Water-Soluble Conductive Blends of Polyaniline and Poly(vinyl alcohol) Synthesized by Two Emulsion Pathways

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ABSTRACT: Water-soluble, electrically conductive polyaniline (PANI)–poly(vinyl alcohol) (PVA) blends of different compositions (10, 30, 50, and 70 w/w) were synthesized by emulsion and inverted emulsion methods with ammonium persulfate and benzoyl peroxide as the oxidants, respectively, with PANI protonated with sulfosalicylic acid. The absorption, Fourier transform infrared, Fourier transform Raman, NMR, and electron paramagnetic resonance (EPR) spectroscopic studies suggested chemical interaction between PANI and PVA. The morphology of the blends depended on the method of synthesis as observed from scanning electron microscopy, X-ray diffraction, and particle size measurements. The blends showed relatively improved mechanical strengths but had lower degradation temperatures than the PANI salt and displayed conductivities as high as 10^{-2} to 10^{-1} S/cm. The blends synthesized by the inverse emulsion method had smaller particle sizes, higher crystallinities, and better mechanical properties. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 583–590, 2005

Key words: blends; emulsion polymerization; conducting polymers; mechanical properties

INTRODUCTION

Progress in the processability of polyaniline (PANI) has resulted in the fabrication of several types of conductive PANI blends[1,2] with such engineering polymers as polystyrene,[3,4] poly(vinyl chloride),[5] and polyamides.[6] There is a demand for blend materials that combine flexibility and high electronic conductivity.[7] Two main pathways have been used for the chemical synthesis of PANI blends. One approach is the dissolution of PANI in a solution or a melt of the industrial polymer.[8–10] The other method, which consists of the polymerization of aniline in the presence of the industrial polymer, is desirable from the technological point of view.[9–12]

Poly(vinyl alcohol) (PVA) is a water-soluble polymer with a high transparency and a good flexibility. Recently, the preparation of PANI–PVA blends and composites has evoked interest.[13–18] PANI–PVA composites have been synthesized by a cosolvation technique with different polar organic solvents.[13] Gospodinova and coworkers[13–15] were the first to synthesize stable PANI–PVA dispersions in an aqueous medium.

The electrochemical characterization of PANI–PVA composite films has been reported.[16,17] A solution dispersion method to synthesize PANI–PVA composites was carried out recently with HCl as the dopant.[18]

In this article, the synthesis by inverted emulsion and emulsion polymerization of PANI–PVA blends with benzoyl peroxide (BPO) and ammonium persulfate as the oxidants, respectively, is described. Traditionally, ammonium persulfate has been used in the polymerization of aniline. Because ammonium persulfate is a strong oxidizing agent and the polymerization of aniline is exothermic, controlling the reaction temperature is rather difficult, and consequently, the reaction may result in polymers with a wide distribution of molecular weights. The removal of the inorganic byproducts (ammonium sulfate) from the polymer produced is also difficult. To overcome this limitation, a mild organic oxidant, namely, BPO, an initiator in many polymerization reactions, has been employed. Here, the excess of oxidant is easily removed with solvents such as acetone used as a nonsolvent in the inverse emulsion process. PANI blends containing 10, 30, 50, and 70 w/w of PVA prepared by the two methods were characterized by various physicochemical techniques, and their properties were compared.

EXPERIMENTAL

Materials

Aniline (Merck, Dorset, UK) was distilled twice *in vacuo*. Chloroform was distilled over calcium chloride.

PVA (weight-average molecular weight ≈ 14,000) and all of the other chemicals were analytical-grade reagents.

Synthesis of PANI–PVA blends

Initially, the ratio of aniline to PVA required to prepare a given blend was determined by the polymerization of aniline under identical conditions. From the yield of PANI sulfosalicylic acid salt obtained, the amount of aniline required to prepare a given blend was determined. By keeping the ratio of aniline to the oxidant constant and by varying the ratio of aniline to PVA, we synthesized blends of different compositions (10, 30, 50, and 70 w/w).

