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Miscibility of polyaniline/poly(vinyl acetate) blends

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A miscible and electroactive polymer blend comprising polyaniline (PANI) as the conductive component and poly(vinyl acetate) (PVAc) as the thermoplastic component was prepared and characterized. The solution-processable conducting PANI was prepared by doping with *p*-phenolsulfonic acid (PSA), which also helps enhance its miscibility with PVAc through hydrogen-bonding interaction. Blends containing 50 wt% or less of PANI-PSA were miscible, as shown by glass transition temperature measurements and a low frequency shift of the carbonyl band of PVAc. Copyright © 1996 Elsevier Science Ltd.

(Keywords: miscibility; polyaniline; poly(vinyl acetate))

INTRODUCTION

Polyaniline (PANI) has recently received much attention because of its high conductivity, environmental stability and low cost. However, the conducting form of PANI is difficult to process owing to its insolubility in common solvents. Extensive research has been directed toward the improvement of the processability of PANI by copolymerization with substituted aniline[1-5] or doping PANI with suitable functionalized protonic acid (FPAs)[6-9].

FPAs such as camphorsulfonic acid, dodecylbenzenesulfonic acid and 5-sulfosalicylic acid possess functional groups which are compatible with non-polar or weakly polar organic solvents, enabling the PANI-FPA salts to dissolve in common organic solvents. The functional groups of FPAs also serve as surfactants to allow mixing between PANI and a variety of polymers such as poly(methyl methacrylate) (PMMA) and polyethylene[6,7,9]. PANI/poly(alkyl methcrylate) blends were also prepared by an emulsion method[10]. However, these studies did not deal with the miscibility behaviour of these blend systems.

Recently, Stockton and Rubner[11,12] reported the miscibility of PANI/poly(*N*-vinyl-2-pyrrolidone) (PVP) blends. Undoped PANI was mixed with PVP by solution casting. Each of the blends containing 3–30 wt% of the undoped PANI exhibited a single glass transition temperature (T_g) indicating miscibility[11]. However, for blends formed from doped PANI, some level of phase segregation was observed[12].

In this paper, we report the miscibility of PANI with poly(vinyl acetate) (PVAc). *p*-Phenolsulfonic acid (PSA) was used as the functionalized protonic acid. It is envisaged that the phenolic groups in the PANI-PSA salt may help to improve its miscibility with other polymers, because poly(*p*-vinylphenol) (PVPh) is miscible with a large variety of polymers through hydrogen-bonding interactions[13-23]. PVAc was chosen as the blend component in view of its miscibility with PVPh[13]. Furthermore, PVAc has a low T_g and may serve as a polymeric plasticizer for PANI which helps to improve processability.

EXPERIMENTAL

Materials

Aniline from Aldrich was double distilled under vacuum before use. Dimethyl sulfonate oxide (DMSO, from Baker), PSA (from Merck) and PVAc (from Aldrich) were used as received. The polyaniline emeraldine salt was prepared by oxidation polymerization. Aniline (1.02 g, 10.9 mmol) was added to 30 ml of aqueous 1.0 M PSA solution at 0–5°C. The solution was kept stirring until the salt of aniline had dissolved. A solution of 1.074 g (3.65 mmol) of $K_2Cr_2O_7$ dissolved in 20 ml H_2O was then added dropwise while keeping the concentration of PSA at 1.0 M. The solution was continuously stirred for 24 h before the green precipitate of PANI-PSA was filtered and washed thoroughly. The precipitate was dried under vacuum for 2 days. $(NH_4)_2S_2O_8$ is the commonly used oxidant for the polymerization of aniline. Since the sulfur/nitrogen ratios of PANI-PSA and its blends are to be measured, any residual $(NH_4)_2S_2O_8$ trapped in PANI-PSA will lead to erroneous results. For this reason, $K_2Cr_2O_7$ was used as the oxidant in the present study.

Polymer blends

Polymer blends were prepared by solution casting from DMSO. DMSO solutions of PANI-PSA (0.7% w/v) and PVAc (4% w/v) were separately prepared. Appropriate amounts of the two solutions were then mixed. The well-mixed solution was transferred to a glass

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dish and dried under vacuum at 40°C for at least 4 days. When the film was visually dry, it was peeled off from the glass substrate by wetting it with cold water. The film was washed copiously with cold water to remove traces of DMSO and subsequently dried *in vacuo* at 60°C for at least a week.

