vinylpyridine) via ion–dipole interactions

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A molecular composite made of ionic Kevlar and poly(4-vinyl pyridine) (PVP) was prepared and studied. TEM observations, as well as a qualitative study of transparency and mechanical strength, indicate that the prepared material is a homogeneous molecular composite. Upon heating, there seems to be no indication of phase separation. It is suggested that the driving force for good miscibility is ion–dipole interactions between ionic groups in ionic Kevlar and ionic dipoles in PVP.

(Keywords: molecular composites; ionic Kevlar; PVP)

Introduction

Conventional fibres for advanced composites, such as carbon fibre and Kevlar [poly(*p*-phenylene terephthalamide)] fibre, are aggregates of fibrils and microfibrils, and therefore they contain many inherent defects which can initiate cracks and lead to premature failure of the composite. The idea of molecular (level) composites[1–3] is based on the fact that an individual rigid-rod molecule, such as a Kevlar molecule, has no defect; therefore, the theoretical strength due to covalent bonds in the backbone chain can be utilized for molecular-level reinforcement. In a sense, this is the ultimate reinforcement in composite materials. It has been shown that reinforcement by rigid-rod molecules is very effective compared with macro-fibre reinforced composites; for example, macro-fibre reinforced composites use as much as 40% of reinforcement, while similar level mechanical properties can be achieved by using as little as several per cent of molecular reinforcement[3]. Moreover, it is well known for macro-fibre composites that increasing aspect ratio (i.e. length divided by diameter) of reinforcer can increase the modulus of the composites up to two orders of magnitude[4]. Following this reasoning, the ultimate reinforcing fibre would again be a single intrinsically rigid-rod molecule[5].

Molecular composites are envisaged to be polymer blends in which rigid-rod molecules are dispersed in a matrix of flexible coil polymer such that the rods act as reinforcers. One of the most extensively studied is the molecular composites of poly(*p*-phenylene benzobisthiazole) (PBZT) in a variety of flexible coil polymers, such as nylon 6,6 and poly(ether ether ketone) (PEEK)[6,7]. A recent review on molecular composites is available[8].

Although the idea of molecular composites is very promising, molecular composites so far developed have drawbacks: the most fundamental problem is that these molecular composites are not in a thermodynamically miscible state, since entropy of mixing is very small as is well known for polymer blends[9,10], and since rod molecules have a strong tendency to segregate[11]. To retain molecular dispersity, a ternary solution (rod polymer/flexible polymer/solvent) is made by dissolving the polymers in a common solvent below the critical concentration, followed by rapid coagulation to make thin films. The rapid coagulation is needed to 'freeze' the miscible rod/coil state to overcome the unfavourable thermodynamic driving force to phase separation. However, many molecular composites are phase separated after this procedure. Although some systems can achieve the miscible blend state, the homogeneous phase morphology is only temporary; for example, phase separation occurs after heating[6]. By reviewing the work on molecular composites, Hwang and Helminiak concluded[12] that a phase separated rigid rod/thermoplastic blend is no better in its physical/chemical properties than a corresponding fibre composite and that the enhanced and desirable properties can only be realized in a true molecular composite, as proposed in the original concept. Therefore, the key to the success of rigid-rod molecular composites technology lies in the molecular dispersity of rigid rods in a matrix material.

It has been suggested, as one means to overcome this problem, that attractive interactions such as hydrogen[13] bonding between rod and coil molecules should be introduced, as is the case for flexible–flexible blends. Even more useful interactions are ionic interactions, such as ion–ion and ion–dipole interactions[14]. It has been shown extensively that ionic interactions can enhance miscibility of polymers that are immiscible without ionic groups. Polymers studied include polystyrene, poly(ethyl acrylate), poly(ethyleneimine) and poly(ethylene oxide). Along this line, it was recently reported that the miscibility of PBZT with poly(2-acrylamido-2-methylpropanesulphonic acid) (HAMPS) was significantly enhanced[15]. They attributed miscibility enhancement to ion–ion interactions, arising from proton transfer from HAMPS to PBZT in acidic solvent, methanesulphonic acid. Although no phase-separated morphology was

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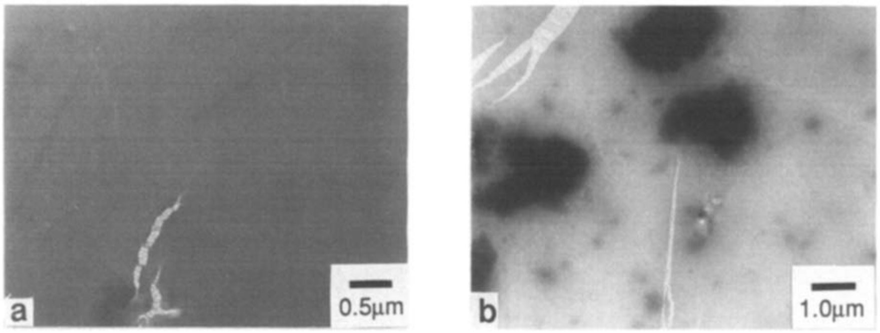

Figure 1 TEM micrographs for blends of ionic Kevlar with (a) PVP and (b) a copolymer of S-VP (50/50)

detected by scanning electron miscroscopy within 500 Å resolution, X-ray diffraction studies indicated a small degree of aggregation of rod molecules.