The effect of oxidant/monomer concentration on the oxidative polymerization of aniline by BPO by the inverted emulsion method was investigated in this laboratory.[19] The yield and the conductivity of PANI increased up to $0.2M$ of the oxidant for $0.1M$ of the monomer. A further increase in the concentration of BPO resulted in decreases in the yield and the conductivity of PANI. Therefore, an oxidant/monomer molar ratio of 2 was employed for the polymerization of aniline by the inverted emulsion method. Similarly, the oxidative polymerization of aniline by ammonium persulfate in aqueous solution as a function of the oxidant/monomer initial molar ratio (r) was investigated by Armes and Miller.[20] The conductivity, yield, elemental composition, and degree of oxidation of the resulting PANI were essentially independent for values of r of less than 1.15. Higher r values resulted in the overoxidation of PANI with a concomitant decrease in conductivity and yield. Therefore, the oxidant/monomer molar ratio was kept at 1.0 for the polymerization of aniline by the emulsion process.

The effect of the oxidant/monomer concentration on the conductivity of blends may be assumed to be the same as that noted for PANI because the conductivity of the blends arise from that of PANI.

Inverted emulsion polymerization

An aqueous solution of sodium lauryl sulfate (an emulsifier), PVA, and the dopant sulfosalicylic acid constituted the continuous phase, and the chloroform solution of aniline with the oxidant BPO constituted the dispersed phase. In a typical experiment, to 24.2 g of BPO in 200 mL of chloroform an aqueous solution (50 mL) of the emulsifier (4.5 g) and an aqueous solution (100 mL, 5.3 g) of PVA were added with stirring. Aniline (4.5 mL) was then added. To the resulting milky white emulsion, 100 mL of aqueous $0.1M$ sulfosalicylic acid was added dropwise with continuous stirring over a period of 30 min. The emulsion gradually turned green. The reaction mixture was put aside for 24 h. The viscous organic phase was sepa-

rated afterward and washed repeatedly with water. It was added to 1.5 L of acetone to break the emulsion and precipitate the blend. The product, which was recovered by filtration as a dark green powder, was washed with acetone and dried *in vacuo* for 36 h.

Emulsion polymerization

An aqueous solution of the oxidant, the dopant, PVA, and the emulsifier formed the continuous phase, whereas a solution of aniline in chloroform constituted the dispersed phase. To an aqueous solution (100 mL) of PVA (5.9 g), 4.5 g of the emulsifier and 12.7 g of sulfosalicylic acid, each in 50 mL of water, were added. To this, 4 mL of aniline in 200 mL of chloroform were added with stirring. To the resulting emulsion, an aqueous solution (100 mL) of ammonium persulfate (11.4 g) was added dropwise over a period of 30 min. The milky white emulsion turned green. The reaction was allowed to proceed for 24 h. The blend was precipitated, washed, and dried as before.

Measurements

The ultraviolet–visible absorption spectra of the blends in dimethyl sulfoxide (DMSO) and water were measured in a Hitachi U-3000 spectrophotometer (Hitachi, Tokyo, Japan). Fourier transform infrared (FTIR) spectra were recorded with a Bruker Equinox 55 instrument (Bruker, Billerca, MA) by the KBr pellet technique. Fourier transform (FT) Raman spectra were obtained with a Bruker RFS100/S spectrometer with a Nd^{3+}:yitrium aluminum garnet (YAG) laser with 30–40 mW of power at the sample. Electron paramagnetic resonance (EPR) spectra were recorded with a Varian E109 spectrometer (Varian Co., San Francisco, CA) operating in the X-band. The sample tube was evacuated to remove the moisture before the spectrum was recorded. To obtain the g (Landé splitting factor) value and spin concentration, the EPR spectra of the samples and charred dextrose as a standard were recorded under identical conditions of microwave frequency (9.05 GHz), microwave power (2 mW), modulation frequency (100 kHz), fieldset (3280 G), scan range (100 or 200 G), modulation intensity (1Gpp), modulation time (0.064 s), and scan time (200 s). Spin concentration was determined by the comparison of the area under the EPR signal of the sample with that of charred dextrose. The calculated areas were likely to be within 5% of the true value.[21] 1H-NMR spectra were measured on a Bruker AMX 400-MHz spectrometer in DMSO-d_6 with tetramethylsilane as an internal reference. Electrical conductivities (direct current) were measured at ambient temperature by the four-probe method. The composites were pressed into pellets by the application of 50 kNm of pressure. The error in the resistance measurements under galvano-

TABLE I
Yield, Conductivity, and Absorption Maximum (λ_{max}) Values of PANI Salt and Its Blends with PVA

