

Miscible Blends of Conductive Polyaniline with Tertiary Amide Polymers

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ABSTRACT: Polyaniline (PANI) was doped with *p*-phenolsulfonic acid (PSA) or 5-sulfosalicylic acid (SSA). The PANI salts were blended with poly(*N*-vinyl-2-pyrrolidone), poly(*N*-methyl-*N*-vinylacetamide), poly(*N,N*-dimethylacrylamide), or poly(2-methyl-2-oxazoline) by solution casting from dimethyl sulfoxide. Blends containing up to 50% by weight of PANI salt were homogeneous and each exhibited a single glass transition temperature, indicating miscibility. Fourier transform infrared spectroscopic studies indicated that the carbonyl groups of the tertiary amide polymers interacted with the PANI salt as evidenced by the development of a shoulder at a lower frequency in the carbonyl stretching band. Electrical conductivities of the blends are in the range 10^{-5} to 10^{-3} S/cm, depending on the blend composition. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1839–1844, 1998

Key words: blends; miscibility; polyaniline; tertiary amide polymers; conductivity; intermolecular interactions

INTRODUCTION

Polyaniline (PANI) is noted for its adequate level of conductivity, good environmental stability, ease of synthesis, and low cost. There have been many studies on blends of PANI with a large variety of polymers such as polystyrene, poly(vinyl chloride), and poly(methyl methacrylate).^{1–12} There are several methods to prepare PANI blends, including solution blending, melt blending, and *in situ* polymerization of aniline in a host polymer matrix. PANI blends offer several advantages such as reducing the amount of PANI necessary for conductivity, increasing the stability of conduction, and enhancing the mechanical properties of PANI.⁵ It has been pointed out since most PANI blends are immiscible the immiscibility may reduce many of the above-mentioned advantages.⁵

Stockton and Rubner⁵ earlier reported that the nonconducting PANI base is miscible with poly(*N*-vinyl-2-pyrrolidone) (PVP) up to 30% by weight of PANI. However, for blends prepared from acid-doped conductive PANI, there was some level of phase segregation as shown by the appearance of microaggregates in the blend films.⁶ Functionalized protonic acids (FPAs) such as dodecylbenzenesulfonic acid (DBSA) and camphorsulfonic acid (CSA) have been used as dopants in place of inorganic acids such as HCl.^{1,2} The FPAs possess functional groups which are compatible with nonpolar or weakly polar organic solvents, enabling the PANI–FPA salts to be soluble in common organic solvents.

Miscibility between two polymers generally requires the presence of favorable intermolecular interaction. If the FPA in PANI–FPA possesses suitable functional groups which are capable of interacting with some functional groups of the other polymer, miscibility may be achieved. We used *p*-phenolsulfonic acid (PSA) and 5-sulfosalicylic acid (SSA) as FPAs to dope PANI in view of

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the ability of hydroxyl and carboxylic acid groups to interact with proton-accepting polymers through hydrogen bonding.^{13,14} PANI-PSA is miscible with poly(vinyl acetate) up to 50 wt % of PANI-PSA in the blend.¹³ PANI-PSA and PANI-SSA are miscible with poly(2-ethyl-2-oxazoline) (PEOx), a tertiary amide polymer, up to 50 wt % PANI-FPA in the blend.¹⁴

We extended our study to blends of PANI-PSA and PANI-SSA with the other tertiary amide polymers, namely, PVP, poly(*N*-methyl-*N*-vinylacetamide) (PMVAc), poly(*N,N*-dimethylacrylamide) (PDMA), and poly(2-methyl-2-oxazoline) (PMOx). Our recent studies have shown that among the tertiary amide polymers PVP and PMVAc show the best ability to be miscible with proton-donating polymers.¹⁵⁻¹⁸

