Preparation, Characterization, Thermooxidative Degradation, and Stability of Polyaniline/Polyacrylonitrile Composites in Terms of Direct-Current Electrical Conductivity Retention

Amir Al-Ahmed,¹ Faiz Mohammad,¹ M. Zaki A. Rahman²

¹Department of Applied Chemistry, Aligarh Muslim University, Aligarh, India ²Department of Chemistry, University Putra Malaysia, Selangor, Malaysia

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ABSTRACT: Electrically conducting composites based on polyaniline and polyacrylonitrile were prepared by two slightly different techniques and were characterized by Fourier transform infrared spectroscopy and scanning electron microscopy. The thermooxidative degradation of the composites was studied by simultaneous thermogravimetric analysis and differential thermal analysis techniques. The stability of the composites in terms of direct-current electrical conductivity retention was studied in an oxidative environment by isothermal and cyclic techniques. The composites were thermally stable under ambient environmental conditions; however, their properties were dependent on the method of preparation. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 437–448, 2006

Key words: conducting polymers; composites; degradation

INTRODUCTION

Composites are 21st century materials used to meet the demand of improved materials and possess a combination of several desirable properties; hence, commercial polymers are always mixed with various other materials, including polymers themselves. Because of their light weight, low cost, low-temperature fabrication, good mechanical strength, and good environmental stability, polymer-based conducting composites have acquired an important position among technologies based on conducting and semiconducting materials.^{1,2} Composites containing an electrically conducting polymer, polyaniline (PANI), and an insulating polymer, polyacrylonitrile (PAN), were selected for this study after careful consideration of the individual merits of the two polymers. PANI occupies a high place among intrinsically conducting polymers because of its ease of preparation, good environmental stability, and good electrical conductivity upon protonic acid doping.³⁻¹⁰ The significant dipolar interactions (~36 kJ/mol), significantly stronger than hydrogen bonding and van der Waals forces, between the -CN groups in the PAN backbone improves its molecular alignment immensely. This interaction stabilizes the orientation of the polymer chains during fiber manufacturing and, thus, enhances the fiber-forming potential of PAN and its melting temperature. Solvents, such as tetrahydrofuran (THF), dimethylformamide, and tetradimethylene sulfone, that can interact with the highly polar —CN groups of PAN can dissolve this polymer. In addition to fibers, PAN is also available in the form of films, sheets, and rods. It has excellent tensile strength, excellent optical clarity, and low water absorption.^{11–14}

EXPERIMENTAL

Materials

The materials used included aniline (99%, Qualigens, India), PAN sheets (Arnan Enterprises, New Delhi, India), THF (99.5%, CDH, New Delhi, India), hydrochloric acid (35%, E. Merck, New Delhi, India), potassium persulfate (98%, CDH, India), and ammonia solution (Qualigens, New Delhi, India). Aniline was doubly distilled before use, and all other materials were used as received.

Preparation of PANI/PAN composites

Doubly distilled aniline was thoroughly mixed in a PAN solution in THF and kept at room temperature (\sim 33°C) for 24 h with occasional stirring. The films were cast from this solution on glass plates with ex-

Correspondence to: F. Mohammad (faizmohammad@lycos.com). Contract grant sponsor: University Grant Commission; contract grant number: UGC Project No. F. 12-7/98(SR-I) (to F.M.).

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Preparation of PANI/PAN1 Composites								
Sample	PAN (g)	THF (mL)	Aniline (g)					
PANI/PAN1-1	2.5	70	0.25					
PANI/PAN1-2	2.5	70	0.5					
PANI/PAN1-3	2.5	70	0.75					
PANI/PAN1-4	2.5	70	1.0					
PANI/PAN1-5	2.5	70	1.25					
PANI/PAN1-6	2.5	70	1.5					
PANI/PAN1-7	2.5	70	1.75					
PANI/PAN1-8	2.5	70	2.0					
PANI/PAN1-9	2.5	70	2.25					
PANI/PAN1-10	2.5	70	2.5					

tremely smooth surfaces by solvent evaporation, which led to the production of PANI/PAN1 composite films, as shown in Table I. In another technique, a viscous solution of PAN (4.6 g) dissolved in aniline (10 g) was prepared by the slow addition of portions of PAN in aniline at room temperature. The films were cast from this solution on the flat glass plates by drying in a closed container for 3 days, which led to the production of PANI/PAN2 composite films.

