

Effects of functionalized protonic acids on the miscibility of polyaniline/poly(2-ethyl-2-oxazoline) blends

C. H. Ong, S. H. Goh* and H. S. O. Chan

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260, Republic of Singapore

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The miscibility of polyaniline (PANI) salts, doped with *p*-phenol sulfonic acid (PSA) or 5-sulfosalicylic acid (SSA), with poly(2-ethyl-2-oxazoline) (PEOx) was studied by differential scanning calorimetry (d.s.c.) and Fourier-transform infra-red spectroscopy (FTi.r.). D.s.c. measurements show a single glass transition temperature (T_g) for each of the blends containing 5–60 wt% of PANI. The T_g value shifts away from that of PEOx with increasing PANI content. FTi.r. studies show the presence of specific interactions between the polymers. The interaction in the PEOx/PANI–SSA system is stronger than that in the PEOx/PANI–PSA system. Electrical conductivities of the blends, determined by four-point probe, range from 10^{-5} to $10^{-3} \text{ S cm}^{-1}$. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Polyaniline (PANI) has attracted considerable scientific interest as it shows not only the mechanical and chemical attributes of polymers but also the electronic properties of semiconductors^{1,2}. However, the salt form of PANI has always been known only as a green intractable powder. Recently functionalized protonic acids (FPAs) have been used as dopants in place of inorganic acids such as HCl^{3–5}. The incorporation of FPAs onto the PANI backbone via a doping process results in improved solubility of PANI–FPA salts in organic solvents^{6–8}.

Blending of PANI with a host polymer can produce desirable properties which are promoted by enhanced compatibility and homogeneity of the two components. Blends of PANI with host polymers such as poly(methyl methacrylate), polyethylene and other thermoplastic have been reported^{8,9}. However, their miscibility behaviour was not discussed. Other systems include composites of PANI dispersed in a thermoplastic matrix¹⁰. Miscibility of PANI–FPAs with a host polymer can be brought about through judicious choice of FPAs which will engage in specific intermolecular interaction with a suitable functional group of the host polymer.

Stockton and Rubner have reported that PANI in its undoped form is miscible with poly(vinyl pyrrolidone) (PVP)¹¹ up to 30% by weight of PANI. However, blends formed by pre-doping the mixed solutions of PVP and PANI in *N*-methyl-2-pyrrolidinone (NMP) with FPAs resulted in phase segregation. The FPAs used were methane sulfonic acid, dodecylbenzene

sulfonic acid and camphor sulfonic acid; either these do not possess functional groups capable of specific interactions with the host polymer, PVP, or the dopant groups are too bulky, which may interfere with specific interaction.

Levon *et al.* recently reported the miscibility of *N*-alkylated PANI with ethylene–vinyl acetate copolymers (EVA)¹². The miscibility was found to depend on the length of the alkyl chain of *N*-alkylated PANI and also on the ethylene content of the copolymer. Complete miscibility occurred between octadecylated PANI and EVA containing 80 wt% of ethylene. The blends were subsequently doped by methane sulfonic acid to render them conductive. Our previous work has shown that PANI doped with *p*-phenol sulfonic acid (PSA) forms miscible blends with poly(vinyl acetate) (PVAc) up to 50 wt% of PANI–PSA through weak hydrogen bonding¹³. With this in mind, we explore the miscibility of PEOx with PANI–FPAs. PEOx is miscible with carboxyl- and hydroxyl-containing polymers through hydrogen bonding involving its carbonyl groups^{14–17}. It was envisaged that PEOx, which possesses carbonyl groups of higher basicity than PVAc, may result in stronger intermolecular interactions with PANI–FPAs. The two FPAs used in this work are PSA and 5-sulfosalicylic acid (SSA), both of which possess hydroxyl groups capable of hydrogen bonding. In the case of SSA, there is an additional COOH group which may further promote miscibility with PEOx. It was also reported that carboxylated polysulfone with a degree of carboxylation greater than 0.93 forms miscible blends with PEOx¹⁸. This further exemplifies that polymers which are sufficiently acidic may form miscible blends with the slightly basic PEOx. Furthermore, SSA-doped

* To whom correspondence should be addressed

PANI has been reported to possess better electrochemical stability of PANI at higher potentials with a solubility of 11% (w/v) in DMSO¹⁹.

EXPERIMENTAL

Materials

Aniline from Aldrich was double distilled and stored under nitrogen in the dark prior to polymerization. Potassium dichromate (from Merck), PSA (from Aldrich), SSA (from Aldrich) and dimethyl sulfoxide (DMSO, from Baker) were used as received. PEOx was provided by the Dow Chemical Company; its number- and weight-average molecular weights are 38 500 and 61 500 g mol⁻¹, respectively, PANI-FPAs were prepared as described previously with a monomer to oxidant ratio of 3/1 in 1.0 M aqueous FPAs solutions¹³. The base form of PANI was obtained by deprotonating its salt form with 0.10 M aqueous NH₃ solution.