EXPERIMENTAL

Materials

PANI-PSA and PANI-SSA were prepared as described previously by oxidation polymerization of aniline in aqueous 1.0M PSA or SSA solution.¹³ PVP with a reported weight-average molecular weight (M_w) of 40 kg/mol was obtained from Scientific Polymer Products (Ontario, NY). PMVAc and PDMA were prepared by free-radical polymerization in 1,4-dioxane at 80°C for 4 h using azobisisobutyronitrile as the initiator. The number-average molecular weight (M_n) and M_w are, respectively, 9.5 and 15 kg/mol for PMVAc and 12 and 20 kg/mol for PDMA. PMOx was prepared by ring-opening polymerization of 2-methyl-2-oxazoline as described previously.¹⁷ The M_n and M_w of PMOx are 12 and 18.5 kg/mol, respectively.

Preparation of Blends

Polymer blends of varying compositions were prepared by solution casting from dimethyl sulfoxide (DMSO). DMSO solutions of PANI-PSA (0.7% w/v), PANI-SSA (0.7% w/v), and tertiary amide polymers (4% w/v) were separately prepared. Appropriate amounts of the two solutions were then mixed. The well-mixed solution was transferred to an aluminum dish and allowed to dry *in vacuo* at 50°C. The resulting blend was further dried *in vacuo* at 90°C for 2 weeks.

Glass Transition Temperature (T_g) Measurements

A TA Instruments 2910 differential scanning calorimeter was used to determine the T_g 's of the sam-

ples. Measurements were made using a heating rate of 20°C/min under a nitrogen purge of 60 mL/min. The initial inflection of the slope of the differential scanning calorimetry (DSC) curve was taken as the T_g .

Fourier Transform Infrared (FTIR) Spectroscopic Measurements

FTIR measurements were made on a Perkin-Elmer 1600 FTIR spectrophotometer; sixty-four scans were signal-averaged at a resolution of 2 cm^{-1} . Samples were prepared by grinding the blend with KBr and compressing the mixture to form a disk. In view of the hygroscopic nature of the tertiary amide polymers, spectra were acquired at 100°C using a SPECAC high-temperature cell equipped with an automatic temperature controller.

Electrical Conductivity Measurements

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

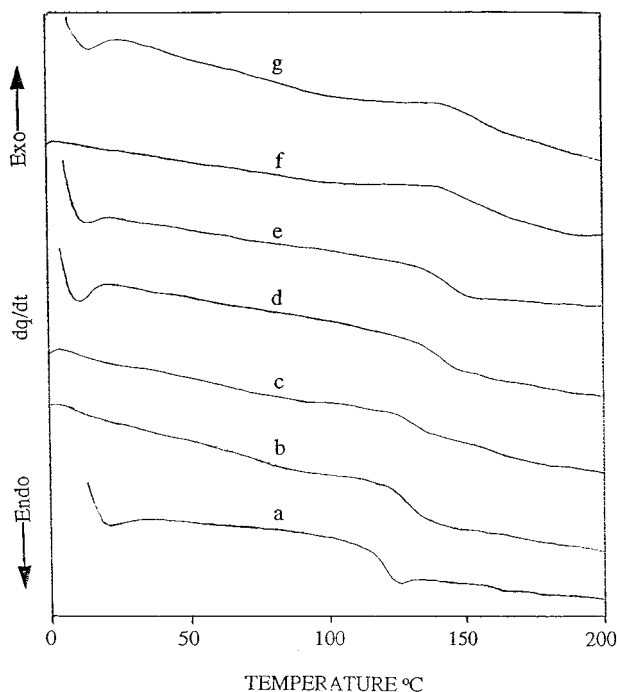


Figure 1 DSC curves of PDMA/PANI-SSA blends: (a) 0, (b) 5, (c) 10, (d) 20, (e) 30, (f) 40, and (g) 50 wt % of PANI-SSA.