Sample	λ_{max} (nm; in DMSO)				Yield (g)	Conductivity (S/cm)
Inverted emulsion method						
PANI	330.0	440.0	630.0	825.0	5.3	5.9×10^{-1}
VA10	316.5	454.5	628.0	—	7.2	4.3×10^{-1}
VA30	302.0	345.5	593.5	—	10.1	1.5×10^{-1}
VA50	306.0	342.0	600.0	—	15.9	2.4×10^{-2}
VA70	301.0	333.5	620.0	—	20.4	—
Emulsion method						
PANI(A)	309.5	378.5	587.0	763.5	5.9	1.3
VA10A	297.0	358.5	571.5	—	6.0	1.4×10^{-1}
VA30A	307.5	—	606.5	—	9.3	1.1×10^{-1}
VA50A	309.5	440.0	604.5	—	12.7	5.8×10^{-2}
VA70A	304.5	—	585.5	—	21.3	—

static conditions with a Keithley model 220 programmable current source (Keithley Instruments, Inc., Cleveland, OH) and a Keithley model 195A digital voltammeter was less than 2%. The scanning electron microscopy (SEM) measurements were carried out with a Jeol JSM 480A scanning electron microscope (JEOL, Tokyo, Japan). X-ray diffraction patterns were recorded in the region of 5–40° with a Jeol JDX-8P X-ray diffractometer with Cu K$_\alpha$ radiation. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were recorded up to 800°C with a SDTA 851E thermal analyzer at a heating rate of 10°C/min under a nitrogen atmosphere. The blends were finely powdered and then palletized with a pressure of 4 tons/cm². Compression testing of these pellets was performed with a DARTEC computer-controlled Servo Hydraulic 9500 compression tester (Dartec Ltd., Stourbridge, UK). Surface microhardness was determined with a Shimadzu 2000 microhardness tester (Shimadzu, Kyoto, Japan). The mean diameter of the particles was measured with Malvern Master Sizer particle size analyzer (Malvern, Worcestershire, UK).

RESULTS AND DISCUSSION

The blends were relatively more soluble in solvents such as DMSO. As the amount of PVA in the blend increased, it became more soluble in warm water. The PANI blends synthesized by the inverse emulsion method that contained 10, 30, 50, and 70 w/w of PVA were designated VA10, VA30, VA50, and VA70, respectively. The blends prepared by the other method were labeled VA10A, VA30A, VA50A, and VA70A, respectively. The yield of the blends obtained by both the methods was high (ca. 95%; Table I).

Absorption spectra

Table I shows the absorption bands of PANI–PVA blends dissolved in DMSO. The spectra of the blends

VA50 and VA50A in DMSO and water, respectively, are given in Figure 1. The absorption spectrum helped to detect the presence or otherwise of the PANI salt and its base. The solution spectrum of the PANI base in DMSO exhibited two bands near 325 and 625 nm. On the other hand, the PANI salt (synthesized with the inverted emulsion method) in DMSO showed four bands at 330, 440, 630, and 825 nm, and that synthesized by the emulsion method also showed four bands, three fairly intense bands at 310, 587, and 764 nm and a weak band at 379 nm. The first band near 325 nm was assigned to the π–π^* transition of the phenyl rings.[22] The second adsorption band at 620 nm was assigned to the exciton transition of the quinoid ring.[22] The remaining bands near 430 and 830 nm of the salt were assigned to polaron transitions.[23]

The blends synthesized by the inverse emulsion method showed three peaks at 300, 350, and 600 nm. The band at 400 nm was very weak, and it was not observed when the PVA content was higher. The conductivity of the blends also decreased (Table I) with
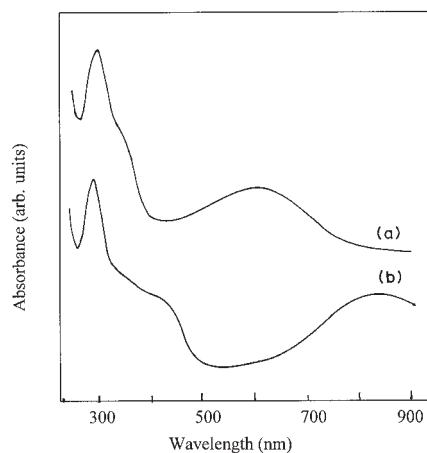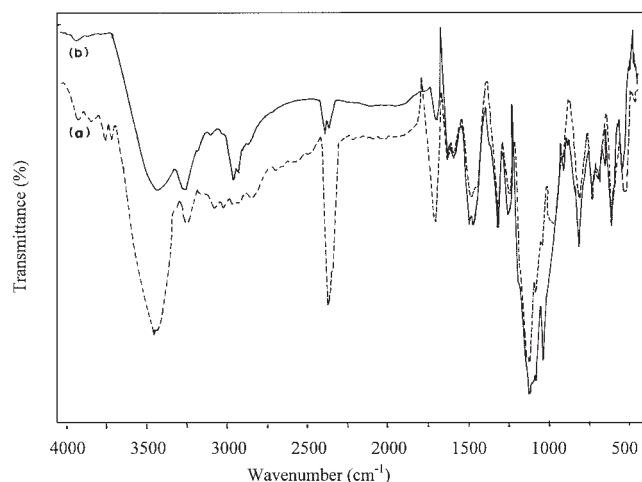