The polymerization of aniline within the PAN matrix was effected by treatment with a potassium persulfate ($K_2S_2O_8$) solution in HCl (1*M*). The composite films were washed with aqueous HCl (1*M*) followed



Figure 1 FTIR spectra of PANI/PAN composites (a) PANI/PAN1-1, (b) PANI/PAN1-2, (c) PANI/PAN1-3, (d) PANI/PAN1-4, (e) PANI/PAN1-5, (f) PANI/PAN1-6, (g) PANI/PAN1-7, (h) PANI/PAN1-8, (i) PANI/PAN1-9, j) PANI/PAN1-10, (k) PANI/PAN2 and (l) PAN and (m) PANI.





Figure 2 SEM photograph of (a) PANI and (b) PAN.

by doubly distilled water until the filtrate was acid free. The composite films prepared in this way were undoped by treatment with an excess of aqueous 1M ammonia. All the composite formulations were redoped by treatment with 1M HCl for 48h prior to experimentation.

Characterization

Fourier transform infrared (FTIR) spectra of PANI/ PAN composites and of PANI were recorded with a PerkinElmer (Spectrum BX, Wellesley, MA) instrument. Scanning electron microscopy (SEM) studies were performed on a LEO 435 VP to examine the difference in the surface morphologies of the composites and their components. Simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on some selected composites with a PerkinElmer (Pyris Dimond) instrument from about 25 to about 650°C at a heating rate of 10°C/min) with a dry-air flow rate of 200 mL/min.

Thermal stability in terms of direct-current electrical conductivity (σ) retention

 σ of the doped composite films was measured with increasing temperature (35–100°C) with a four-in-line probe σ -measuring instrument (Scientific Equipments, Roorkee, India). σ was calculated with the following equations:

$$\rho = \rho_o / G_7 (W/S) \tag{1}$$

$$G_7(W/S) = (2S/W) \ln 2$$
 (2)

$$\rho_o = (V/I)2\pi S \tag{3}$$

$$\sigma = 1/\rho \tag{4}$$

where $G_7(W/S)$ is a correction factor, which is a function of thickness of the sample as well as probe spacing, and where *I*, *V*, *W*, and *S* are the current (A), voltage (V), thickness of the film (cm), and probe spacing (cm), respectively, and ρ and ρ_o are the corrected and uncorrected registivities (ohm-cm), respectively, and ρ and ρ_0 are the corrected and uncorrected registivities (ohm-cm), respectively.¹⁵

The isothermal stability of the composite films in terms of σ retention was carried out on selected composite films at 50, 70, and 90°C in an air oven. The σ measurements were carried out at intervals of 15 min. The thermal stability of the composite films in terms of σ retention was also studied by repeatedly measurement of the four-in-line probe σ on films with increasing temperature from 35 to 100°C. The measurements were repeated in this temperature range five times at intervals of 45 min.

RESULTS AND DISCUSSION

Preparation of the composites

When aniline is oxidized in an acidic (HCl) aqueous medium with potassium persulfate ($K_2S_2O_8$), the protonated conducting form of PANI (PANI/HCl) is produced, as given in the following unbalanced redox reaction:

The dark green PANI prepared in this manner was of high molecular weight, as very few (<0.5%) oligomers could be extracted from it on soxhlation for 24 h. The yield of the polymer was more than 50% after washing and drying.^{16–20}



Figure 3 SEM photographs of PANI/PAN composites: (a) PANI/PAN1-1, (b) PANI/PAN1-3, (c) PANI/PAN1-5, (d) PANI/PAN1-7, (e) PANI/PAN1-9, and (f) PANI/PAN2.

