

# Spectral and Thermal Studies on Polyaniline–Epoxy Novolac Resin Composite Materials

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**ABSTRACT:** Polyaniline–epoxy novolac resin composite materials (PANI–RESIN) were prepared by emulsion polymerization technique and characterized by infrared and electronic absorption spectra, conductivity, particle size, and thermogravimetric and differential scanning calorimetric analysis. The conductivity of PANI–RESIN samples decreased with the addition of the RESIN as 0.1, 0.02, and 0.04 S/cm for 25, 50, and 75% addition of the RESIN, respectively. TGA thermograms of PANI–RESIN samples are more or less similar to those of polyaniline salts (PANI), which were stable up to 225°C. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3507–3512, 1999

**Key words:** antistatic materials; composite materials; DSC analysis; polyaniline–epoxy novolac resin; thermogravimetric analysis

## INTRODUCTION

Electrically conducting polymers are promising materials for various applications. The implementation of practical applications has been facilitated by the improvement of the processibility of conducting polymers. Many investigations concerning polyaniline and its derivatives have been reported with interesting results and attractive applications, such as lightweight batteries,<sup>1</sup> electrochromic displays,<sup>2,3</sup> electroluminescent devices,<sup>4</sup> electrochemical actuators,<sup>5</sup> schottky diodes,<sup>6</sup> gas separators,<sup>7</sup> and photonic devices<sup>8</sup>

The electrical voltage generated by friction on plastic materials amounts to a few thousand volts, but even a 20-V surge of static electricity can be sufficient to destroy highly sensitive microelectronic components. This problem can be solved only by using materials with antistatic properties. Electrically conducting polymers offer

reliable and convenient means of preventing static charges. The conductivity of conducting polymers is not necessarily high and the resistivity in the range  $10^1$  to  $10^9$  ohm cm could be used for antistatic and charge dissipative applications. Polyaniline has been found to be a very effective material for antistatic applications.<sup>9</sup>

Antistatic materials may be employed for the following applications to control static electricity: protective packaging, antistatic floors, antistatic bench tops, antistatic shoes, wrist straps, etc. Epoxy resins are used for floor applications. Since polyaniline is electrically conductive and possesses good environmental stability, polyaniline–epoxy novolac resin composite materials (PANI–RESIN) may be used for antistatic floor applications.

The PANI–RESIN samples were prepared by emulsion polymerization technique and characterized by infrared and electronic absorption spectra, conductivity, particle size analysis, and thermogravimetric and differential scanning calorimetric analysis.

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**Table I** Typical Properties of the Prepared Epoxy Novolac Resin

Properties	Values
Specific gravity at 25°C	1.21–1.22
Refractive index	1.582–1.584
Viscosity at 25°C (cP)	21,800–22,500
Epoxy equivalent value	205
Volatiles at 150°C	18%

## EXPERIMENTAL

### Materials

Reagent-grade aniline [E. Merck, India] was vacuum-distilled under nitrogen prior to use. Reagent-grade phenol, formaldehyde, epichlorohydrin, *p*-toluenesulfonic acid, sodium laurylsulfate, ammonium persulfate, and dichloromethane were used as purchased.

### Synthesis

#### *Preparation of Epoxy Novolac Resin (RESIN)*

Epoxy novolacs were synthesized by the usual procedure, that is, by preparing a low molecular weight novolac from phenol and formaldehyde in the presence of acid catalyst. The novolac so obtained was made to react with epichlorohydrin in the presence of a basic catalyst, such as sodium hydroxide, resulting in production of an epoxy novolac resin. Typical properties of the epoxy novolac resin is shown in Table I.