Table I Characteristics of PMVAc Blends

Composition (wt % PANI)	PMVAc/PANI-PSA		PMVAc/PANI-SSA	
	T_g (°C)	Conductivity (S/cm)	T_g (°C)	Conductivity (S/cm)
5	134	3.5×10^{-5}	135	7.8×10^{-5}
10	136	7.6×10^{-5}	137	9.3×10^{-5}
20	138	9.1×10^{-5}	139	4.6×10^{-4}
30	141	3.8×10^{-4}	142	7.8×10^{-4}
40	142	6.2×10^{-4}	144	1.1×10^{-3}
50	143	8.6×10^{-4}	145	1.7×10^{-3}

samples. To exclude moisture, samples were kept in an oven at 100°C for 1 h prior to the measurements.

RESULTS AND DISCUSSION

Miscibility Studies

Various binary blends of PANI-PSA or PANI-SSA with PVP, PMVAc, PDMA, and PMOx were prepared. The well-mixed solutions were clear for all blend compositions before casting. Blends containing 5 or 10 wt % of PANI-PSA or PANI-SSA were green and transparent; those containing 20–50 wt % of PANI-PSA or PANI-SSA were dark green in color but were also homogeneous by visual inspection. All the homogeneous blends were flexible. It is of interest to note that the blends of PVP with PANI doped with methane sulfonic acid (MSA), CSA, or DBSA showed some level of phase separation.⁶ However, the present work shows that blends of PVP with PANI-PSA or PANI-SSA are homogeneous up to 50 wt % of PANI salt. The results demonstrate the advantage of using dopants such as PSA and SSA which possess hy-

droxyl and carboxylic acid groups capable of interacting with PVP. In contrast, MSA, CSA, and DBSA do not possess interacting functional groups. However, blends containing 60 wt % or more of PANI-PSA or PANI-SSA were brittle and showed signs of phase separation, and these blends were not further studied.

The T_g values of PVP, PMVAc, PDMA, and PMOx as cast from DMSO are 168, 133, 117, and 65°C, respectively. The samples were dried under the same conditions as were those of the blends. Figure 1 shows the DSC curves of various PANI-SSA/PDMA blends. These curves clearly show that the T_g value of the blend gradually shifts to a higher temperature with increasing PANI-SSA content in the blend. Similar trends on the change of the T_g value with composition were also observed for PANI-PSA/PDMA, PANI-SSA/PMVAc, PANI-PSA/PMVAc, PANI-SSA/PMOx, and PANI-PSA/PMOx blend systems (Tables I–III). Figure 2 shows the DSC curves of various PANI-SSA/PVP blends. In this case, the T_g value of the blend gradually decreases with increasing PANI-SSA content in the blend. PANI-PSA/PVP blends also showed a similar trend of their

Table II Characteristics of PDMA Blends

Composition (wt % PANI)	PDMA/PANI-PSA		PDMA/PANI-SSA	
	T_g (°C)	Conductivity (S/cm)	T_g (°C)	Conductivity (S/cm)
5	120	4.5×10^{-5}	120	5.1×10^{-5}
10	122	9.8×10^{-5}	123	8.7×10^{-5}
20	126	2.7×10^{-4}	129	2.4×10^{-4}
30	130	5.6×10^{-4}	134	6.7×10^{-4}
40	133	8.7×10^{-4}	138	9.6×10^{-4}
50	137	1.3×10^{-3}	140	2.1×10^{-3}

Table III Characteristics of PMOx Blends

Composition (wt % PANI)	PMOx/PANI-PSA		PMOx/PANI-SSA	
	T_g (°C)	Conductivity (S/cm)	T_g (°C)	Conductivity (S/cm)
5	69	1.7×10^{-5}	70	2.2×10^{-5}
10	74	2.6×10^{-5}	77	3.6×10^{-5}
20	79	6.5×10^{-5}	83	8.7×10^{-5}
30	84	2.3×10^{-4}	89	3.1×10^{-4}
40	88	7.8×10^{-4}	95	9.7×10^{-4}
50	92	1.1×10^{-3}	100	1.9×10^{-3}