The color change from dark green to sky blue is associated with the neutralization of positive charges on the protonated PANI chains. The process may be treated as *n*-type doping of a *p*-type-doped polymer in which the polymer passes through an insulating state. Schöllhörn and Zagefka²¹ suggested a redox reaction for ammonia or amine intercalation into layered metal chalcogenides, which was further supported by the work of Foot and Shaker.²² On the basis of the disproportionation reaction of ammonia, as suggested by these researchers, an analogous reaction was suggested by Mohammad²³ for the undoping of polythio-

IGA and DIA Studies of PANI and PAN								
	DT	A	TGA					
Sample	Peak temperature (°C)	Comment	Temperature range (°C)	Weight loss (%)				
PANI	512	Exo	0–92 92–275 275–475 475–658	4.42 2.25 44.53 48.77				
PAN	370 406	Endo Exo	0–54 54–213 213–410	1.01 6.33 92.4				

TABLE II TGA and DTA Studies of PANI and PAN

Endo-endothermic peak; exo-exothermic peak.

phene by water. The overall chemical reactions are given in the following equations:

$$8NH_3 \rightarrow 6NH_4^+ + 6e^- + N_2$$
 (6)

$$PTH^{+} \longrightarrow BF_{4}^{-} + NH_{4}^{+} + e^{-} \rightarrow PTH + NH_{4}BF_{4} \quad (7)$$

$$6H_2O \rightarrow 4H_3O^+ + 4e^- + O_2$$
 (8)

$$PTH^{+} \longrightarrow BF_{4}^{-} + H_{3}O^{+} + e^{-} \rightarrow PTH + HBF_{4} \cdot H_{2}O$$
(9)



Figure 4 TGA and DTA of (a) PANI and (b) PAN.

			1		
	DT	A	TGA		
Sample	Peak temperature (°C)	Comment	Temperature range (°C)	Weight loss (%)	
PANI/PAN1-1			0–44	0.81	
	372	Endo	44-270	7.59	
	409	Exo	270-400	88.01	
	497	Exo	400-592	3.56	
PANI/PAN1-3			0-53	0.79	
	373	Endo	53-245	5.07	
	402	Exo	245-400	86.45	
	487	Exo	400-570	7.65	
PANI/PAN1-5			0-62	1.40	
	362	Endo	62-243	4.40	
	394	Exo	243-401	84.80	
	488	Exo	401-545	9.33	
PANI/PAN1-7			0-72	2.5	
	347	Endo	72–272	5.17	
	392	Exo	272-381	81.25	
	456	Exo	381-485	10.87	
PANI/PAN1-9			0–92	3.95	
	362	Endo	92-271	6.97	
	374	Exo	271-390	79.38	
	497	Exo	390-575	9.42	
PANI/PAN2			0–93	6.98	
			93-280	6.68	
	362	Exo	280-374	44.82	
	492	Exo	374–595	40.56	

TABLE III TGA and DTA Studies of PANI/PAN Composites

Endo = endothermic peak; exo = exothermic peak.

$$HBF_4 \cdot H_2 O \to HF + BF_3 + H_2 O \tag{10}$$

The charge neutralization reaction depends on the rate of chemical reaction between the polymer and dopant, which in turn, depends on the reactivity of the polymer chain and the basic strength of the dopant.²³ The basic strength of water is very low; hence, it does not act as an undoping agent in the case of PANI. However, a neutralization reaction for the undoping of the PANI component of the composites by ammonia is suggested by the following reaction:

$$[PANI(PAN)]^{+n}(nCl^{-}) + nNH_{4}^{+} + ne^{-} \rightarrow$$
$$PANI(PAN) + nNH_{4}Cl \quad (11)$$

The method of film casting from the solution of PAN in THF mixed with different quantities of aniline followed by the polymerization of aniline within the PAN matrix was successfully demonstrated in the preparation of the PANI/PAN1 composite films. The PANI/PAN2 composite films were successfully prepared by dissolution of PAN in aniline followed by the polymerization of aniline within the PAN matrix



Figure 5 TGA and DTA of PANI/PAN composites: (a) PANI/PAN1-1, (b) PANI/PAN1-3, (c) PANI/PAN1-5, (d) PANI/PAN1-7, (e) PANI/PAN1-9, and (f) PANI/PAN2.

in the form of dark black films with almost uniform thicknesses.

