Molecular composites

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Abstract: Molecular composites were prepared with the following polymers as the rigid components: (1) sulfonated poly (*p*-phenylene terephthalamide), PPTS, (2) the cupric or zinc salts of PPTS and (3) poly (3-alkylthiophenes) where the alkyl group is octyl or dodecyl. Evidences for the dispersion of the rigid component on a molecular scale in the matrix were obtained from NMR relaxation times. The nature of the specific interaction between PPTS and poly (4-vinyl pyridine) was identified by NMR chemical shifts and infrared spectroscopy.

Introduction

The term molecular composites was coined in the seventies to describe polymeric materials in which a fraction of the molecules had extended conformation to form the "reinforcing fiber" in a matrix of coiled molecules. Since then, numerous attempts have been made to construct such molecular composites. However, except in a few cases,[1-8] the majority of the experiments resulted in rodlike molecules aggregating with themselves in distinct domains.

PPTS   **POT**
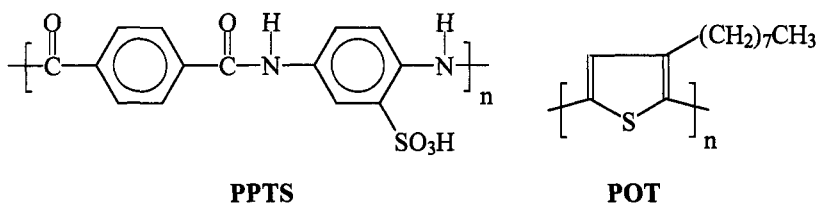
We have previously reported on molecular composites[7] comprised of a rigid polymer, sulfonated poly (*p*-phenylene terephthalamide), PPTS, and three flexible macromolecules, namely, poly (vinyl pyridine), PVPy, poly (vinyl pyrrolidone), PVP and poly (vinyl alcohol). Glass transition temperatures and NMR relaxation time measurements were the principal tools to provide evidences of miscibility, on a molecular scale, in these composites. We now wish to present infrared spectroscopic data on the PPTS-poly (vinyl pyrrolidone) system which support the identification of interacting groups made earlier on the basis of NMR data alone. We have also prepared new molecular composites consisting of poly (vinyl pyridine) and Cu^{+2} and Zn^{+2} salts of PPTS. Additionally, we shall report on recent work in which the rigid components contain long alkyl side chains, in particular, poly (3-octylthiophene) and poly (3-dodecylthiophene).

Experimental

The synthetic procedure for sulfonated poly (*p*-phenylene terephthalamide) was that described by Salamone[9] and by Vandenberg.[10] The Cu^{+2} and Zn^{+2} salts were prepared by neutralizing the sulfonic acid group with cupric or zinc acetate.

Poly (3-alkylthiophene) samples were obtained through the courtesy of Neste Oy, Finland. Poly (ethylene-*co*-vinyl acetate) containing 20% by weight of vinyl acetate units, EVA 20, was provided by Neste Oy (Finland).

Results and Discussion

1. PPTS-PVP blends

The miscibility of the PPTS-PVP blends have already been discussed in Ref. 7 and will not be repeated here. In what follows, we shall present infrared and ^{13}C NMR chemical shift data in our effort to identify the nature of specific interaction between the two component polymers. There are three possible types of hydrogen bonding in PPTS itself, namely, between amide-amide, sulfonic acid-sulfonic acid, and amide-sulfonic acid groups. When PPTS is blended with PVP, the carbonyl group of PVP, being a disubstituted amide and a strong hydrogen bond acceptor, can form hydrogen bonds with either the amide or the sulfonic acid group of PPTS, or both. ^{13}C CP/MAS NMR spectra in the region of PVP carbonyl carbon resonance is shown in Fig. 1 as a function of blend composition. The resonance at 175.5 ppm shifts progressively downfield as PPTS content increases. In the 60% PPTS blend, the shift is ~2ppm; the magnitude of the shift is comparable to that reported for PVP-poly (vinyl alcohol)[11] blends. The observation is also consistent with the known sensitivity of PVP carbonyl resonance to hydrogen bonding; for example, the chemical shift was observed at 172.9 ppm in chloroform but 178.8 in aqueous solutions.[12]
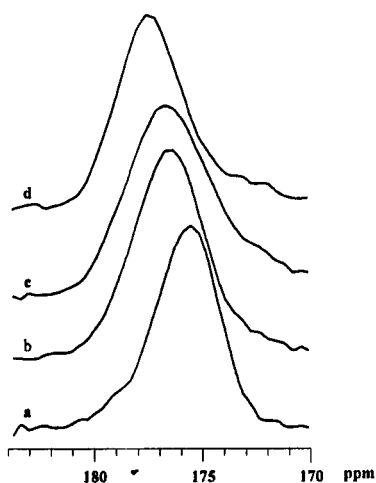

Fig. 1 ^{13}C spectra of carbonyl resorance of PVP in PPTS/PVP blends: (a) PVP; (b) 20/80; (c) 40/60; (d) 60/40.