Figure 1 Electronic absorption spectra of PANI–PVA blends: (a) VA50 in DMSO and (b) VA50A in water.

Figure 2 FTIR spectra of (a) PANI sulfosalicylic acid salt and (b) its blend VA50.

decreasing intensity of the polaron peak at 400 nm. The blends prepared by the emulsion method exhibited only two peaks around 310 and 600 nm. The absence of the other two peaks around 430 and 820 nm was due to the poor solubility of the blends in DMSO. The blends with higher PVA contents (e.g., 50, 30, and 70) prepared by either method were soluble in water and gave rise to three peaks near 300, 425, and 850 nm (Fig. 1), whereas those with lower PVA contents were insoluble in water. The absorption spectra of the blends confirmed the presence of PANI in the salt form. The absorption spectrum of a film of an electrochemically synthesized PVA blend has been reported to show bands at 330, 420, 580, and 800 nm.[17]

FTIR and FT Raman spectra

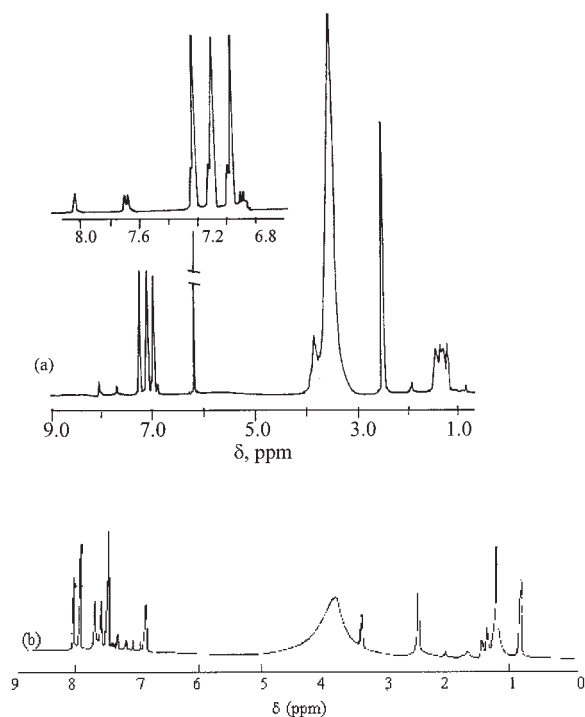The FTIR spectra of PANI sulfosalicylic acid salt and its blend with PVA, VA50, are given in Figure 2. The peak at 1573 cm^{-1} in the PANI salt spectrum, due to the C=C stretching vibration of the benzenoid ring, shifted to a lower wave number (1555 cm^{-1}) in the blends, indicating a decrease in polaron delocalization.[11] The intensity of the peak at 1470 cm^{-1} in the blends increased with increasing PVA content in the blend (Fig. 2). Both PANI salt and PVA showed bands in this region, which were assigned to C=N stretching of the quinoid ring, which was caused by the protonation of PANI (1466 cm^{-1}) by the dopant, and the CH$_2$ bending (1432 cm^{-1}) of PVA.[24] The band shifted in the spectra of the blends, and the change in the intensities suggested chemical interaction between PANI and PVA, which may have been through hydrogen bonding.[25] This was supported by the increase in the broadness of the peak at 3300 cm^{-1} in the spectra of the blends.