FTIR studies

The band corresponding to the out-of-plane bending vibrations of the C—H bond of *p*-disubstituted benzene rings appeared at 824 cm⁻¹. The bands corresponding to the stretching vibrations of N—B—N and N=Q=N structures appeared at 1497 and 1587 cm⁻¹, respectively, where —B— and =Q= are the benzenoid and quinoid moieties in the polymer. The bands corresponding to the vibration mode of the N=Q=N ring and the stretching mode of the C—N bond appeared at 1143 and 1302 cm⁻¹. The FTIR spectrum supported the presence of the benzenoid and quinoid moieties in the PANI. The characteristic broad band for the C \equiv N group in PAN appeared around 1995 cm⁻¹. Two characteristic bands for CH₂ appeared around 1451 and 750 cm⁻¹ for the bending and rocking vibrations, respectively. In PANI/PAN1 composites, the gradual increase in the intensities in the bands corresponding to PANI and the decrease in the bands corresponding to PAN supported the gradual increase in the PANI composite, the FTIR spectra became slightly different from their parent compounds. Some peaks appeared clearly, whereas some others were not observed due to a very broad

TABLE IV	ature Dependence of σ (S/cm) of HCI-Doped PANI/PAN Composites	· · · · · · · · · · · · · · · · · · ·

Tempe

	AN2 -3)					~	~	•			_		_	~	
	$PANI/P_{\ell}$ ($\sigma imes 10^{\circ}$	1.6850	1.7118	1.7394	1.7394	1.7679	1.7679	1.7697	1.7394	1.7118	1.6850	1.6591	1.6340	1.5859	1.5406
	$\begin{array}{l} \mathrm{PANI/PAN1-10}\\ (\sigma \times 10^{-4}) \end{array}$	4.4411	4.5798	4.7276	4.8852	5.0970	5.2261	5.4094	5.6766	5.8769	5.9819	6.2350	6.3444	6.5257	6.7674
	$\begin{array}{l} \mathrm{PANI/PAN1-9}\\ (\sigma \times 10^{-4}) \end{array}$	4.1959	4.2935	4.4487	4.5586	4.7339	4.9232	5.1284	5.4300	5.6807	5.9555	6.1541	6.4780	6.7135	6.9669
	$\begin{array}{l} \mathrm{PANI/PAN1-8}\\ (\sigma \times 10^{-4}) \end{array}$	4.3317	4.4864	4.8315	5.2341	5.3927	5.8830	6.0560	6.3444	6.5257	6.8519	7.4129	7.6133	8.0362	8.5090
cm)	$\begin{array}{l} \mathrm{PANI/PAN1-7}\\ (\sigma \times 10^{-4}) \end{array}$	5.7727	5.9695	6.1802	6.3291	6.5664	6.7348	7.0042	7.2961	7.3988	7.6133	7.7252	7.7812	7.8974	8.0170
σ (S/	$\begin{array}{l} \mathrm{PANII/PAN1-6}\\ (\sigma \times 10^{-4}) \end{array}$	4.7904	4.8448	4.9575	5.1367	5.3683	5.5831	5.8157	6.0685	6.3444	6.5427	6.9788	7.2195	7.2851	7.4127
	$\begin{array}{l} {\rm PANI/PAN1-5}\\ (\sigma \times 10^{-4}) \end{array}$	3.4162	3.5061	3.6063	3.8066	4.0241	4.2680	4.5204	5.1152	5.5910	6.0169	6.5081	7.1221	8.2273	8.7947
	$\begin{array}{l} {\rm PANI/PAN1-4}\\ (\sigma \times 10^{-4}) \end{array}$	3.0532	3.2210	3.3308	3.4483	3.6639	3.7578	3.8567	4.0710	4.2480	4.3748	4.5094	4.6525	4.7276	4.8852
	$\begin{array}{l} \mathrm{PANI/PAN1-3}\\ (\sigma \times 10^{-4}) \end{array}$	1.5498	1.6042	1.7172	1.7879	1.8181	1.8749	1.9771	2.1466	2.2276	2.3262	2.4224	2.4631	2.5485	2.5703
	$\begin{array}{l} \text{PANI/PAN1-2}\\ (\sigma \times 10^{-4}) \end{array}$	1.0950	1.1312	1.1641	1.1931	1.2235	1.2425	1.2824	1.3033	1.3249	1.3397	1.3626	1.3782	1.4107	1.4190
	Temperature (°C)	35	40	45	50	55	60	65	70	75	80	85	06	95	100