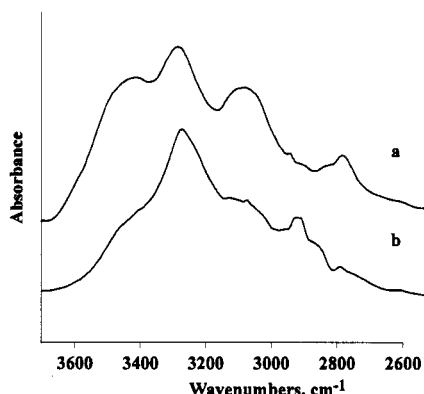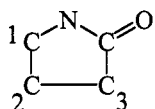
Fig. 2 FTIR spectra of PPTS (a) and difference spectrum from the 60/40 blend; (b) in the range 2600-3800 cm^{-1}.

The interaction of the PVP carbonyl group with PPTS also causes changes in the resonance peak of C3 in the pyrrolidone ring .

According to the literature,[13] the resonance peaks of the various ring carbons appeared at 38.7 ppm for C1, 19.5 ppm for C2 and 32.4 ppm for C3; these peaks were also observed in our experiments. Upon blending with PPTS, there appeared near the C3 resonance another peak at 36.2 ppm which increased in intensity as the PPTS content was increased.

The effect of interpolymer interaction was also seen in the NMR spectra of PPTS. The chemical shifts of the ring carbons in PPTS are C_α at 134 ppm, C_β at 130.5 ppm and C_γ at 122 ppm. A downfield shift of ~2.5 ppm was seen for C_α in the 40% PVP blend but the shift increased to ~4 ppm in the 90% blend. The C_β resonance also showed a downfield shift of ~1.5 ppm. The carbonyl carbon and C_γ, on the other hand, are relative insensitive to the addition of PVP.
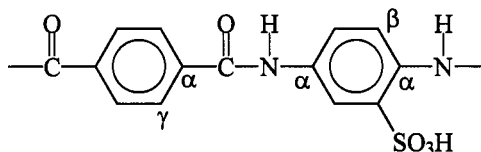
FTIR spectra in the range of 3000-3500 cm^{-1} show peaks at 3309 and 3470 cm^{-1}, respectively. The locations of the two peaks are the same as those reported for another sulfonated aromatic polyamide, poly [(p-phenylene terephthalamide) propanesulfonate].[14] The band at 3470 cm^{-1} is attributable to "free" —NH groups,[15,16] while the band at 3309 cm^{-1} is believed to be due to the stretching vibration of the hydrogen bonded NH group.[17] We note that the position of the latter band is ~20 cm^{-1} lower than that found in poly (p-phenylene terephthalamide), PPTA. The absorption bands in the blends are generally broad in this region and difficult to deconvolute. Accordingly, we did not analyze these peaks in any detail except to point out that systematic spectral change occurred upon blending.

Instead, we have focused our attention on the absorption near 3815 cm^{-1} which can be assigned to —OH stretching of the sulfonic acid groups which form a cyclic dimer via hydrogen bonding.[18] Upon blending PPTS with PVP, this peak was reduced in intensity (see the difference spectra in Fig. 2b) while a new peak appeared at ~2950 cm^{-1} which, according to the literature,[16] was seen typically in the spectra of sulfonic acids as due to OH stretching. When these results are taken together with the NMR chemical shift of the PVP carbonyl, we are led to think that the most likely mode of interaction in the composite is the replacement of the sulfonic acid dimer between adjacent PPTS chains by SO_3H-PVP carbonyl hydrogen bonding. (However, we can not rule out the possibility of NH-carbonyl interaction although there are complicating factors in data interpretation.)