X-ray photoelectron spectroscopy (X.p.s.) measurements

Core-level spectra were obtained on a VG ESCA/SIMSLAB MK II with Mg Kα radiation. The samples were mounted onto a VG sample holder with double-sided adhesive tape. The binding energies were referenced to the hydrocarbon component in the C1s envelope, defined at 285.0 eV to compensate for surface charging. The surface stoichiometries were obtained from peak area ratios corrected with the appropriate sensitivity factors and were subject to $\pm 10\%$ error. Spectral deconvolution was carried out using Gaussian component peaks with constant full widths at half-maximum for all components in a particular spectrum.

Thermal analysis

A TA Instruments 2910 differential scanning calorimeter was used to determine T_gs of samples. Measurements were carried out at a heating rate of $10^\circ\mathrm{C\,min^{-1}}$ under N_2 purge at $60\,\mathrm{ml\,min^{-1}}$. In this study, the initial inflection of slope in the differential scanning calorimetry (d.s.c.) curve was taken as the T_g. The thermal stability of various blends in air was evaluated with a TA Instruments 2950 thermogravimetric analyser and was compared to that of the parent polymers and their physical mixture.

*Fourier transform infra-red (*FT*i.r.) spectroscopic measurements*

Infra-red spectra were obtained using a Perkin-Elmer 1600 *FT*i.r. spectrophotometer. The PVAc sample was prepared by casting its tetrahydrofuran solution onto KBr disc. Blends were ground in liquid nitrogen and then dispersed in KBr to form discs.

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 based on at least 10 pairs of readings at different points on both sides of the samples.

RESULTS AND DISCUSSION

X.p.s. characterization

Blends containing 5, 10, 15, 25, 40 and 50 wt% of PANI-PSA salt were prepared and are denoted as B*xx*, where *xx* represents the percentage of PANI-PSA. Blends containing 15 wt% or less of PANI-PSA were green and transparent; those containing 25 wt% or more of PANI-PSA were dark green but also appeared to be homogeneous by visual inspection. Blends with low PANI-PSA content were flexible while those containing 40 and 50 wt% of PANI-PSA were brittle. Blends containing 60 wt% or more of PANI-PSA showed gross phase separation into a top PVAc layer and a bottom PANI-PSA layer; these blends were not further examined.

The characteristics of PANI-PSA and various blends are summarized in *Table 1*. *Figures 1–3* show the C1s, N1s and S2p core-level spectra of PANI-PSA, B15 and B40.

The C1s peak of the PANI-PSA tailed towards the high binding energy end, indicating the presence of a long-range disordered conjugation. The C1s peak can be deconvoluted into five environments: C–C or C–H at 285 eV, C–N, C=N or C–O at 286.1 eV, C–N$^+$, C=N$^+$ at 287 eV, C=O at 287.8 eV and O–C=O at 289.5 eV. The presence of environments at 287.8 and 289.5 eV suggests some surface oxidation of the PANI-PSA sample. The C1s peaks of the two blend samples can similarly be deconvoluted into five environments, but they appear at higher binding energies owing to the low conductive nature of the blends. The presence of PVAc in

Table 1 Composition of blends

Sample	Feed composition	Surface composition from X.p.s.
PANI-PSA	$C_9H_{7.5}N_1S_{0.5}O_2$	$C_{9.42}N_1S_{0.42}O_{1.83}$
B50	$C_{13.02}H_{13.50}N_1S_{0.5}O_{3.98}$	$C_{10.10}N_1S_{0.36}O_{6.13}$
B40	$C_{14.77}H_{16.15}N_1S_{0.5}O_{4.88}$	$C_{14.96}N_1S_{0.34}O_{9.17}$
B25	$C_{20.48}H_{25.27}N_1S_{0.5}O_{7.9}$	$C_{19.04}N_1S_{0.37}O_{4.45}$
B10	$C_{43.50}H_{59.21}N_1S_{0.5}O_{19.23}$	$C_{42.11}N_1S_{0.49}O_{41.52}$
B05	$C_{83.13}H_{118.68}N_1S_{0.5}O_{39.06}$	$C_{79.89}N_1S_{0.48}O_{33.02}$