band in the region. The spectral assignments used in the characterization of these materials were from refs. 24–27. The FTIR spectra of PANI, PAN, and the PANI/PAN composites are shown in Figure 1.

SEM studies

The percolation threshold in composites is related to the homogeneity of the mixing of individual components; hence, SEM studies were performed. In addition to the small difference in the surface morphology of the PANI/PAN1-1 composites from that of the PANI/PAN2 composites, the SEM photographs of the composites supported the homogeneity of the composites and the uniformity of the film surface, as evident in Figures 2 and 3.

TGA studies

In the case of undoped PANI, the initial weight loss of -4.4% up to 100°C was due to the removal of the moisture present in the polymer. An extremely small weight loss of about 2.3% up to 275°C suggested that the PANI still contained some volatile material, most probably the doping agent, HCl, and that it was thermally stable up to 275°C under oxidative conditions. The onset temperature of the thermooxidative degradation of PANI was observed at 275°C, accompanied by a massive weight loss of 93.3% up to about 650°C, with no residue left behind. A strong exothermic peak in DTA at 512°C corresponded to this degradation. In the case of PAN, the initial weight loss of around 6% up to 254°C indicated its good thermal stability. One endothermic peak at 370°C may be attributed to the melting of PAN. The TGA curve indicated that about 90% weight loss between 254 and 400°C was due to thermooxidative degradation, which was supported by one sharp exothermic peak. The details of the TGA and DTA of undoped PANI and PAN are presented in Table II and Figure 4.

For the PANI/PAN1 composites, the initial weight loss of 5–7% up to 270°C suggested that the composites still contained some volatile materials, most probably, the doping agent, HCl, along with water. A small endothermic peak around 370°C was attributed to the melting of PAN. The onset temperature of thermooxidative degradation was 270°C, which was associated with a massive weight loss beyond this temperature, which was further supported by a simultaneous exothermic peak in DTA. The initial part of the weight loss was associated with the thermooxidative degradation of the composites. The last part of this step was associated with the thermooxidative degradation exclusively of PANI, as the weight loss percentage slightly increased with increasing PANI content in the composites. In PANI/PAN2, a four-step weight loss was observed. The initial weight loss of 6% up to



Figure 6 Temperature dependence of σ of PANI/PAN composites: (a) PANI/PAN1-2, (b) PANI/PAN1-3, (c) PANI/PAN1-4, (d) PANI/PAN1-5, (e) PANI/PAN1-6, (f) PANI/PAN1-7, (g) PANI/PAN1-8, (h) PANI/PAN1-9, (i) PANI/PAN1-10, and j) PANI/PAN2. T stands for temperature (K).

100°C was associated with the loss of water. Beyond this temperature, another 6% weight loss up to 280°C was attributed to the loss of the doping agent, HCl. In the next two steps, a weight loss in TGA was observed where the weight loss in both steps was almost equal. The weight loss of 40% in the last step was associated with the thermooxidative degradation exclusively of PANI because PAN degrades completely at around 400°C. The extent of about 100% weight loss up to about 600°C, with no residue left behind, suggested that there was no chemical reaction between the components of the composite during thermooxidative degradation; this leads to the formation of thermally stable polynuclear organics.^{26,28–31} The TGA details of PANI/PAN1 and PANI/PAN2 are given in Table III and Figure 5.