The Raman spectra of the blends were closer to that of PANI sulfosalicylic acid salt, even for the blends with higher PVA content. For the blends synthesized by the inverted emulsion method, the band at 1170 cm^{-1} assignable to the out-of-plane C—H bending in the PANI salt became broad with increasing PVA content in the blend. The peak at 1352 cm^{-1} due to N—H bending mode of the PVA salt shifted by about 16 cm^{-1} in the blend. The peak also became broader with increasing PVA content. This shift and broadening of the band indicated the presence of hydrogen bonding in the blends. The broad asymmetric peak at 1592 cm^{-1} in the salt spectrum assigned to C—C ring stretching vibration also registered a shift by about 8 cm^{-1} in the spectra of the blends. The band at 1533 cm^{-1}, which was of medium intensity in the spectrum of PVA salt, diminished in intensity in the blend with increasing PVA and almost disappeared in the spectrum of VA70. The FTIR and FT Raman spectra of the blends synthesized by the inverse emulsion method were

TABLE II
EPR Parameters for PANI-PVA Blends

Sample	g	ΔH (G)	Spin concentration (spins/g)	A/B ratio
Inverted emulsion method				
PANI	2.0037	1.40	2.2287×10^{20}	0.9700
VA10	2.0025	2.50	3.6324×10^{18}	0.9783
VA30	2.0031	3.00	4.7755×10^{18}	1.0580
VA50	2.0031	5.00	1.0067×10^{18}	1.0680
VA70	2.0046	1.75	1.3162×10^{18}	1.0560
Emulsion method				
PANI(A)	2.0048	1.75	4.2298×10^{18}	1.0286
VA10A	2.0028	2.00	3.2980×10^{18}	0.9765
VA30A	2.0032	2.00	3.2952×10^{18}	1.0145
VA50A	2.0037	3.00	3.1940×10^{18}	1.0806
VA70A	2.0034	2.25	9.4270×10^{17}	1.0909

Figure 3 ^{1}H-NMR spectrum of (a) the blend VA50A and (b) PANI sulfosalicylic acid salt.

more resolved than those of the blends synthesized with the other method.

EPR spectra

Table II presents the spin concentrations, line widths (ΔHs), g values, and ratios of the height of the positive to the negative peak (A/B peak ratio) obtained from the EPR spectra of the blends. The ambient-temperature EPR spectra of the blends showed a single signal without a hyperfine structure similar to those observed for the PANI sulfosalicylic acid salt. The ΔH, g values and A/B ratios of the blends prepared by both methods were similar. The A/B ratio was nearly unity, indicating that the spins were of the free-electron type. ΔH showed considerable variation from 1.4 to 5.0 G. In general, the ΔH value was lower (2.0–3.0 G) for the PANI salt, whereas it was greater, about 8.0–12.0 G, for the PANI base.[21] Thus, the narrow ΔHs indicated the presence of PANI in the salt form in the blends. As the amount of PVA in the blend increased, the spin concentration decreased and became nearly constant ($\sim 10^{18}$ spins/g).

For the blends synthesized by the emulsion method, the spin concentration was nearly constant (10^{18} spins/g) up to VA50A, and with a further increase in PVA content, there was a drop in the spin concentration to 10^{17} spins/g. Although the conductivity of the salt was much higher than that of the blends, their spin concentrations were similar in magnitude (10^{18}

spins/g). Thus, there seemed to be no definite correlation between conductivity and spin concentration for the blends, as shown in Tables I and II.

NMR spectra

The spectra of the blends exhibited peaks arising from the PANI salt and from PVA (Fig. 3). Signals due to —CH and —OH protons, which appeared at δ 1.4 and 4.1 ppm, respectively, in the spectrum of PVA, underwent an upfield shift by 0.2–0.3 ppm in the blend. The —NH and quinoid ring protons occurring at 3.81 and 7.30 ppm, respectively, in the PANI salt shifted upfield in the blend by 0.4 and 0.1 ppm, respectively, due to the interaction between PANI and PVA. The signals in the region of δ 8.0 and 7.7 ppm arose from the dopant sulfosalicylic acid.[19] Blends with higher PVA contents had higher solubility in DMSO and good NMR spectra.