Preparation of polymer blends

Binary blends of PEOx with PANI-PSA, PANI-SSA or PANI-base of varying compositions were prepared by solution casting from DMSO on an aluminium dish. The well-mixed solution was left to dry *in vacuo* at 50°C. The films were further dried *in vacuo* at 90°C for at least two weeks.

The PEOx/PANI-base blends were also re-doped by suspending the films over 1.0 M aqueous PSA or SSA solution in a closed container for two days. The re-doped blends were further dried *in vacuo* at 90°C for two weeks.

Glass transition temperature (T_g) measurements

The T_g s of various blends were measured with a TA Instruments 2910 differential scanning calorimeter. The

measurements were carried out at a heating rate of 20°C min⁻¹ under a nitrogen purge at 60 ml min⁻¹. The initial onset of the change of slope in the d.s.c. curve of the second and subsequent runs represents the T_g .

Fourier transform infra-red spectroscopic characterization

Samples for FTi.r. analysis were prepared by grinding the polymer blend film, and dispersed in KBr to form discs. Spectra were acquired at elevated temperature using a SPECAC high-temperature cell equipped with an automatic temperature controller mounted on a Perkin-Elmer 1725X FTi.r. spectrophotometer; sixty-four scans were signal-averaged at a resolution of 2 cm⁻¹.

Electrical conductivity

Conductivity measurements were carried out on a four-point probe connected to a Keithley voltmeter constant-current source system. The conductivities were deduced on the basis of at least ten pairs of readings at different parts on both sides of the samples.

RESULTS AND DISCUSSION

Miscibility

A series of PANI/PEOx blends of various compositions was prepared. The well-mixed solutions were clear for all compositions before casting. For blends containing 15 wt% or less of PANI-PSA or PANI-base, the films were transparent and homogeneous by visual observation. For PANI-SSA blends, optical clarity remained so with PANI-SSA content as high as 20 wt%. The optical clarity at lower PANI content gives a good indication of miscibility. Although blends with higher PANI content were dark in colour, they were homogeneous, as evidenced from the uniform colour of film when observed using a light microscope.

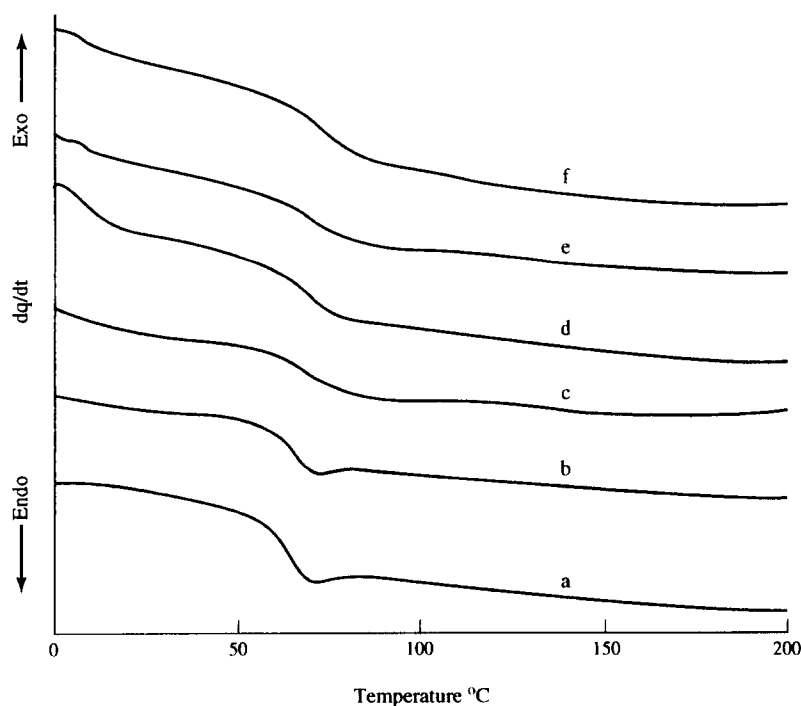


Figure 1 D.s.c. curves of PEOx/PANI-base system: (a) PEOx; (b) 5; (c) 10; (d) 20; (e) 30 and (f) 40 wt% PANI-base