Stability in terms of σ retention

The PANI/PAN composites showed an enhanced electrical conductivity on exposure to HCl due to the involvement of a charge-transfer reaction between the PANI component of the composites and the doping agent, HCl,^{32,33} as given in the following equation:

$$[PANI(PAN)] + nHCl \rightarrow [PANI-H(PAN)]^{+n}(nCl^{-})$$
(12)

The electrical conductivities of the composite films were measured from 35 to 100°C and were found in the semiconducting region, as presented in Table IV. All the PANI/PAN1 composite samples, in principle, followed the Arrhenius equation for temperature de-



Figure 6 (*Continued from the previous page*)

pendence of electrical conductivity, as shown in Figure 6. This suggests the semiconducting nature of the HCl-doped composites. No semiconductor-to-metal transition was observed. However, the electrical conductivity of the HCl-doped PANI/PAN1-1 composite in the insulating region suggested that the PANI concentration in this composite was well below the percolation threshold.

The PANI/PAN2 composite deviated from the Arrhenius equation around 55°C, and the electrical conductivity started decreasing after 65°C. This behavior was attributed to a semiconductor-to-metal transition and to the approach nearer to the glass-transition temperature of the composite.

Five composite samples (PANI/PAN1-3, PANI/ PAN1-5, PANI/PAN1-7, PANIPAN1-9, and PANI/ PAN2) were selected to study the stability of electrical conductivity under isothermal conditions at 50, 70, and 90°C. The temperature of the composite films was maintained at the temperature of study, and the σ was measured every 15 min in an accelerated aging experiment. The electrical conductivity measured with respect to the time of accelerated aging is presented Table V and Figure 7. For PANI/PAN1, the electrical conductivity was quite stable at 50, 70, and 90°C; this supported the fact that the electrical properties of the composites were sufficiently stable below 90°C under a thermooxidative atmosphere. In the PANI/PAN2 composites, the electrical conductivity was stable up to 70°C and then started decreasing slowly with time at 90°C, which was attributed to the loss of the dopant, the chemical reaction of the dopant with the polymer, and the semiconductor-to-metal transition and the approach nearer to the glass-transition temperature of the composite.

Two composites samples (PANI/PAN1-9 and PANI/PAN2) were selected to study the stability in terms of the σ retention by a cyclic technique. The PANI/PAN1-9 composite showed a gradual decrease in electrical conductivity up to cycle 3, and after that, the electrical conductivity increased toward cycle 5. This was attributed to the removal of moisture, annealing, and crystallization of the polymer, which created a homogeneous doping of the polymer and decreased the percolation threshold, as evident in Table VI and Figure 8. In PANI/PAN2, σ increased up to cycle 3, decreased a little in cycle 4, and increased in cycle 5. This variation in the electrical conductivity of composite was attributed to the same reasons described previously. The measured data of the electrical conductivity of PANI/PAN2 is presented in Table VII, and the Arrhenius plots are shown in Figure 9.

CONCLUSIONS

Chemically prepared conducting polymers are difficult to process by solution or melt techniques because they are intractable and degrade well before melting. We successfully prepared conducting composite films with PANI, an electrically conducting polymer, within the matrix of an insulating polymer, PAN. The insulating polymer selected for this study possessed good

			σ (S cm)			
Temperature (°C)	Time (min)	$\frac{\text{PANI/PAN1-3}}{(\sigma \times 10^{-4})}$	$\begin{array}{c} \text{PANI/PAN1-5} \\ (\sigma \times 10^{-4}) \end{array}$	$\begin{array}{c} \text{PANI/PAN1-7} \\ (\sigma \times 10^{-4}) \end{array}$	$\begin{array}{c} \text{PANI/PAN1-9}\\ (\sigma \times 10^{-4}) \end{array}$	PANI/PAN2 ($\sigma imes 10^{-3}$)
50	0	1.5442	3.6913	5.2011	3.6387	1.9587
	15	1.5623	3.6913	5.2531	3.5932	2.1986
	30	1.5829	3.8066	5.6686	3.6797	2.1986
	45	1.5967	3.9294	5.9262	3.7661	1.7670
	60	1.6021	4.0604	6.2084	4.0305	1.9248
70	0	2.2320	3.9256	5.3604	4.0445	1.6079
	15	2.2454	4.1873	5.3062	4.0496	2.2444
	30	2.2454	3.3186	5.5885	4.2230	2.3420
	45	2.2558	3.3951	6.1802	4.2660	1.5613
	60	2.2662	3.4894	6.3291	4.4987	1.8574
90	0	2.2047	6.7674	5.8368	6.5885	1.6054
	15	2.2351	7.1654	5.7099	6.7177	1.3293
	30	2.2558	5.5369	5.9024	6.1179	1.3459
	45	2.2454	5.2962	5.9024	5.9069	1.2520
	60	2.2558	5.2962	5.9695	5.9069	1.1838