Conductivity

Table I shows the conductivity of the blends. The conductivity of the PANI salt synthesized by the emulsion method was much higher than that synthesized by the other method. However, the conductivity was similar for blends of the same composition (Table I). The conductivities of the blends synthesized by both methods were rather high ($\sim 4 \times 10^{-2}$ to 2×10^{-2} S/cm). The room-temperature conductivity depended strongly on the volume fraction of PANI in the blend. Electrical conductivity can be interpreted on the basis of a hopping mechanism between polaronic clusters.[26] Gospodinova et al.[15] reported a conductivity of 10^{-3} S/cm for a PANI dodecyl benzene sulfonic acid (DBSA) (90)–PVA (10) blend synthesized by a colloidal dispersion method, wherein particles of the two components of the blend were dispersed in a xylene–water mixture. The particle size also influenced the conductivity.[15] Chen and Hwang[23] synthesized PVA blends with sulfonic acid ring substituted PANI by mixing the constituents in water. The conductivities of the blends containing 30 and 50% of PVA were reported to be 10^{-3} and 10^{-4} S/cm, respectively, which were nearly two orders of magnitude lower than those obtained for the blends in this study. Temperature-dependent studies have revealed that the conductivity of PANI–PVA blends depend on the composition and morphology of the conducting phase.[27] The higher conductivity of the blends obtained by these methods was attributed to the more homogeneous protonation of the imine nitrogens. The conductivity of VA70 and VA70A, which could not be palletized, were not measured.

TGA

Table III summarizes the results of the TGA and DTA studies of the blends. The weight-loss patterns in the

TABLE III
TGA and DTA Data for PANI-PVA Blends

Sample	First step	Second step	Third step	Fourth step	E_a (kJ/mol)	Peak temperature (°C) for the endotherm[b]				
Inverted emulsion method										
PANI	64–158 (3.3)		267–400 (29.4)	495	68.96	120 (375.7)		301 (165.7)		573 (35.3)
VA10	40–161	179–214 (0.8)	272–406 (17.8)	462	14.90	107 (148.2)	203 (4.6)	286 (99.5)		603 (51.0)
VA30	40–140 (1.8)	193–233 (4.4)	279–367 (10.8)	421	29.50	102 (63.7)	202 (58.1)	295 (61.2)		623 (285.13)
VA50	45–122 (1.9)	210–267 (9.8)	307–343 (1.6)	411	25.80	95 (160.7)	209 (123.6)	302 (42.3)	440 (47.2)	597 (382.7)
VA70	40–112	173–229 (12.9)	273–385 (6.2)	446	11.80	105 (46.4)	183 (92.5)	276 (63.7)	449 (37.7)	603 (376.0)
Emulsion method										
PANI(A)	40–156 (3.0)		265–390 (22.6)	496	51.00	110 (406.8)		306 (332.2)		
VA10A	40–144 (1.1)		210–382 (5.7)	476	27.70	104 (145.9)		260 (151.9)		591 (70.9)
VA30A	40–120 (2.5)		187–374 (6.7)	487	21.50	101 (90.0)	196 (42.1)	260 (74.9)		606 (152.5)
VA50A	40–134	197 (18.2)			17.28	100 (47.2)	205 (410.6)		466 (57.0)	610 (432.8)
VA70A	40–136		197–338 (26.8)	423	10.70	95 (203.3)	203 (259.2)		494 (90.7)	573 (340.4)

ᵃ Weight loss percentage values are in parentheses.
ᵇ Heat of degradation $\Delta H(J/g)$ values are in parentheses.

TGA curves of blends followed that of the PANI salt. Interestingly, the blends prepared by the inverted emulsion method showed a four-step weight loss. The first weight loss step of about 2% around 40–160°C was attributed to a loss of moisture. The second step, between 180 and 230°C, was due a loss of water molecules that were strongly bound along with a small amount of the dopant, oligomers, and some of the acid-catalyzed degradation products of PVA.[10] The weight loss in the second step increased with the amount of PVA in the blend. The loss of the dopant sulfosalicylic acid occurred in the third step, between 270–400°C. The fourth step, above 420°C, corresponded to the degradation of the blend. The TGA of pure PVA showed weight loss between 200 and 300°C, followed by a further weight loss between 350 and 450°C, leaving a residue of nearly 10 wt %. The elimination of side groups occurred at lower temperatures followed by the breakdown of the polymer backbone at higher temperatures.[28] The degradation temperature of the blends was lower than that of PANI sulfosalicylic acid salt but higher than that of PVA.[25] When the amount of PVA in the blend increased, the degradation temperature was lowered from 460 to 410°C (Table III). The DTA thermograms of the blends also showed four endotherms (Table III) consistent with the four-step weight loss observed in the TGA curves.