T_g values as a function of composition (Table IV). We were unable to detect with certainty the glass transitions of PANI-SSA and PANI-PSA from their DSC curves. The difficulty in the detection of the glass transition of PANI is also exemplified in Figures 1 and 2. The glass transition of the blend broadens considerably with increasing PANI content in the blend. Thus, for PANI and blends with high PANI contents, the glass transitions are likely to be so broad that it becomes very difficult to pinpoint the onset of the glass transition. It is also difficult to estimate the T_g values of PANI-PSA and PANI-SSA by extrapolation. Based on the T_g plot as shown in Figure 3,

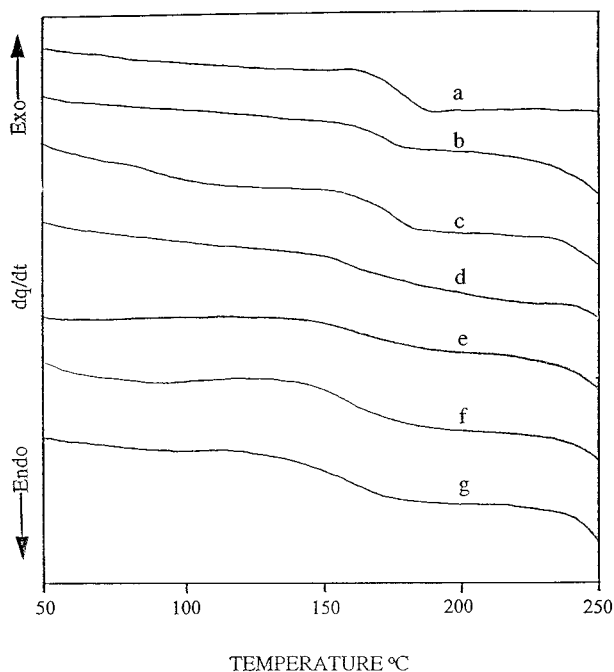


Figure 2 DSC curves of PVP/PANI-SSA blends: (a) 0, (b) 5, (c) 10, (d) 20, (e) 30, (f) 40, and (g) 50 wt % of PANI-SSA.

the T_g value of PANI-PSA is expected to be around 120°C using the T_g values of PMOx and PVP blends and around 150°C using the T_g values of PDMA and PMVAc blends. Nevertheless, the existence of a composition-dependent T_g and the homogeneous appearance of the blends can be taken to indicate miscibility.