#### *Preparation of Polyaniline-*p*-Toluene Sulfonic Acid Salt (PANI)*

The experimental procedure adopted for the preparation of polyaniline-*p*-toluene sulfonic acid salt was described elsewhere.<sup>10</sup>

#### *Preparation of Polyaniline-Epoxy Novolac Resin (PANI-RESIN)*

In a typical experiment, 120 mL of dichloromethane solution containing 4.5 mL of aniline and 5 g of RESIN was placed in a 1-L flask. To this solution, an aqueous solution of 4.5 g of sodium laurylsulfate (45 mL) was added and a gel like emulsion was obtained. To this emulsion, 250 mL of an aqueous solution containing 22.82 g of ammonium persulfate and 19.02 g of *p*-toluenesulfonic acid was added dropwise for 15 to 20 min under

constant stirring. The reaction mixture was kept for 4 h and the precipitated PANI-RESIN was washed with 4 L of distilled water; finally, the product was dried at 100°C for 24 h. Using this procedure 25, 50, and 75% of PANI in PANI-RESIN samples were prepared.

### Characterization

#### *Fourier-Transform Infrared (FTIR) Spectra*

Infrared spectra of the polymer samples were recorded on a Bomem MB 100 spectrometer. The spectra were measured at room temperature on the samples dispersed in KBr disk pellets.

#### *Electronic Absorption Spectra*

Absorption spectra of the polymer samples were recorded at room temperature on a Hitachi U3400 spectrophotometer. Dilute solutions of the polymer samples in *N,N*-dimethylformamide (DMF) were used. The absorption spectra of the solutions were measured in the range 900–250 nm.

#### *Conductivity*

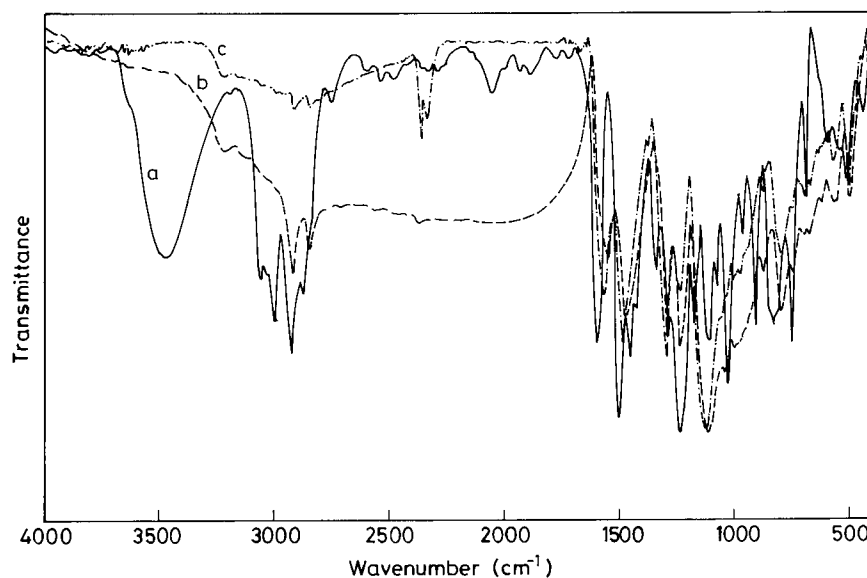
Electrical conductivity (DC) of the polymer samples in the form of compacted disk pellets was measured by a four-probe method with a Keithley Model 230 A constant current source and Model 195 A digital voltmeter. The pellets were obtained by subjecting the polymer samples to a pressure of 950 kg/cm<sup>2</sup>. Conductivity was calculated based on the average of at least three pairs of readings taken at different points on the pressed pellet.

#### *Particle Size*

Particle size analysis of the polymer samples in aqueous medium was carried out with a particle size analyzer (Malvern Mastersizer X).

#### *Density and Water Absorption*

Density and water absorption of the polymer samples were measured at room temperature on the pressed pellets obtained by subjecting the samples to a pressure of 950 kg/cm<sup>2</sup>. Pellet density was calculated from mass per unit volume of the pressed pellet. Water absorption was measured by immersing the pellets in distilled water for 24 h at room temperature and the samples were removed after 24 h and the surface moisture was wiped off with a tissue paper. From the weight of the samples before and after water absorption,



**Figure 1** FTIR spectra of (a) RESIN, (b) PANI : RESIN (50 : 50), and (c) PANI.

the percentages of water absorption of the samples were calculated.