The thermograms of the blends obtained by the emulsion method generally showed a three-step weight loss. The second step commenced early for these blends. It indicated that the loss of strongly bound water and the dopant occurred simultaneously. Blends synthesized by the emulsion method underwent degradation at a somewhat higher temperature than those prepared by the inverse emulsion method.

The energy of activation (E_a) for the degradation of the blends was calculated by with the Horowitz and Metzger method.[29] A computerized thermal analysis system recorded the weight of the sample and its temperature at regular intervals for the entire duration of the thermogravimetric experiment. A plot of ln {ln $[(W_0 - W_f)/(W_t - W_f)]$} against θ was made, where W_0 is the initial weight of the sample, W_f is the final weight of the sample, W_t is the weight of the sample at time t, and $\theta = T - T_s$, where T is the temperature of the sample and T_s is the temperature where $[(W_t - W_f)/(W_0 - W_f)] = 1/e$. A straight line with a slope of $(E_a \times 10^3)/RT_s^2$ was obtained, where R is the gas constant. E_a was calculated from the slope. Table III shows that E_a for the degradation of the blends was much lower (10.7–29.5 kJ/mol) than that of PANI sulfosalicylic acid salt. This seemed to be consistent with the lower degradation temperatures for the blends than for the PANI salt.

Morphology

The SEM photographs of the PANI salt and its blends were obtained as such except for VA70 and VA70A, which were surface-coated with gold before SEM was performed. The blends synthesized by both the methods exhibited spherical morphology with two distinct phases of PVA and PANI. However, the inverse emulsion method yielded particles with a mixed morphology of spheruloids and fibrillar natures for the VA50 blend, indicating the oxidant's role in the determination of the morphology. The particles were sharp edged with a lamellar structure on one side, whereas the other side was comparatively smoother. The pure PANI sulfosalicylic acid salts possessed a granular morphology.

The blends with compositions of 90/10 and 70/30 showed a smooth surface on one side, whereas the other side was rugged and possessed an irregular terrain. PVA was dispersed in the PANI matrix. On

the other hand, chemically synthesized PANI–PVA blends (8% PVA w/w) with potassium dichromate as the oxidant has been reported to display a flake-like morphology.[9] When the amount of PVA in the blend increased, the morphology tended toward a fibrillar nature. For VA50, the fiber pattern was prominent, but this was not so when the oxidant was ammonium persulfate, as shown in Figure 4. This kind of mixed fibrillar and granular morphology has been observed for a chemically prepared blend with $NaIO_3$ as the oxidant.[12] However, unlike this case, the previous PANI–PVA blend was covered with an electrochemically inactive PVA matrix. When the PVA content was increased to 70 w/w, the boundary between the two polymers was minimized, which showed that the blend was not a simple mixture of its constituents.

The diffraction pattern was recorded on a glass plate with the samples as powders. The VA50A and VA70A blends were difficult to grind into fine powders, and hence, these samples were dissolved in warm water and cast into films to record their X-ray diffraction pattern. PVA showed a sharp peak at 19.5° and exhibited a high degree of crystallinity, which was due to the strong intermolecular and intramolecular hydrogen bonding, as suggested by Bunn.[30] The PANI salt synthesized by the inverse emulsion method was more crystalline than that obtained by the other method, and the patterns for the PANI sulfosalicylic acid salts were typical of semicrystalline/amorphous materials. Similar X-ray diffraction patterns were observed for PANI–PVA blends prepared by both methods. The crystallinity of PVA was still observable in the blend. The number of Bragg's peaks in the blend decreased with increasing PVA content; for example, from four for VA10 to two for VA70. The peak at 19.5° narrowed, but its intensity increased when the PVA content in the blend increased. On the other hand, the peak at 25° broadened and became less intense from VA10 to VA70. The intensity of the peak at 19.5° due to the crystalline portion of PVA decreased, although the content of PVA was high, indicating strong interactions between the two components of the blend. This could have also been attributed to the formation of hydrogen bonding between PANI and PVA.[31]