FTIR Characterization

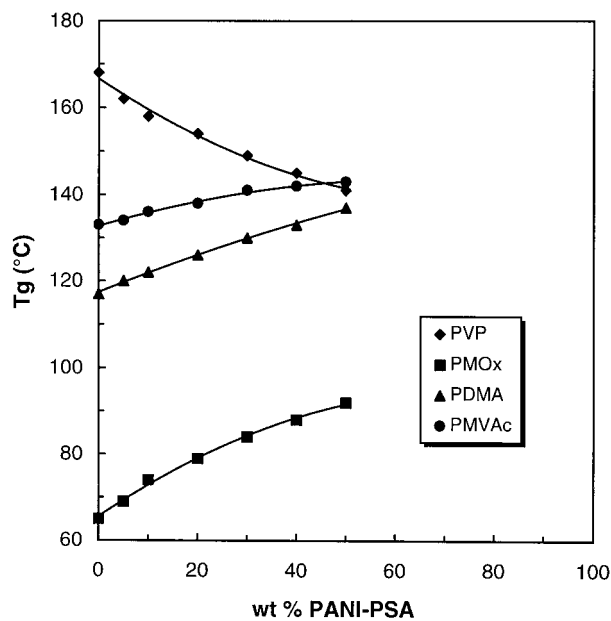
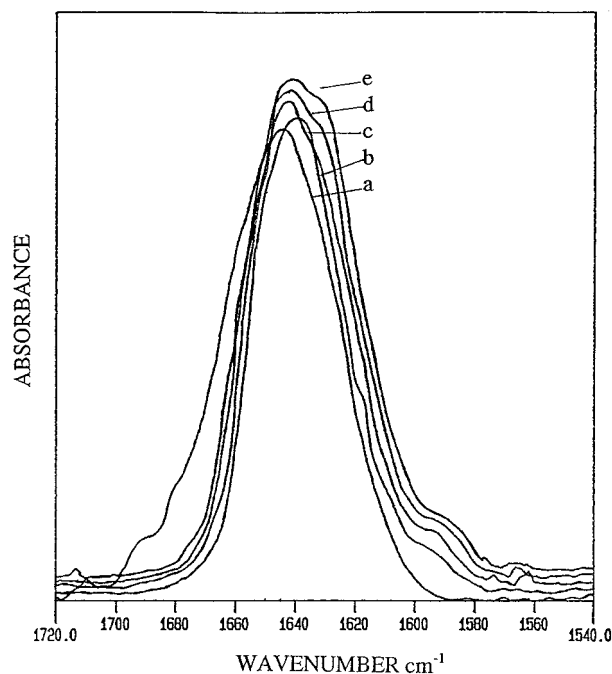
It is well known that tertiary amide polymers interact with proton-donating polymers via hydrogen bonding through their carbonyl groups and such interactions are evidenced from FTIR studies. Figure 4 shows the FTIR spectra in the carbonyl stretching region of various PANI-PSA blends at 100°C. The carbonyl band of PDMA is centered at 1644 cm^{-1} (curve a). When a small amount of PANI-PSA is added to PDMA, the center of the carbonyl band shifts to a lower frequency, showing that the carbonyl groups are interacting with PANI-PSA (curve b). A further increase of PANI-PSA content in the blend leads to the development of a shoulder band at 1630 cm^{-1} which is ascribed to the carbonyl groups hydrogen-bonded to the hydroxyl groups in PANI-PSA. The difference in frequency between the hydrogen-bonded carbonyl band and the free carbonyl band ($\Delta\nu$) is 14 cm^{-1} , which is larger than that observed in the PEOx/PANI-PSA blend system (8 cm^{-1}) reported previously.¹⁴ Figure 5 shows the FTIR spectra of various PDMA/PANI-SSA blends. The addition of PANI-SSA leads to the development of a shoulder band at 1628 cm^{-1} . The $\Delta\nu$ value of the PDMA/PANI-SSA blend system (16 cm^{-1}) is slightly larger than that in the PDMA/PANI-PSA blend system. The FTIR spectra of the other blend systems show the same features as those of the PDMA/PANI blend system and these spectra are not shown here.

Table IV Characteristics of PVP Blends

Composition (wt % PANI)	PVP/PANI-PSA		PVP/PANI-SSA	
	T_g (°C)	Conductivity (S/cm)	T_g (°C)	Conductivity (S/cm)
5	162	5.2×10^{-5}	160	6.6×10^{-5}
10	158	8.2×10^{-5}	157	8.8×10^{-5}
20	154	1.5×10^{-4}	152	3.8×10^{-4}
30	149	5.4×10^{-4}	146	7.3×10^{-4}
40	145	1.0×10^{-3}	141	9.4×10^{-4}
50	141	1.5×10^{-3}	136	3.1×10^{-3}