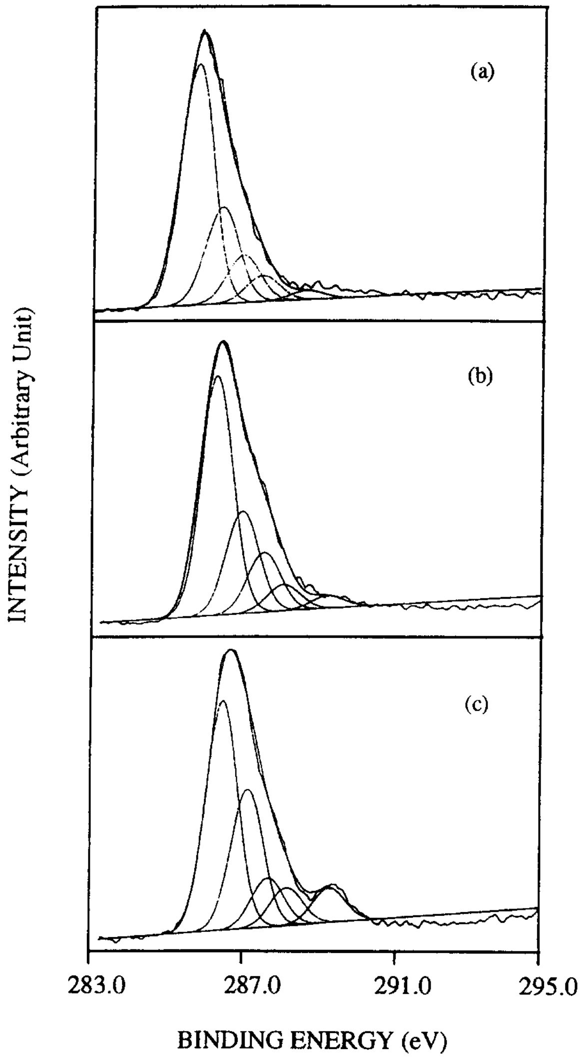

Figure 1 C1s X.p.s. spectra of (a) PANI-PSA, (b) B15 and (c) B40

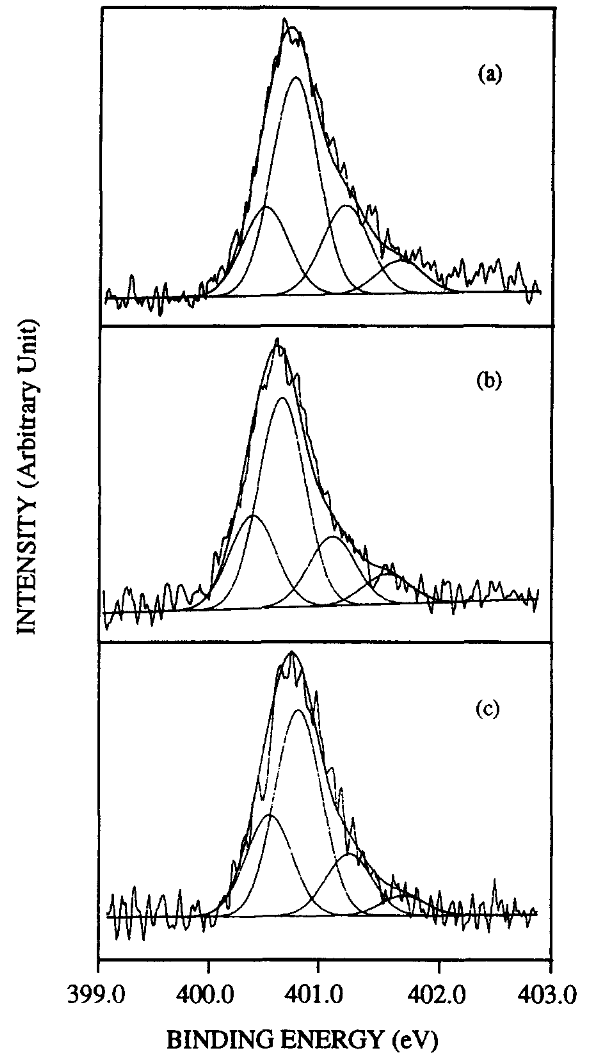

Figure 2 N1s X.p.s. spectra of (a) PANI-PSA, (b) B15 and (c) B40

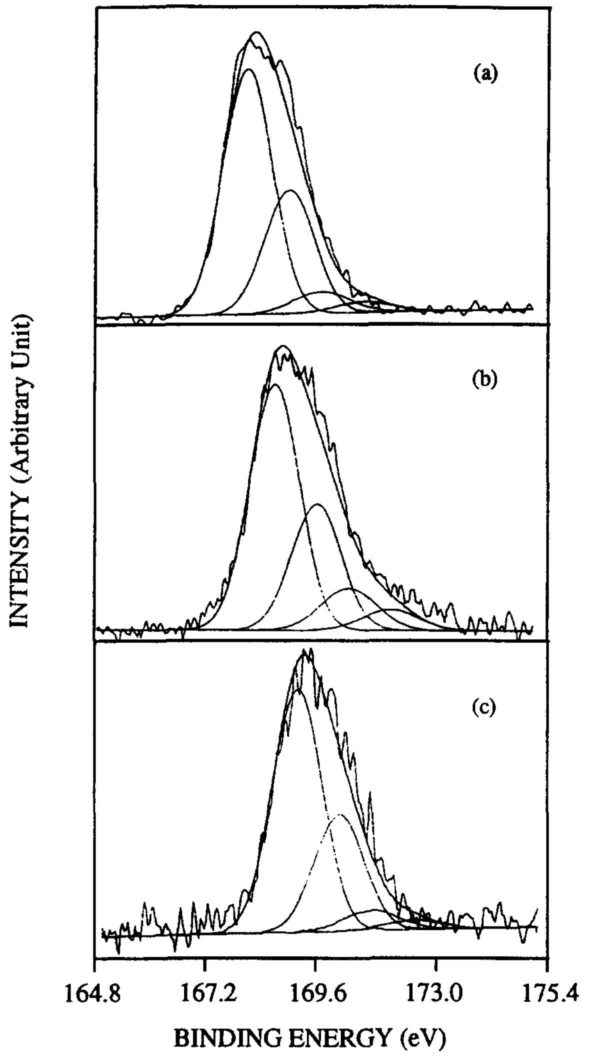

Figure 3 S2p X.p.s. spectra of (a) PANI-PSA, (b) B15 and (c) B40

the blend is also evidenced from the increased intensities of the C–O, C=O and O–C=O environments.

The N1s peak of PANI-PSA can be deconvoluted into four environments: N=C at 399.4 eV, N–C at 400.2 eV, $^+$N=C at 401.6 eV and $^+$N–C at 403.1 eV. Similarly the N1s peaks of the blends can be deconvoluted into the four environments and the various environments agree quite well with those of PANI-PSA, suggesting that no structural change or charge transfer reaction had occurred during the blending process.

The S2p peak of PANI-PSA shows a major component with S2p$_{3/2}$ binding energy at 168 eV, characteristic of covalently bonded $-SO_3^-$ species. The presence of residual DMSO in the sample is evidenced by the two minor components at higher binding energies. The S2p peaks of the two blend samples are similar to that of PANI-PSA, but they are displaced to higher binding energies.

The $S^-:N^+$ ratios, which give an indication of the degree of doping, of various blends are shown in *Table 2*. The ratios are fairly constant, indicating that PANI-PSA was not appreciable deprotonated in DMSO.

Miscibility studies

The d.s.c. curves of various blends and PVAc are shown in *Figure 4*. The PVAc sample for d.s.c. measurements was prepared by solution casting from DMSO and dried under the same conditions as the blend samples. The T_g of PANI-PSA is difficult to detect by d.s.c. As compared to PVAc, the T_g values of various blends shift to higher temperatures with increasing PANI-PSA content. Thus, the glass transition behaviour and the homogeneous appearance of the blends indicate miscibility between PANI-PSA and PVAc.

Table 2 Characteristic of blends

Sample	$S^-:N^+$ ratio	Binding energy (eV)	Conductivity (S cm^{-1})
PANI-PSA	1:0.75	285.0	2.5×10^0
B50	1:0.78	286.7	7.5×10^{-4}
B40	1:0.71	287.1	9.3×10^{-5}
B25	1:0.79	287.2	2.9×10^{-5}
B15	1:0.77	287.9	8.8×10^{-6}
B05	1:0.67	288.1	1.2×10^{-6}
PVAc	–	288.5	–