TABLE VStability of σ of PANI/PAN Composites (Under Isothermal Conditions)



Figure 7 Isothermal stability of (a) PANI/PAN1-3, (b) PANI/PAN1-5, (c) PANI/PAN1-7, (d) PANI/PAN1-9, and (e) PANI/PAN2 composites in terms of retention of σ with respect to time at 50, 70, and 90°C.

TABLE VI Stability of σ of the PANI/PAN1-9 Composite (Cyclic Technique)

Temperature	$\sigma imes 10^{-4}~({ m S/cm})$							
(°C)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5			
35	3.3154	2.5585	2.3294	2.7381	4.1071			
40	3.6707	2.6453	2.4011	2.8902	4.1488			
45	3.7138	2.6909	2.4773	3.0014	4.2442			
50	3.8066	2.7870	2.6012	3.1214	4.3440			
55	3.9042	2.9447	2.6909	3.3207	4.5030			
60	3.9530	3.0602	2.8376	3.4682	4.6155			
65	4.2296	3.2515	3.0602	3.7160	4.8585			
70	4.4784	3.5471	3.2515	3.9018	5.0581			
75	4.9118	3.7160	3.4682	4.2181	5.3514			
80	5.2505	4.0018	3.6296	4.4592	5.6807			
85	5.6395	4.2181	3.8066	4.5903	5.8610			
90	5.8564	4.3353	4.0018	4.8772	6.1541			
95	6.3444	4.4592	4.2181	5.0346	6.3663			
100	6.6202	4.5903	4.4592	5.3818	6.5936			



Figure 8 Stability of σ of the PANI/PAN1-9 composite (cycle technique).

TABLE VII Stability of σ of the PANI/PAN2 Composites (Cyclic Technique)

Temperature	$\sigma imes 10^{-3}$ (S/cm)								
(°C)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5				
35	1.6096	1.6591	1.8278	1.1982	1.5629				
40	1.6591	1.6850	1.8594	1.2117	1.6096				
45	1.6850	1.7118	1.8920	1.2255	1.6591				
50	1.7118	1.7118	1.9258	1.2396	1.6850				
55	1.7394	1.7118	1.9258	1.2540	1.7118				
60	1.7394	1.7118	1.9258	1.2540	1.7118				
65	1.7394	1.6850	1.8920	1.2396	1.7679				
70	1.7118	1.6591	1.8920	1.2255	1.6850				
75	1.6850	1.6096	1.8594	1.2117	1.5859				
80	1.6591	1.5621	1.8278	1.1851	1.4978				
85	1.6096	1.5189	1.7679	1.1596	1.4773				
90	1.5621	1.4743	1.7118	1.1352	1.4005				
95	1.5406	1.4379	1.6591	1.1118	1.3314				
100	1.4773	1.4005	1.6096	1.0893	1.1851				



Figure 9 Stability of σ of the PANI/PAN2 composite (cycle technique).

film-forming properties along with various other individual merits.

The electrical properties of the composite materials were of good quality, as almost all of the composites showed a great increase in their electrical conductivity from the insulator to the semiconducting region after doping with hydrochloric acid. All of the composite materials were successfully characterized for their electrical properties, and with FTIR, SEM and TGA, we found that the materials had good standards.

Thermal stability and stability in terms of retention of σ were also fairly good as studied by several experimental techniques. Most of the formulations of the composites so prepared were suitable for use in electrical and electronic applications below 90°C under an ambient atmosphere.