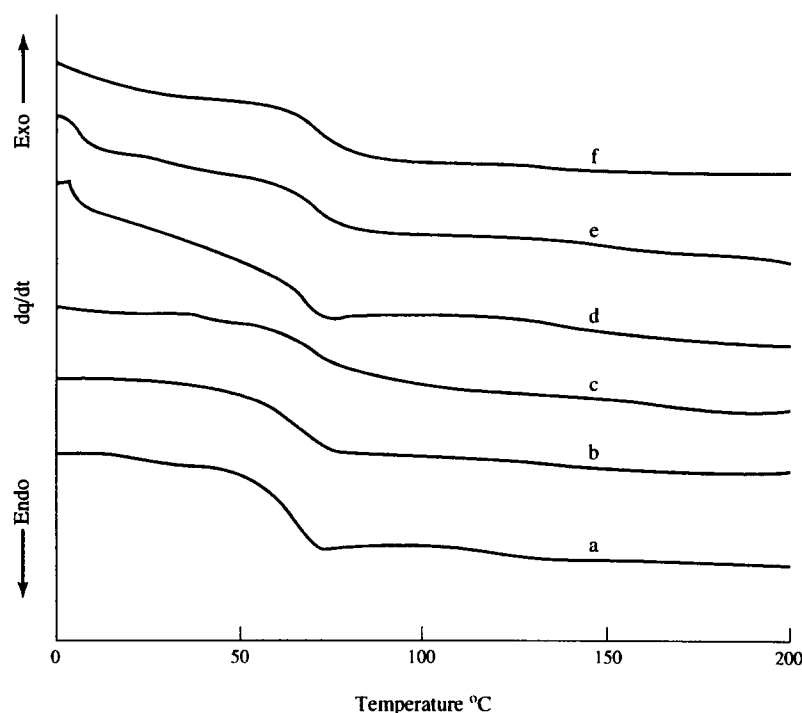


Figure 2 D.s.c. curves of PEOx/PANI-PSA system: (a) PEOx; (b) 5; (c) 10; (d) 20; (e) 30 and (f) 40 wt% PANI-PSA

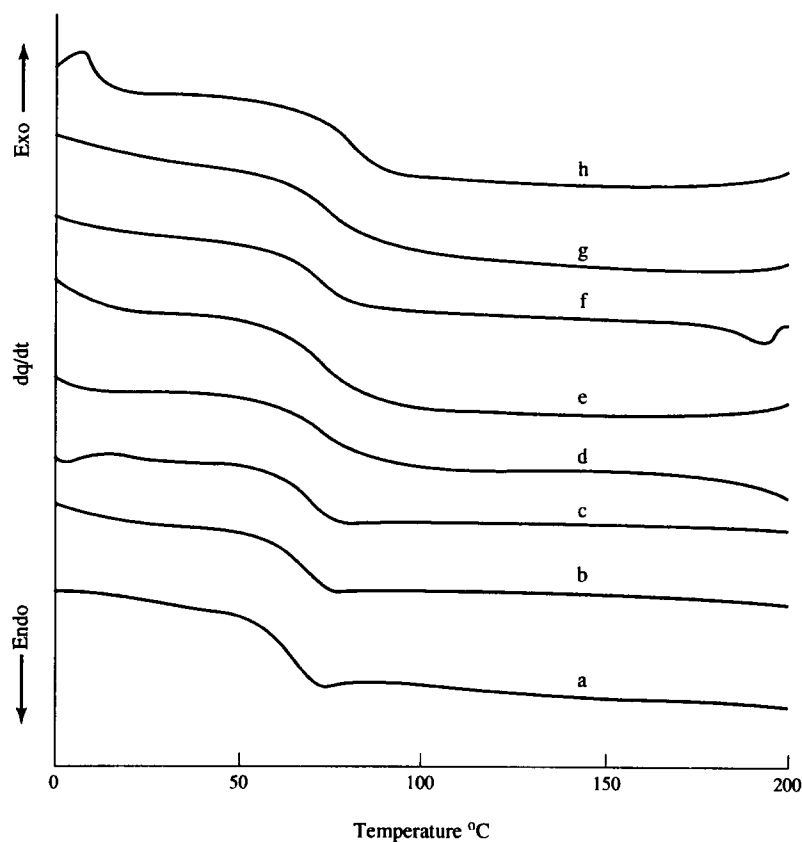


Figure 3 D.s.c. curves of PEOx/PANI-SSA system: (a) PEOx; (b) 5; (c) 10; (d) 20; (e) 30; (f) 40; (g) 50 and (h) 60 wt% PANI-SSA

For blends containing 50 wt% or more of PANI-base, 60 wt% or more of PANI-PSA or 70 wt% or more of PANI-SSA, particulate aggregates were observed to be dispersed in the sample, indicating phase separation. However, when PEOx/PANI-base blends were re-doped with PSA or SSA, phase segregation was observed when the PANI content was 10 wt% or more.