As mentioned earlier, PVPh is miscible with PVAc[13]. *FT*i.r. studies show the existence of hydrogen-bonding interactions between the phenolic hydroxyl groups and the acetate carbonyl groups[13]. *Figure 5* shows the *FT*i.r. spectra of PVAc and blends in the carbonyl absorption region. The carbonyl stretching vibration of PVAc occurs at 1739 cm^{-1}. Upon blending with PANI-PSA, the carbonyl band gradually shifts to lower frequencies, indicating that the carbonyl groups are interacting with some functional moieties of PANI-PSA. The extent of frequency shift of the carbonyl band is small but comparable to that observed in polycaprolactone/phenoxy blends[24]. In contrast, the addition of PVPh to PVAc leads to the development of a band at 1714 cm^{-1} (ref. 13). Thus, the interactions between PVAc and PANI-PSA are weaker than those between PVAc and PVPh. The hydroxyl band and the N–H band in PANI-PSA overlap, preventing the observation of any changes of these bands upon blending with PVAc.

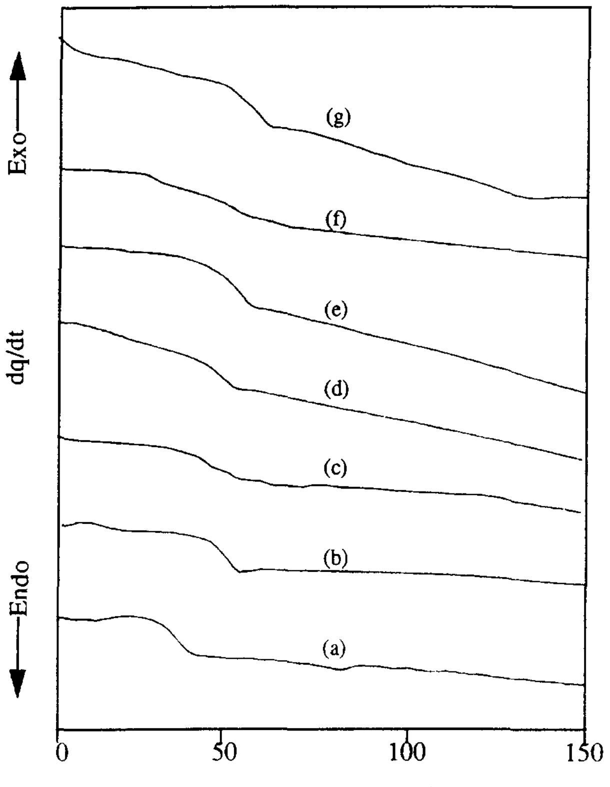

Figure 4 D.s.c. curves of (a) PVAc, (b) B05, (c) B10, (d) B15, (e) B25, (f) B40 and (g) B50

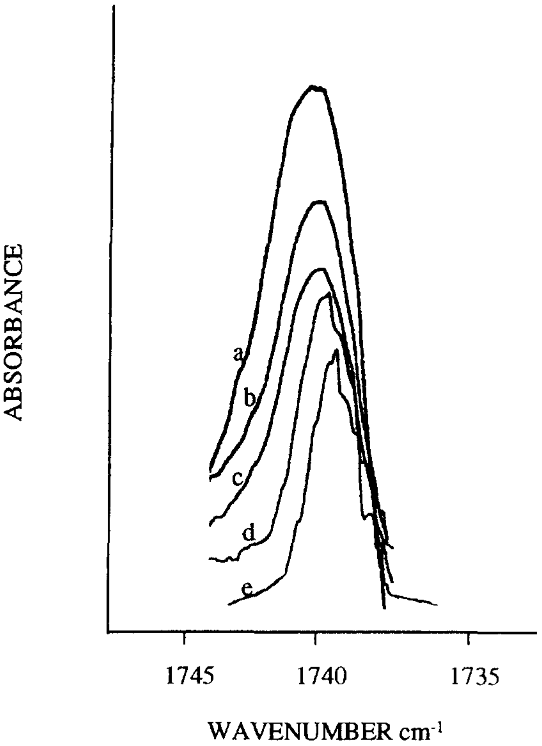

Figure 5 *FT*i.r. of the carbonyl group in (a) PVAc, (b) B05, (c) B10, (d) B25 and (e) B40

The interaction between the polymers can also be noted from the oxidative degradation curves through thermogravimetric analysis (t.g.a.) studies. T.g.a. curves of the polymers, a PANI-PSA/PVAc (1 : 3) blend and a PANI-PSA/PVAc (1 : 3) physical mixture, are given in *Figures 6* and *7*. The degradation of PANI occurs in three stages. The first stage is the loss of absorbed moisture and solvent from room temperature to around 150°C. The second stage, occurring between 150 and 350°C, is due to the loss of acid dopant in PANI salt and the degradation of PVAc chain. The final degradation of the polymer occurs from 350 to 650°C. The t.g.a. curve of the physical mixture can easily be resolved into that due to PANI, which shows a sharp loss in weight at around 390°C, and that due to PVAc which consists of two weight loss steps at approximately 430°C and 500°C.