The particle size measurements could not be made for VA70 and VA70A, as they could not be ground into fine powder. The mean diameters of the blend particles are given in Table IV. The particle size of the blend was in the range 84–430 μm, which increased with increasing PVA. The particle size of PANI sulfosalicylic acid salt synthesized by the emulsion method was significantly smaller than that of the salt prepared by the other method.
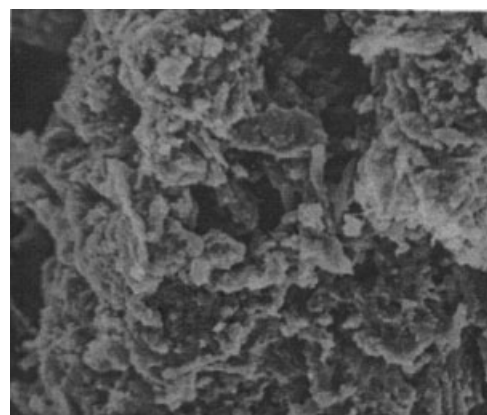
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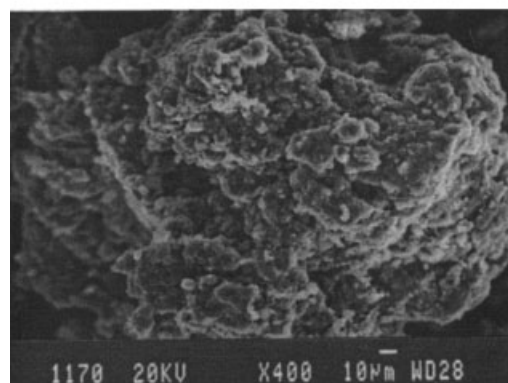
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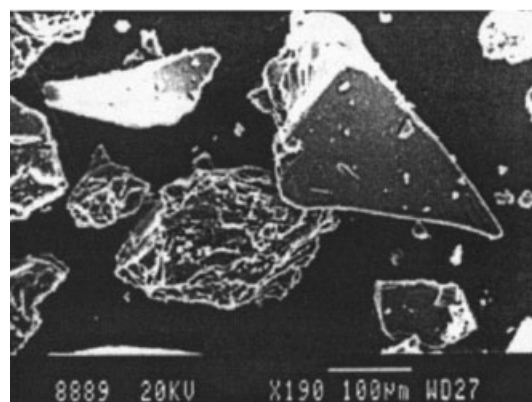
(c)

Figure 4 SEM photographs of the blends (a) VA50 and (b) VA50A and (c) PANI sulfosalicylic acid salt.

Mechanical properties

The values of compression strength and surface hardness for the blends are given in Table IV. The mechan-

TABLE IV
UCS, Surface Hardness, and Particle Size Data for PANI-PVA Blends

Sample	UCS (kg/mm^2)	Surface hardness (microvickers)	Mean diameter (μm)
Inverted emulsion method			
PANI	—	—	124.9
VA10	2.606	39.6	126.8
VA30	2.885	23.1	305.3
VA50	6.068	22.8	314.8
Emulsion method			
PANI(A)	—	—	83.5
VA10A	4.029	31.6	196.8
VA30A	2.924	16.8	270.9
VA50A	3.253	11.1	430.6

ical strength, that is, ultimate compression strength (UCS), increased when the amount of PVA in the blend increased but did not show any regular trend. The nature of the break changes with increasing PVA content from a sudden to a fragmental pattern. That these blends could sustain stress even after the commencement of fracture was revealed by the fragmental pattern, and thus, they had comparatively better mechanical strengths.

The surface hardness measurements were made on the blends made into pellets under a compact pressure of 7 tons and heat treated at 120°C for 2.5 h. The load applied was 25 g for a period of 2 s. The surface hardness depended on a number of parameters, such as the particle size, compact pressure applied, and heat treatment before measurements, and it decreased with increasing content of PVA in the blend. The surface hardness of the blends synthesized by the inverse emulsion method was significantly higher than that of the blends prepared by the other method.

CONCLUSIONS

Water-soluble conductive blends of various compositions (w/w) of sulfosalicylic acid protonated PANI with PVA were synthesized. Two methods—emulsion method with conventional ammonium persulfate as the oxidant and the inverse emulsion method with BPO as a new mild oxidant were tested. Absorption and EPR spectra revealed the presence of PANI in the salt form. The degradation temperature and also E_a of degradation decreased with increasing PVA content. The blends synthesized by the inverted emulsion method had smaller particle sizes, higher crystallinities, and better mechanical properties.

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