#### Thermogravimetric Analysis (TGA)

TGA thermograms of the polymer samples were recorded using a Perkin-Elmer thermogravimetric analyzer TGA-7 in the presence of oxygen up to 650°C, at a heating rate of 10°C/min.

#### Differential Scanning Calorimetry (DSC) Analysis

DSC of the polymer samples were recorded using a Differential Scanning Calorimeter DSC-2C Perkin-Elmer in the presence of oxygen up to 350°C at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Infrared Spectra

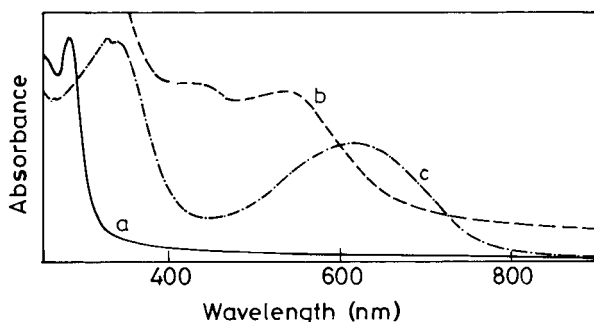
The infrared spectra of RESIN, PANI-RESIN, and PANI samples recorded in the range 4000–400  $\text{cm}^{-1}$  are shown in Figure 1. The vibrational bands observed for PANI are explained on the basis of the normal modes of polyaniline; a band at 2930  $\text{cm}^{-1}$  is assignable to the aromatic CH stretch, 1590 and 1490  $\text{cm}^{-1}$  bands to the benzene and/or the quinone ring deformations, a 1310  $\text{cm}^{-1}$  band to the CN stretch of a secondary aromatic amine, and a 820  $\text{cm}^{-1}$  band to an aromatic CH out-of-plane bending. In the region of 1010–

1170  $\text{cm}^{-1}$ , aromatic CH in-plane-bending modes are usually observed. For PANI, a strong band characteristically appears at 1155  $\text{cm}^{-1}$ , which has been explained as an electronic band or a vibrational band of nitrogen quinone. The CH out-of-plane-bending mode has been used as a key to identify the type of substituted benzene. For the polymer salt, this mode was observed as a single band at 820  $\text{cm}^{-1}$ , which fell in the range 800–860  $\text{cm}^{-1}$  reported for a 1,4-substituted benzene.

Generally, the infrared spectra of all three samples (i.e., 25, 50, and 75% of PANI in PANI-RESIN samples) are very nearly the same and the bands at 2900, 1250, 1100, and 1000  $\text{cm}^{-1}$  were due to RESIN in the present study.

### Electronic Absorption Spectra

Very small quantities of soluble PANI-RESIN and PANI samples were dissolved in DMF. The electronic absorption spectra of the solutions were measured and the results are shown in Figure 2. The electronic absorption spectra of polyaniline base and polyaniline salts have been reported widely in the literature. The absorption spectrum of polyaniline base<sup>11,12</sup> shows two distinct absorption bands located between 315–345 and 610–650 nm, depending on the preparation and/or processing conditions of polyaniline. Polyaniline salts<sup>11,13</sup> obtained from the base by treatment with acids show three absorption bands at 325–



**Figure 2** UV-Visible spectra of (a) RESIN, (b) PANI : RESIN (50 : 50), and (c) PANI.

360, 400–430, and 780–825 nm, respectively. Cao et al.<sup>13</sup> reported the absorption spectra of polyaniline–camphorsulfonic acid salt films cast from *m*-cresol or dimethylformamide solutions. It showed three absorption bands, including a band around 800 nm.