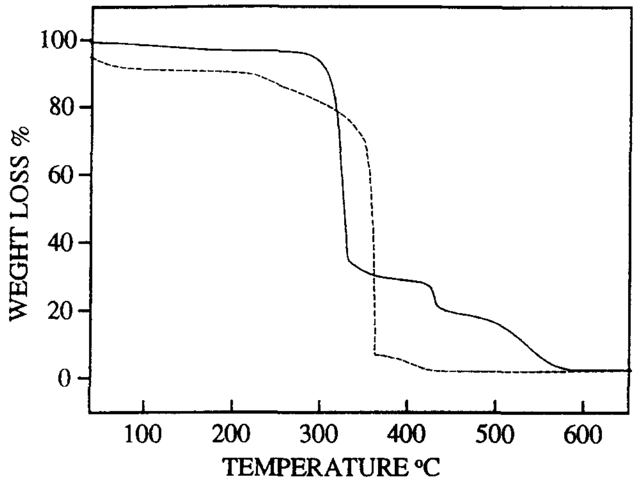

Figure 6 T.g.a. curves of (- - -) PANI-PSA and (—) PVAc

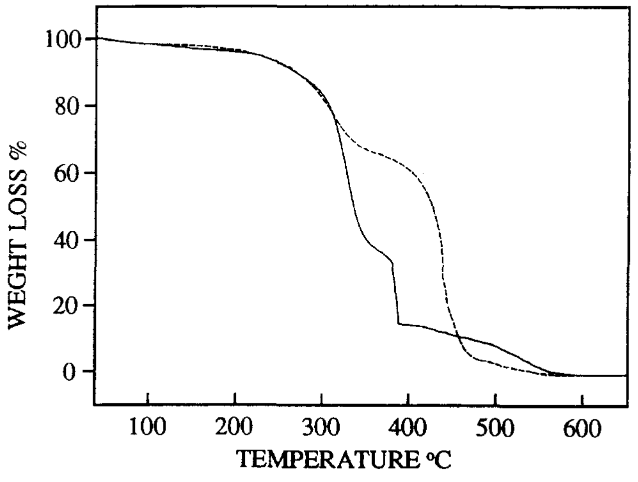

Figure 7 T.g.a. curves of 1 : 3 PANI-PSA/PVAc (- - -) blend and (—) physical mixture

These steps, however, are not observed in the t.g.a. curve of the blend, suggesting the presence of interaction between the polymers which alters the degradation pattern.

Conductivity

Conductivity measurements were taken on both sides of the films. The sides exposed to the atmosphere give lower conductivity values, but their values do not differ significantly from those obtained from the sides touching the glass substrate. The reasons for the slight difference in conductivities could be due to the escape of dopant into the atmosphere together with the solvent during evaporation, or due to the polar characteristic of the glass substrate which has a tendency to draw the dopant towards its surface. Thus, the mean value of both sides is taken as the conductivity of the blend. The results are presented in *Table 2*. The conductivities of the blends are 10^5 times lower than that of the PANI, owing to dilution with insulating PVAc component. The shift in the X.p.s binding energies of the C1s hydrocarbon component of the blends, form the reference at 285 eV, are also shown in *Table 2*. The shift correlates well with the decreasing order of conductivity from PANI-PSA, through the blend, to PVAc.

CONCLUSIONS

PANI-PSA/PVAc blends containing 5–50 wt% of PANI-PSA are miscible as shown by the presence of a single T_g, which shifts to a higher value with increasing PANI-PSA content. *FT*i.r. spectroscopic studies show the presence of intermolecular interactions between PANI-PSA and the carbonyl groups in PVAc. The conductivity of the blend decreases with increasing amount of PVAc. X.p.s. studies show no structural change of PANI-PSA upon blending with PVAc.

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