The miscibility of polymer blends is commonly ascertained through T_g measurements. The existence of a composition-dependent T_g is taken to indicate miscibility. The reported T_g values of PANI vary widely²⁰⁻²⁴. Wei *et al.*²⁴ found that the T_g values of PANI measured by dynamic mechanical analysis were in the range of 140–220°C, depending on the residual

N-methyl-2-pyrrolidinone content in the cast film. We were unable to detect the T_g s of PANI-SSA and PANI-PSA by d.s.c., and Conklin *et al.*²⁵ were also unable to observe the T_g of PANI by d.s.c. On the other hand, the T_g of PEOx is easily measured by d.s.c. A T_g value of 55°C was found for DMSO-cast PEOx film dried under the same condition as the blends.

Figures 1-3 show the d.s.c. curves of various PEOx/PANI-base, PEOx/PANI-SSA and PEOx/PANI-PSA blends. These curves clearly show that T_g increases with increasing PANI content in the blend. The existence of a single composition-dependent T_g in each blend, together with its optical clarity, is taken to indicate miscibility. There is no further increase in T_g for blends of higher PANI content, indicating that a miscibility limit is reached. This is consistent with the presence of particulate aggregates as observed by microscopy in blends of higher PANI content. The results also show that SSA affords a higher miscibility limit with PEOx than PSA. It

Table 1 T_g values of PEOx and PANI system

Wt% PANI	PANI-PSA blend (°C)	PANI-SSA blend (°C)	PANI-base blend (°C)
0	55	55	55
5	58	59	57
10	60	60	59
20	61	62	60
30	62	64	62
40	63	65	62
50	64	68	—
60	—	71	—

is also noted that the T_g of a PANI-SSA blend is higher than that of the corresponding PANI-PSA blend, as shown in Table 1. This may be an indication that PEOx interacts more strongly with PANI-SSA than with PANI-PSA, giving rise to a more rigid chain structure. Further discussion on interpolymer interaction will be given in the following section.

Fourier transform infra-red spectroscopy characterization

FTi.r. is commonly used to investigate the miscibility behaviour of polymer blends involving hydrogen-bonding interaction^{15,26,27}. The frequency shifts of hydroxyl and carbonyl bands indicate the relative strength of this interaction. To exclude moisture from the samples due to the hygroscopic nature of PEOx, all the FTi.r. measurements were carried out at elevated temperatures.

Figure 4 shows the carbonyl stretching region of PEOx and PEOx/PANI-base blends, recorded at 100°C. PEOx (curve a) has a strong absorption centred at 1648 cm⁻¹ for the free carbonyl band. With the addition of PANI-base, the band shifted towards a lower frequency, indicating the existence of intermolecular hydrogen-bonding interaction. In terms of the frequency shifts of the carbonyl band, the interpolymer hydrogen-bonding between PEOx and PANI is rather weak, but comparable to that between PEOx and poly(enamino nitrile)²⁸.

An increase in thermal energy reduces the average strength of intermolecular interaction and decreases the

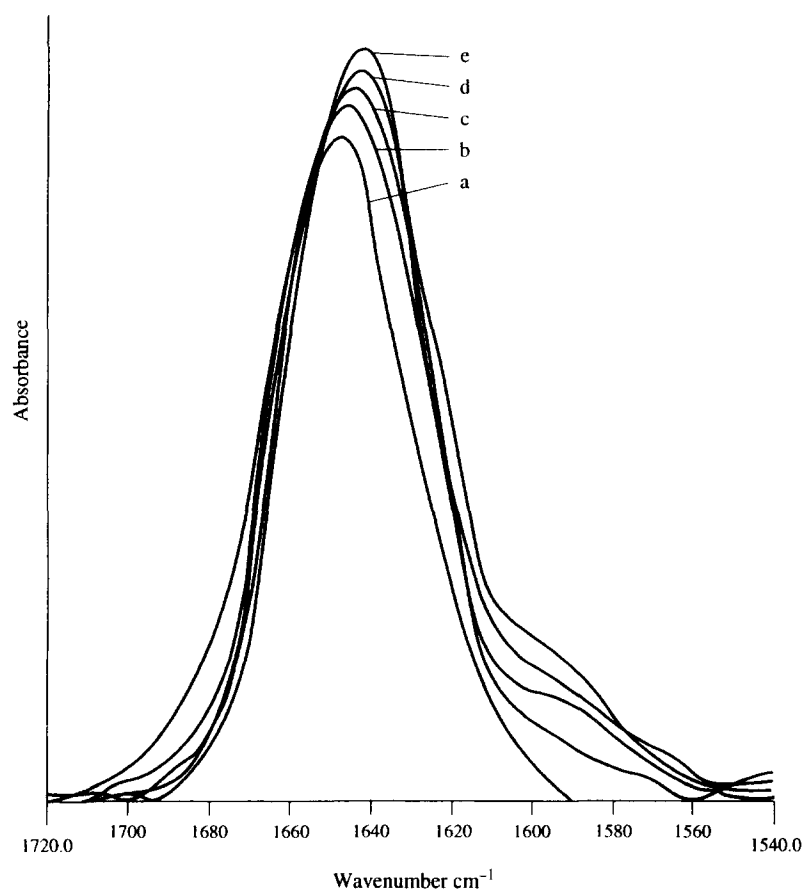


Figure 4 FTi.r. spectra, recorded at 100°C, of the carbonyl stretching region of PEOx/PANI-base blends containing: (a) 0; (b) 5; (c) 10; (d) 20 and (e) 30 wt% of PANI-base