In this work, we exploit ion–dipole interactions to achieve miscibility between ionic Kevlar molecules and flexible PVP molecules.

Experimental

Ionic Kevlar, i.e. poly(*p*-phenylene terephthalamide propane sulphonate) (PPTA-PS) was prepared by the alkylsulphonation reaction of the Kevlar pulp (Du Pont) according to the method reported by Gieselman and Reynolds[16]. Incorporation of ionic groups was successful, since these polymers were dissolved in a polar solvent, dimethylformamide (DMF), and polyelectrolyte behaviour was observed by viscosity and light scattering. PVP and a copolymer of styrene with 4-vinylpyridine (50/50) (S-VP) were purchased from Scientific Polymer Products, Inc.[2]. Each polymer was dissolved in DMF separately, followed by mixing under stirring. The transparent light yellow solution was then cast on microscope slides. The films were floated off the glass slides onto the surface of distilled water and picked up on a ductile copper grid for TEM observation. The microstructure of these thin films was observed by a transmission electron microscope (JEM-100 CXII) operating at 100 kV.

Results and discussion

Figure 1 shows the TEM micrographs for blends of ionic Kevlar with PVP and a copolymer of S-VP (50/50). The weight fraction of ionic Kevlar is 20%. It seems that no phase-separated morphology is detected for the PVP/matrix blend, while a second phase, mainly made of ionic Kevlar of various sizes and shapes, is clearly seen for the S-VP/matrix blend.

As mentioned in the Introduction, it is suggested that strong attractive interactions are needed to render miscible otherwise immiscible polymer mixtures, especially when one of the components has a rigid-rod-like conformation. In our case, it is expected that ion–dipole interactions are responsible for the miscibility enhancement, since the functional groups involved are ion pairs (i.e. sodium sulphonate) in ionic Kevlar and ionic dipoles in PVP molecules. Ion–ion interactions arising from proton transfer to nitrogen atoms is inconceivable for our system. It is pointed out[14] that to make ion–dipole interactions effective as miscibility enhancers, the polar polymer should have many dipoles as is the case for PVP which has ionic dipoles at every repeat unit. As seen in *Figure 1b*, when the number of dipoles is reduced to half, a sign of immiscibility is seen. This is partly due to a decrease in interacting groups as described above, as well as potential immiscibility between styrene segments and ionic Kevlar. The fact that pyridine groups can interact more strongly than phenyl groups with ionic groups is also evident from the following observation. When thin films cast on glass slides were floated off onto distilled water, it was observed that the PVP films were difficult to remove from the surface of the glass, which has many ionic groups, while the PS films were easily removed. This result is due to ion–dipole interaction between ionic dipoles in PVP and ionic groups in glass.

Indirect evidence, although qualitative and preliminary, for miscibility enhancement in our system is also available. The film samples of ionic Kevlar/PVP blend are transparent and light yellow in colour, which is an indication of miscibility[9] on a scale down to 0.1 μm. The films of ionic Kevlar/PVP are more ductile compared to ionic Kevlar/S-VP copolymer films as well as to films of other immiscible blend systems that include ionic Kevlar as a reinforcer, which tend to be brittle. This is yet another indication of good miscibility[9]. Finally, it should be added that heat treatment so far has not developed any sign of phase separation as has been seen in many molecular composites[6].

Although promising, the results presented are still preliminary and much work needs to be done to demonstrate the usefulness of our system as a molecular composite. These studies should include determination of the following: (1) the degree of miscibility, by various methods with different length scale; (2) the conformation of ionic Kevlar in the solid state; and (3) the deformation and fracture behaviour of the blend film specimens, as compared with those of PVP films.

In summary, a thermodynamically miscible molecular composite was made from ionic Kevlar and PVP. The interactions between those polymers responsible for the observed miscibility are considered to be ion–dipole interactions between sodium sulphonate groups in ionic Kevlar and polar groups, including nitrogen atoms, in PVP. More detailed characterization of this system, as well as a study of its deformation and fracture behaviour, is under way and will be reported.

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