References

- 1. Sharma, S. C. Composite Materials; Narosa: New Delhi, 2000.
- 2. Bott, D. C. In Handbook of Conducting Polymers; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 2.
- MacDiarmid, A. G.; Chiang, J. C.; Halpern, M.; Huang, W. S.; Mul, S. L.; Somasiri, L. D.; Wu, W.; Yamger, S. L. Mol Cryst Liq Cryst 1985, 12, 173.
- Paul, E. W.; Ricco, A. J.; Wrighton, M. S. J Phys Chem 1985, 89, 1441.
- MacDiarmid, A. G.; Epistin, A. J. Faraday Discuss Chem Soc 1989, 88, 317.
- 6. Chiang, J. C.; MacDiarmid, A. G. Synth Met 1986, 13, 193.
- Abraham, D.; Bharathi, A.; Suramanyam, S. V. Polym Commun 1996, 37, 5295.
- 8. Ding, L.; Wang, X.; Gregory, R. V. Synth Met 1999, 104, 73.
- 9. Trivedi, D. C. Ind J Chem Sect A 1994, 33, 552.
- 10. Gök, A.; Sari, B. J Appl Polym Sci 2002, 84, 1993.
- 11. Cowie, J. M. G. Polymer Chemistry and Physics of Modern Materials; Billing & Sons, Guilford: London, 1973.
- Billmeyer, F. W., Jr. Text Book of Polymer Science; Wiley: New York, 1994.
- Misra, G. S. Introductory Polymer Chemistry; Wiley Eastern: New Delhi, 1993.
- Gowariker, R.; Viswanathan, N. V.; Sreedhar, J. Polymer Science; New Age International: New Delhi, 1999.

- 15. Chiang, J. C.; MacDiarmid, A. G. Synth Met 1986, 13, 193.
- 16. Cao, Y.; Andereatta, A.; Heeger, A. J.; Smith, P. Polymer 1989, 30, 2305.
- 17. Armes, S. P. Synth Met 1987, 20, 367.
- Vogel's Textbook of Practical Organic Chemistry; Furniss, B. S.; Hannaford, A. J.; Rogers, V.; Smith, P. W. G.; Tatchell, A. R., Eds.; English Language Book Society: London, 1987.
- Instruction Manual; Scientific Equipment and Services: Roorkee, India, 2000.
- Naarmann, H.; Strohriegel, P. In Handbook of Polymer Synthesis; Kricheldorf, H. R., Ed.; Marcel Dekker: New York, 1992; Part B.
- 21. Schöllhörn, R.; Zagefka, H. D. Angew Chem Int Ed Engl 1997, 16, 199.
- 22. Foot, P. J. S.; Shaker, N. G. Mater Res Bull 1983, 18, 173.
- 23. Mohammad, F. J Phys D: Appl Phys 1998, 31, 951.
- 24. Rao, C. N. R. Chemical Application of Infrared Spectroscopy; Academic: New York, 1963.

- Silverstein, R. M.; Bassler, G. C.; Morrillch, T. C., III. Spectrometric Identification of Organic Compounds; Wiley: New York, 1981.
- 26. Samui, A. B.; Patankar, A. S.; Satpute, R. S.; Dev, P. C. Synth Met 2002, 125, 423.
- 27. Kalsi, P. S. Spectroscopy of Organic Compounds; New Age International: New Delhi, 2001.
- Keattch, C. J.; Dollimore, D. An Introduction to Thermogravimetry; Heyden: London, 1975.
- 29. Palaniappan, S.; Narayana, B. H. J Polym Sci Part A: Polym Chem 1994, 31, 2431.
- Mzenda, V. M.; Goodman, S. A.; Auret, F. D.; Prinsloo, L. C. Synth Met 2002, 127, 279.
- Piont, N. J.; Shah, P. D.; Kohol, P. K. Phys Rev B: Condens. Matter 1996, 53, 10690.
- 32. MacDiarmid, A. G. Synth Met 2002, 125, 11.
- 33. Heeger, A. J. Synth Met 2002, 125, 23.