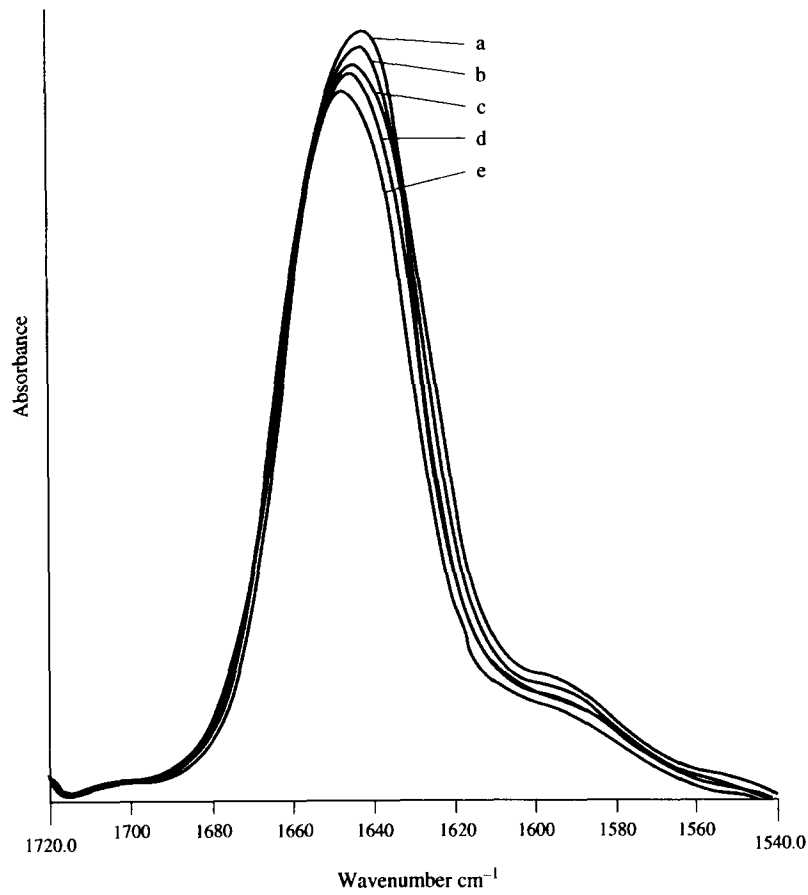


Figure 5 FTi.r. spectra of the carbonyl region of PEOx/PANI-base blends containing 30 wt% of PANI-base recorded at: (a) 100; (b) 120; (c) 140; (d) 160 and (e) 180°C