In the present study, PANI showed only two bands, one broad band around 630 nm and another band at 325 nm. It should be noted that no change in the absorption spectra was observed even after the solution was left for 48 h. This confirms the presence of polyaniline base in the sample and the conspicuous absence of an absorption band around 800 nm in the absorption spectra of PANI, which indicates that the salt is not soluble and only the base part is soluble in DMF.

The electronic absorption spectrum of RESIN showed an absorption band at 280 nm. The electronic absorption spectra of all the PANI–RESIN samples were very nearly the same and showed one band at 275 nm (not shown in Fig. 2 due to overscaling) due to RESIN. Two humps around 410 and 515 nm were due to a lower-wavelength

shift of the conjugation band of PANI. This result indicates that the conjugation of PANI is affected by the surrounding RESIN in the PANI–RESIN samples.

### Particle Size

Particle sizes for PANI and PANI–RESIN samples were measured and tabulated in Table II. Particle size for PANI was found to be 170  $\mu\text{m}$ . The particle size of the PANI–RESIN samples increased with the addition of RESIN as 200, 275, and 410  $\mu\text{m}$  for 25, 50, and 75% addition of RESIN, respectively.

### Conductivity

The conductivity of PANI and PANI–RESIN samples was measured using a four-probe method and the results are tabulated in Table II. The conductivity of PANI was 2.0 S/cm and the conductivity of RESIN–PANI decreased with the addition of RESIN as 0.1, 0.02, and 0.04 S/cm for 25, 50, and 75% addition of RESIN, respectively.

### Density

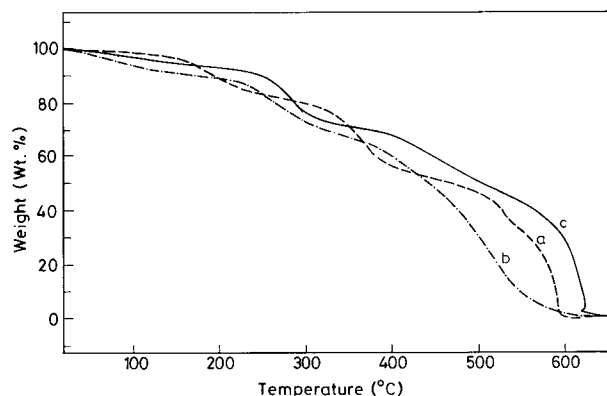
The density of RESIN, PANI, and PANI–RESIN samples was measured and the results tabulated in Table II. The density of RESIN and PANI was the same (1.2  $\text{g}/\text{cm}^3$ ) and that of the PANI–RESIN samples varied from 1.11 to 1.18  $\text{g}/\text{cm}^3$ . The density before and after water absorption was found to be nearly the same.

### Water Absorption

PANI have been found to contain water in substantial amounts (0.78 water molecules per mo-

**Table II** Conductivity, Density, Water Absorption, and Particle Size Values of PANI, PANI–RESIN, and RESIN Samples

Properties	PANI	PANI–RESIN Ratio (wt %)			RESIN
		75 : 25	50 : 50	25 : 75	
Conductivity (S/cm)	2.0	0.1	0.02	0.04	$>10^{-10}$
Density ( $\text{g}/\text{cm}^3$ )					
Before water absorption	1.22	1.14	1.11	1.16	1.21
After water absorption	1.20	1.17	1.12	1.18	—
Water absorption (%)	16	14.1	10.7	6.7	0.02
Particle size ( $\mu\text{m}$ )	170	200	275	410	—