Supporting evidence that the sulfonic acid group was involved in the interaction can also be obtained from the spectral features of the sulfonic acid vibration modes. The effect of the interactions on the symmetric stretching band of the SO$^-$ ion is shown in Fig. 3. The PPTS spectra in this frequency region is characterized by two partially overlapped absorptions, one at ~1026 cm^{-1} due to the symmetric stretching band of the SO$^-$ ion and the other at ~1017 cm^{-1} due to the ring mode vibration. The symmetric stretching band of the SO$^-$ ion was known to be sensitive to cation species, self-association, and distance between the ion and the cation.[18,19] In the 40% PVP blend, this stretching band shifted to ~1022 cm^{-1} along with an apparent decrease in the band width, presumably because the self-association of the sulfonic acid groups was replaced by interactions with the PVP. This interpretation is in line with the spectral features of the acid O-H band in Fig. 2.
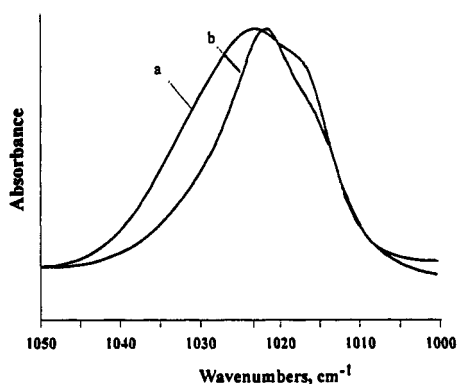

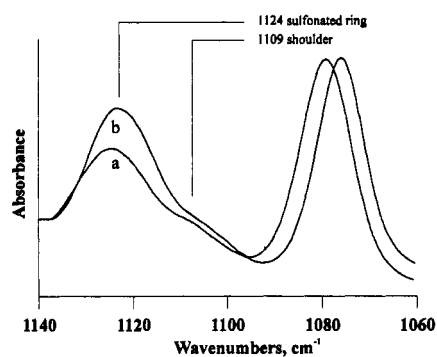Fig. 3 FTIR spectra of PPTS (a) and substracted spectrum from the 60/40 blend; (b) in the range 1000-1050 cm^{-1}.

Fig. 4 FTIR spectra of PPTS (a0 and difference spectrum from the 60/40 blend; (b) in the range 1060-1140 cm^{-1}.

Changes were also observed for vibrations of the aromatic ring to which the sulfonic acid group was attached (Fig. 4). In the neat PPTS, three bands were detected: 1124 cm^{-1} for the C-H in-plane bending of the sulfonated ring, ~1109 cm^{-1} (shoulder) for the C-H in-plane bending of the non-sulfonated ring, and ~1079 cm^{-1} for the in-plane skeleton vibration of the sulfonated ring. These ring vibrations are strongly influenced by substituents and, therefore, may be also informative about the interactions involving their substituents.[18] In the 40% PVP blend, the two bands associated with the sulfonated ring obviously shifted to the lower frequencies, while the bands resulted from the non-sulfonated ring shown little change in the position.

2. Blends of PPTS-Zn or PPTS-Cu and poly (vinyl pyridine)

The miscibility of PPTS and PVPy has already been studied in Ref. 7. We have now extended our investigation to blends comprised of Zn^{+2} and Cu^{+2} salts of PPTS. The zinc sulfonate moiety has attracted a great deal of attention in recent miscibility studies. In the course of our study, we were unable to determine the T_g's of the PPTS salts because degradation and side reactions set in before glass transition. Accordingly, we again relied on NMR relaxation time measurements. The results are listed in TABLE 1. It is seen that the spin lattice relaxation times (T_1) of the blends are much shorter than the values predicted from the linear equation[20]

$$k_{blend} = k_A(N_A / N_T) + k_B(N_B / N_T) \qquad (1)$$

where k is the relaxation rate $(1/T_1)$, and the subscripts A and B denote the component polymers respectively; N_A and N_B are the number of protons of A and B polymers in the blend and N_T is the total number of protons. The rotating frame relaxation times $(T_{1\rho})$ also show similar deviations. Such deviations are usually indicative of strong interaction between polymers which alter the path lengths of spin diffusion or the relaxation mechanism.[21]

TABLE 1. ^1H relaxation of PPTS-M^{+2}/PVPy blends

T_1, sec			$T_{1\rho}$, msec		
MPPTS, %	Zn	Cu	MPPTS, %	Zn	Cu
100	0.81	0.20	100	9.6	7.8
86	0.54	—	86	9.0	—
75	0.38	0.10	75	8.7	4.8
50	0.36	0.03	50	6.0	4.1
25	0.65	0.04	25	5.9	3.8
0	1.60	1.60	0	6.5	6.5