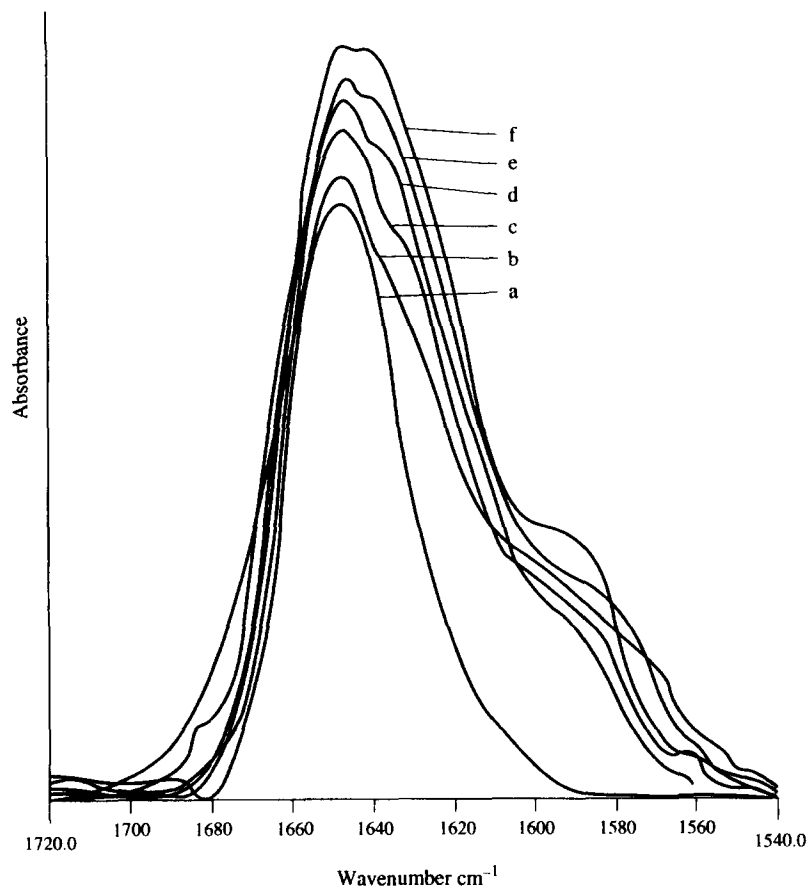


Figure 6 FTi.r. spectra, recorded at 100°C, of the carbonyl stretching region of PEOx/PANI-PSA blends containing: (a) 0; (b) 5; (c) 10; (d) 20; (e) 30 and (f) 40 wt% of PANI-PSA

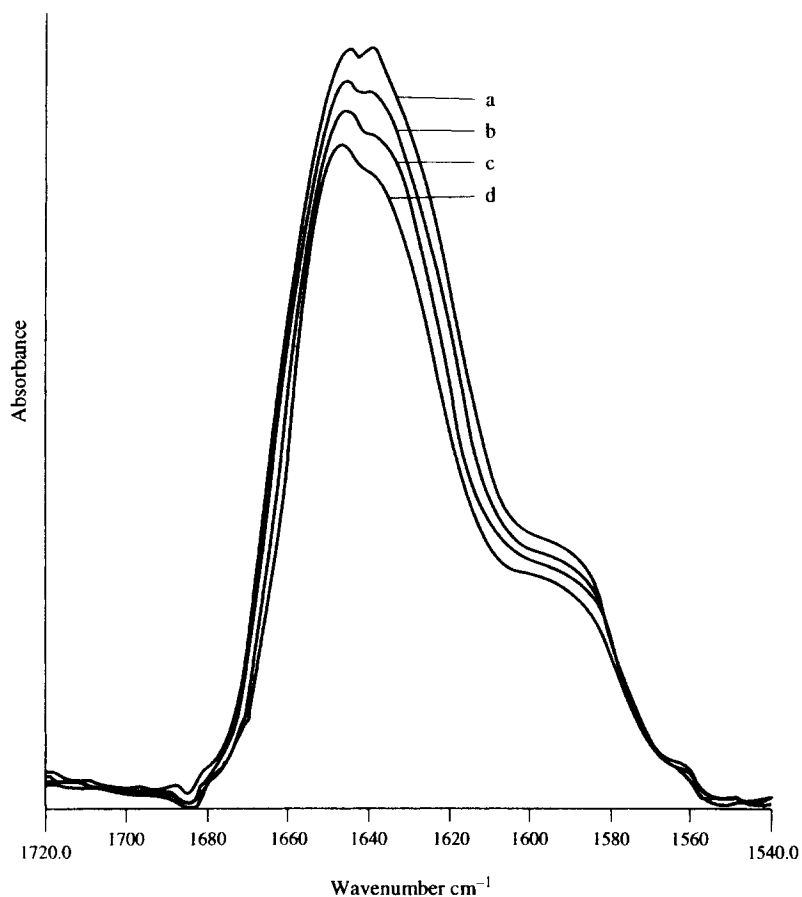


Figure 7 FTi.r. spectra of the carbonyl region of PEOx/PANI-PSA blends containing 40 wt% of PANI-PSA recorded at: (a) 100; (b) 120; (c) 140 and (d) 160°C