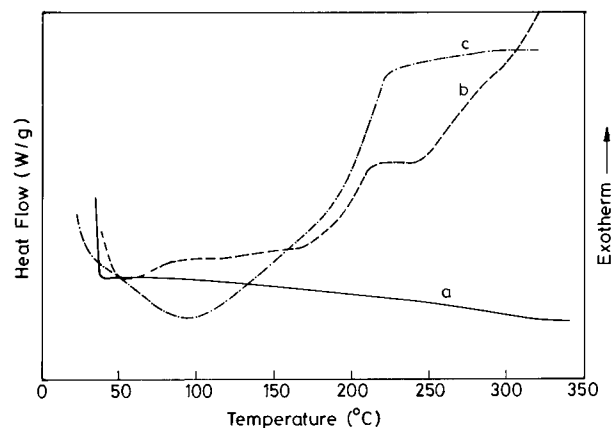


**Figure 3** TGA thermograms of (a) RESIN, (b) PANI : RESIN (50 : 50), and (c) PANI.

meric unit).<sup>14</sup> The amount of water present in the polyaniline has been calculated using a thermogravimetric analyzer by several workers.<sup>15,16</sup> They have reported that polyaniline contains up to 10 to 15% water. In the present study, the percentage of water absorption for RESIN, PANI, and PANI-RESIN samples was measured and the results tabulated in Table II. The percentage of water absorption for RESIN was found to be substantially less (0.02%), whereas for PANI it was observed around 16%. The percentage of water absorption for PANI-RESIN decreased with the addition of RESIN as 14.1, 10.7, and 6.7% for 25, 50, and 75% addition of RESIN, respectively.

#### Thermogravimetric Analysis (TGA)

TGA thermograms of RESIN, PANI, and PANI-RESIN samples are shown in Figure 3. TGA thermogram of RESIN showed a 16% weight loss up to 245°C, which was due to the evolution of volatile matter, and then underwent complete degradation around 600°C. The TGA thermogram of PANI showed an 11% weight loss occurs up to 260°C, which was due to the presence of moisture,



**Figure 4** DSC thermograms of (a) RESIN, (b) PANI : RESIN (50 : 50), and (c) PANI.

and then underwent degradation, and that the complete weight loss occurred around 625°C.<sup>17</sup> The TGA thermogram of PANI-RESIN (75% PANI) sample was more or less similar to that of PANI and was stable up to 225°C.

#### Differential Scanning Calorimetry (DSC)

DSC thermograms of RESIN, PANI, and PANI-RESIN samples were recorded up to 350°C and are shown in Figure 4. A DSC thermogram of PANI showed one endotherm around 85°C due to the moisture in the sample. However, a DSC thermogram of PANI-RESIN samples showed one exotherm around 210°C, depending upon the amount of RESIN used. The peak around 210°C is due to the thermal dedoping of *p*-toluene sulfonic acid.<sup>17-19</sup> The start, maxima, and end temperatures for PANI-RESIN samples are shown in Table III. However the exotherm maxima increased as 215, 220, and 260°C for 25, 50, and 75% addition of PANI, respectively.

**Table III** DSC Thermogram Data for PANI, RESIN, and PANI-RESIN Samples

Sample	Endotherm (°C)	Exotherm			Difference (°C)
		Start (°C)	Maxima (°C)	End (°C)	
PANI	85	—	—	—	—
RESIN	—	—	—	—	—
PANI 25%	—	170	215	240	70
PANI 50%	—	180	220	235	55
PANI 75%	—	235	260	280	45

## CONCLUSIONS

The Infrared spectra of all three PANI-RESIN samples are nearly the same and show bands due to PANI and RESIN. The conjugation of polyaniline is affected by the addition of RESIN. The conductivity of the PANI-RESIN samples decreased with the addition of RESIN as 0.1, 0.02, and 0.04 S/cm for 25, 50, and 75% addition of RESIN, respectively. The particle size of the PANI-RESIN samples increased with the addition of RESIN. The density of the PANI-RESIN samples was found to be nearly the same. The water absorption for the PANI-RESIN samples decreases with the addition of RESIN. The TGA thermograms of the PANI-RESIN samples were more or less similar to that of PANI and were stable up to 225°C.

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