The frequency shift, $\Delta\nu$, gives an indication of the relative strength of intermolecular interactions. For the PANI-PSA blends, the $\Delta\nu$ value decreases in the order PVP (15 cm^{-1}) = PMVAc (15 cm^{-1}) > PDMA (14 cm^{-1}) > PMOx (12 cm^{-1}) > PEOx (8 cm^{-1}). For the PANI-SSA blends, the $\Delta\nu$ value decreases in the order PVP (17 cm^{-1}) = PMVAc (17 cm^{-1}) > PDMA (16 cm^{-1}) > PMOx (15 cm^{-1}) > PEOx (10 cm^{-1}). Therefore, the ability of the tertiary amide polymer to interact with PANI is in the order PVP = PMVAc > PDMA > PMOx > PEOx. The order is consistent with our previous studies of blends of tertiary amide polymers with various hydroxyl-containing polymers.¹⁵⁻¹⁸ Our studies have consistently shown that among the five tertiary amide polymers PVP and PMVAc have the best ability to interact with

other polymers. We have proposed that the steric effect is an important factor governing the interacting ability of these polymers.¹⁶ The carbonyl groups of PDMA, PMOx, and PEOx are only one bond length away from the main chains, while those of PVP and PMVAc are two bond lengths away from the main chains. Therefore, the carbonyl groups of PVP and PMVAc are more accessible for interaction with other polymers. Similarly, the steric effect can also account for the difference in the interacting ability between PMOx and PEOx.^{17,19} As compared with PEOx, the smaller methyl groups in PMOx allow the carbonyl groups

**Figure 3** T_g plot for PANI-PSA blends.**Figure 4** FTIR spectra, recorded at 100°C, in the carbonyl region of PDMA/PANI-PSA blends: (a) 0, (b) 20, (c) 30, (d) 40, and (e) 50 wt % of PANI-PSA.

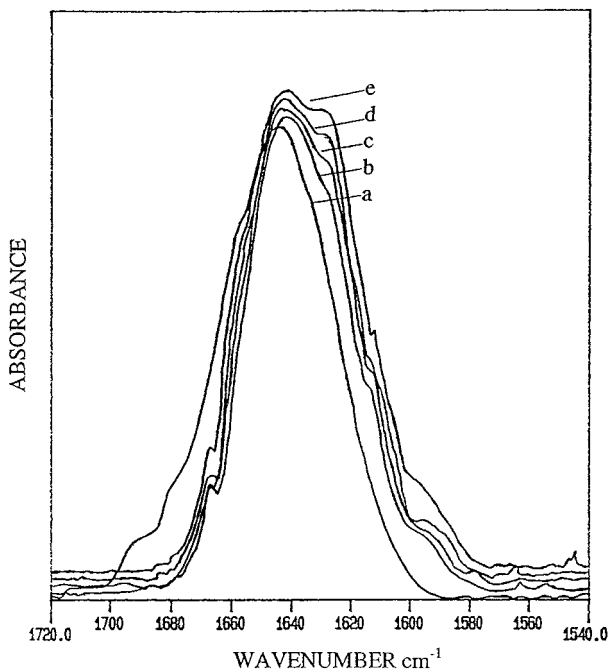


Figure 5 FTIR spectra, recorded at 100°C, in the carbonyl region of PDMA/PANI-SSA blends: (a) 0, (b) 20, (c) 30, (d) 40, and (e) 50 wt % of PANI-SSA.

to be more accessible for interaction. The frequency-shift values also indicate that the interactions between PANI-SSA and various tertiary amide polymers are slightly more intense than are those between PANI-PSA and the tertiary amide polymers. The presence of two interacting functional groups, hydroxyl and carboxylic acid groups, in SSA may account for the observation.

Electrical Conductivity

Tables I-IV show the electrical conductivities of various blends. The conductivity increases with increasing PANI in the blend. For blends containing 50 wt % of PANI-PSA or PANI-SSA, the conductivities are in the order of 10^{-3} S/cm.

CONCLUSIONS

Miscible blends of PANI-PSA or PANI-SSA with tertiary amide polymers up to 50 wt % of the PANI

salt can be prepared. Electrical conductivities of the blends range from 10^{-5} to 10^{-3} S/cm, depending on the blend composition. FTIR studies show that the ability of the tertiary amide polymer to interact with the PANI salt is in the order PVP = PMVAc > PDMA > PMOx > PEOx.

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