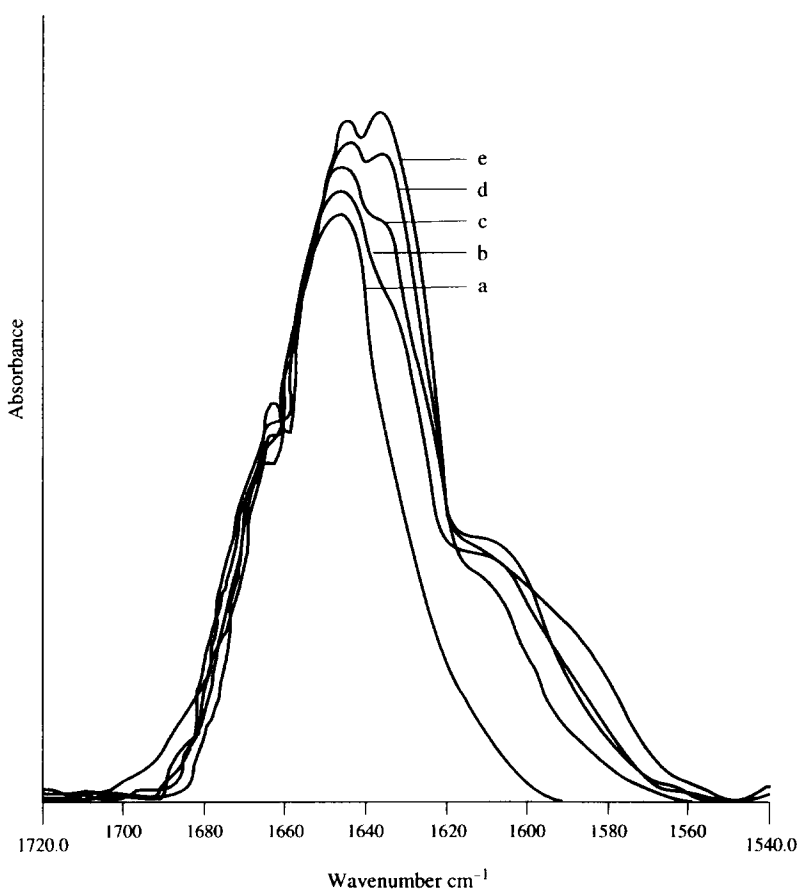


Figure 8 FTi.r. spectra, recorded at 100°C, of the carbonyl stretching region of PEOx/PANI-SSA blends containing: (a) 0; (b) 10; (c) 20; (d) 50 and (e) 60 wt% of PANI-SSA

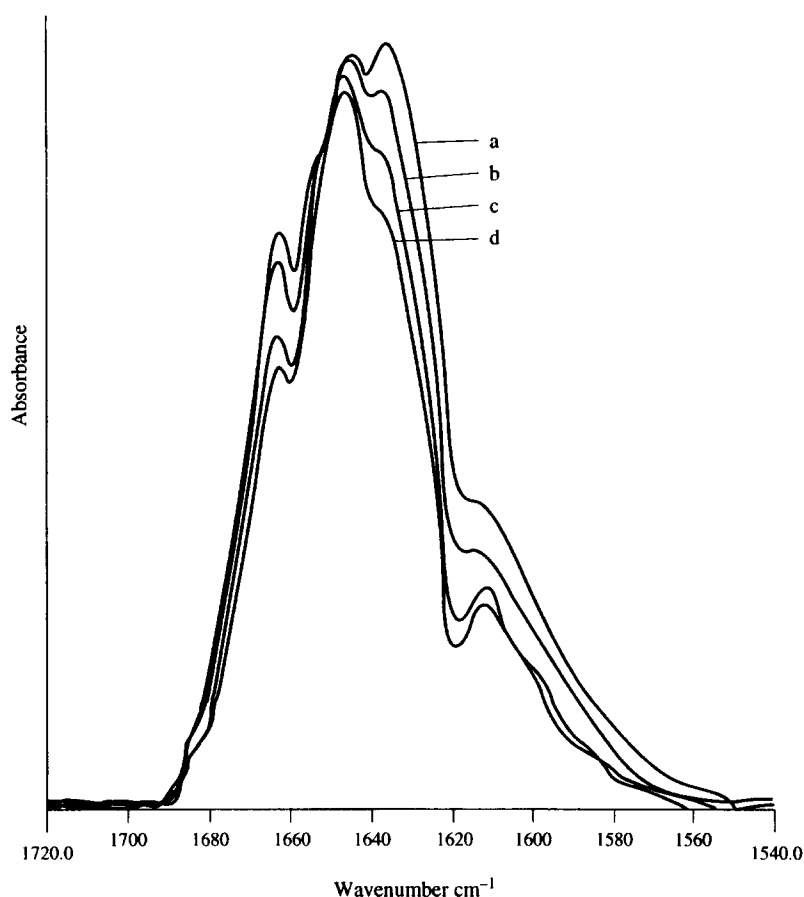


Figure 9 FTi.r. spectra of the carbonyl stretching region of PEOx/PANI-SSA blends containing 60 wt% of PANI-SSA recorded at: (a) 100; (b) 120; (c) 140 and (d) 160°C

Table 2 Conductivities of blends

Wt% PANI	PANI-PSA blend (S cm ⁻¹)	PANI-SSA blend (S cm ⁻¹)
100	2	3
5	5.2×10^{-6}	1.1×10^{-5}
10	1.4×10^{-5}	3.5×10^{-5}
20	3.4×10^{-5}	4.7×10^{-5}
30	6.1×10^{-5}	9.5×10^{-5}
40	7.4×10^{-4}	4.3×10^{-4}
50	1.7×10^{-3}	2.0×10^{-3}
60	—	2.9×10^{-3}

number of interactions that occur. *Figure 5* depicts the spectra in the carbonyl region of a PEOx/PANI-base blend containing 30 wt% of PANI over a temperature range of 100–180°C. The spectra shift back towards higher frequency as the interaction is shattered when temperature is increased. This confirms that the shift in frequency is a result of intermolecular hydrogen bonding interaction.