3. Blends containing poly (3-alkylthiophene)

Poly (3-octylthiophene) has a rigid main chain to which the octyl groups are attached. It is partially miscible with a copolymer of ethylene and vinyl acetate, EVA 20. The phase behaviors of this binary system, deduced from optical microscopy, are shown in Fig. 5. Blends containing 80% or more EVA are miscible. The melting points of EVA were depressed slightly in the blends which remained optically clear at temperatures above the EVA melting point (~93°C) until 180°C at which the experiment was terminated. Blend containing 70% EVA appeared to be miscible at room temperature but became heterogeneous at about 100°C. The 30 and 40% EVA blends were heterogeneous at room temperature. The dashed line in Fig. 5 represents the probable location of the phase boundary. To confirm the existence of the miscible region in EVA rich blends, we carried out NMR relaxation time measurements.
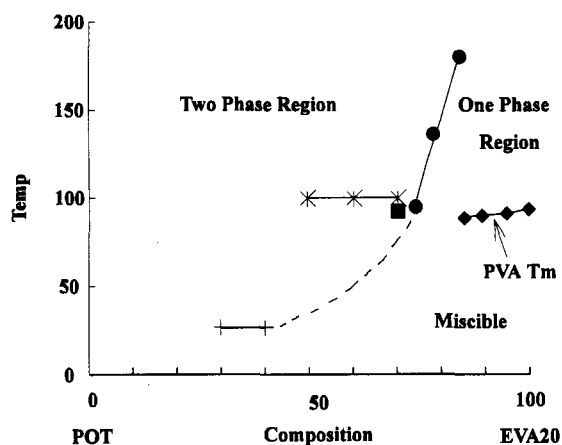

Fig. 5 Proposed phase disgram of poly (3-octylthiophene) and poly (ethylene-co-vinyl acetate) blends.

The results are shown in Fig. 6. A single T_1 was observed for each blend in the composition range studied; furthermore, the magnitude of T_1 increases progressively with POT content.
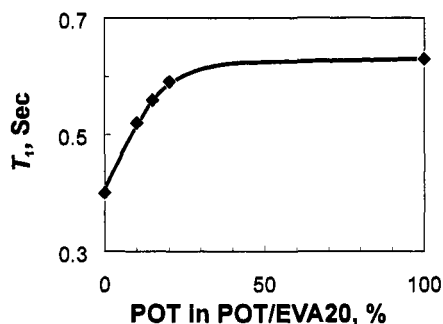

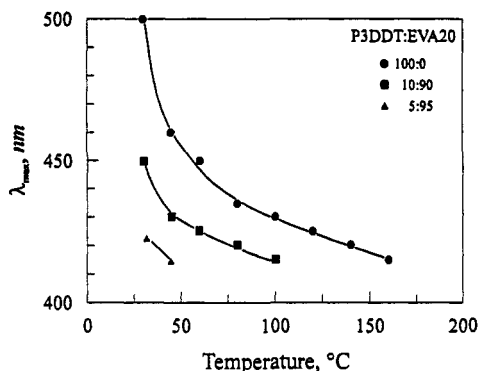Fig. 6 NMR T_1 relaxation times of POT EVA blends.

Fig. 7 Solvatochromism of poly (3-dodecylthiophene)-EVA blends.

Mixing on a molecular scale between poly (3-dodecylthiophene) and EVA produces a strong solvatochromatic effect. Solvatochromism in PDDT-EVA 20 blends can be seen in Fig. 7 in which the UV absorption maxima are plotted as a function of temperature for PDDT and blends containing 5 and 10% PDDT, respectively. The wavelength at absorption maximum, λ_{max}, decreased from 500 to about 415 nm when a PDDT film was heated from 30° to 160°C—thermochromism. The absorption maximum in a 10% PDDT blend was located at 450 nm at 30°C, a considerable shift from the λ_{max} of PDDT itself. The λ_{max} in a 5% PDDT blend was further lowered to about 424 nm. In both blends, the λ_{max} values were also seen to shift to shorter wavelengths as temperature was raised. At each temperature, the λ_{max} values of the blends were shorter than the corresponding wavelength for PDDT. Shifts in the absorption maxima are usually interpreted in terms of changes in the conjugation length of the system,[22] in this case the thiophene backbone. The observed solvatochromism in the present system is therefore suggestive of conformational changes of PDDT when mixed with EVA 20.

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