Figure 6 shows the spectra in the carbonyl stretching region of PEOx and PEOx/PANI-PSA blends recorded at 100°C. With the addition of PANI-PSA, a shoulder at 1640 cm⁻¹ gradually developed. The development of this shoulder band is attributed to carbonyl groups in PEOx hydrogen-bonded with the hydroxyl groups in PANI-PSA. The difference in frequency between the hydrogen-bonded and non-hydrogen-bonded carbonyl is small compared to that in PEOx/poly(ethylene-co-methacrylic acid) (EEMA) blends reported by Lichkus *et al.*¹⁵. This observation

indicates that the intermolecular hydrogen-bonding interaction between PEOx and PANI-PSA is weaker than that between PEOx and EEMA. However, the interaction is stronger than that between PEOx and PANI-base. Thus, the presence of PSA improves the miscibility of PANI with PEOx.

Figure 7 shows the spectra in the carbonyl region of a PEOx/PANI-PSA blend containing 40 wt% of PANI-PSA, recorded as a function of temperature. As envisaged, the intensity of the hydrogen-bonded carbonyl peak at 1640 cm⁻¹ decreases as the temperature is raised from 100 to 160°C. This affirms that the peak at 1640 cm⁻¹ arises from intermolecular hydrogen-bonding interaction.

Figure 8 depicts the infrared spectra in the carbonyl stretching region of PEOx and PEOx/PANI-SSA blends, recorded at 100°C. Unlike PANI-PSA, PANI-SSA shows absorptions in this region at 1672 and 1611 cm⁻¹, attributed to a free SSA carbonyl stretching band and an intramolecular hydrogen-bonded SSA carbonyl stretching band respectively. This to some extent results in a complicated stretching pattern in this region. However, an obvious new peak at 1638 cm⁻¹ was detected, which belongs neither to that of the SSA nor to the free carbonyl stretching band of PEOx. To evaluate this new peak, spectra of a blend with 60 wt% of PANI-SSA were acquired across a temperature range of 100–160°C. The spectra in *Figure 9* show that the intensity of this new peak at 1638 cm⁻¹ decreases as the temperature is raised. Thus this new band can be assigned to that of the intermolecular hydrogen-bonded carbonyl stretching band of PEOx.

The frequency shift, $\Delta\nu$, which is the difference in frequency between the hydrogen-bonded and the free carbonyl stretching band of PEOx in the blends, gives an indication of the relative average strength of intermolecular interactions. In the case of PEOx/PANI-PSA, $\Delta\nu$ is 7 cm^{-1} , while that of the PEOx/PANI-SSA is 10 cm^{-1} for the same composition ratio of PEOx and PANI at 140°C . These results suggest that the intermolecular interaction between PEOx and PANI-SSA is stronger than that between PEOx and PANI-PSA, which in turn is stronger than that between PEOx and PANI-base. This, to a certain extent, is in agreement with the larger shift of T_g values in the PEOx/PANI-SSA blends.

Electrical conductivity

Conductivity measurements were taken on both sides of the films. Due to the hygroscopic nature of the blends, samples were kept in an oven at 100°C for at least 1 h prior to measurements, to exclude moisture. A mean value of 10 readings was taken as the conductivity of the blend, and the results are tabulated in Table 2. The conductivities range from 10^{-3} – 10^{-5} S cm^{-1} for both the PEOx/PANI-PSA and PEOx/PANI-SSA blends, though the conductivities are always slightly higher for the PEOx/PANI-SSA blends. This is so because the conductivity of the pure PANI-SSA (3 S cm^{-1}) is higher than that of PANI-PSA (2 S cm^{-1}). The higher conductivity achieved in pure PANI-SSA could be due to improved structural order, as suggested by Beyer and Steckenbiegler²⁹. The post-doped PEOx/PANI film also showed conductivity within the same range. However, the measured values at different points on each sample were more inconsistent than for those prepared from as-doped PANI blend; thus the conductivities are not reported.

CONCLUSIONS

PEOx forms miscible blends with PANI up to 40 wt% of PANI-base, 50 wt% of PANI-PSA and 60 wt% of PANI-SSA. The miscibility is affirmed by the presence of a single composition-dependent T_g . FTi.r. studies reveal that intermolecular hydrogen bonding is more pronounced in the PEOx/PANI-SSA blends than in the PEOx/PANI-PSA blends. Conductivity studies show that these blends, although miscible, have much lower conductivity than the PANI-FPAs and that the value decreases with increasing PEOx content. However, unlike other composites¹², conductivity for these miscible

blends is a continuous function without an observed percolation threshold.

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