

# Thermoplastic Blend of Polyaniline with Polyvinyl Chloride-Nitrile Rubber

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**ABSTRACT:** Polyaniline doped with ( $\pm$ )-camphor sulfonic acid was blended with polyvinyl chloride/nitrile rubber. The thermoplastic blend was characterized for its conductivity, mechanical and dynamic mechanical properties, and microwave response. The blend was found to be compatible in nature. Loss component of relative permittivity increased with polyaniline content. Storage modulus in-

creased with polyaniline content, whereas  $\tan \delta$  showed decline. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1217–1222, 2006

**Key words:** conducting polymer; thermoplastic blend; dynamic mechanical properties; storage modulus; permittivity

## INTRODUCTION

Conducting polymers have attracted considerable attention because of their potential application in the field of energy storage,<sup>1–3</sup> electromagnetic interference shielding,<sup>4,5</sup> photoelectronic device,<sup>6,7</sup> transistor and microelectronic device,<sup>8</sup> sensors,<sup>9,10</sup> corrosion inhibition,<sup>11–13</sup> and so on. Polyaniline (PANI) is relatively popular because of easy availability of raw materials, easy synthesis route, excellent stability in air, and relatively high temperature. However, doped PANI is generally insoluble and difficult to work. It was a tremendous achievement when camphor sulfonic acid, dodecyl benzene sulfonic acid, and alkylene phosphates were proposed and demonstrated for their doping action.<sup>14–18</sup> The resulting materials were conducting, and it was possible to work on them by casting films.

Over the years, there is rapid growth of techniques for imparting conductivity to commodity plastics by incorporating PANI. Initial attempts involved counter ion induced processibility,<sup>19,20</sup> in situ polymerization in presence of polymer latex,<sup>21</sup> and coating on various substrates.<sup>22,23</sup> As the attempts to innovate better processes gained momentum other processes such as melt blending and vulcanization were reported.<sup>24–27</sup> It was found that the combined characteristics of matrix polymer and doped PANI determine the resulting morphology and electrical conductivity of blend. Interaction level between PANI and matrix polymer determines PANI particles dispersion mode in the

matrix. Whatever the blend is, it must possess some optimum properties, such as mechanical strength and electrical conductivity. Various blends normally find use in specific applications. It is always a gain if more than one application can be combined in a single blend. In a recent publication preparation of PANI and diene rubber blend was reported.<sup>28</sup> It was proposed that chlorine and ozone can form charge transfer complexes with double bonds.<sup>29–32</sup> The presence of chlorine or ozone will alter the electrical conductivity of conducting blend, which in turn can be utilized for quantitative sensing of these gases. The same blend can be used for other purposes, such as antistatic, microwave absorbing structures, and so on.

In the present work, attempts have been made to make thermoplastic blend of PANI with polyvinyl chloride/nitrile rubber (PVC-NBR) by using simple and environment friendly method and characterize it for various properties.

## EXPERIMENTAL

### Materials

Polyvinyl chloride/nitrile rubber (PVC-NBR) blend of 70/30 (w/w) composition received from Kosyn, Korea (KNB 35 L, % acrylonitrile: 35) was used as received. Ammonium persulfate (AP) (AR), hydrochloric acid (36% aq., AR), ammonia solution (25% aq., AR; s.d Fine Chem), DL-camphor sulfonic acid (CSA) (pure grade, Aldrich), stearic acid (processing aid) (AR grade; from s.d Fine Chem), phenol formaldehyde resin (softening point: 89°C, methylol content: 14.8%; Romit Resins, India) were used without further purification. Aniline (AN) (Merck) was freshly distilled before use.

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## Methods

### Synthesis of PANI-CSA

PANI-HCl was synthesized by following the method of MacDiarmid et al.<sup>33</sup> About 9.3 g (0.1M) of AN was dissolved in 500 mL of 1N HCl and cooled to  $-5^{\circ}\text{C}$ . About 22.8 g (0.1M) of AP dissolved in 50 mL 1M HCl (chilled) was added dropwise under stirring. Stirring was continued for 2 h, and the solid product was separated by filtration. The residue was thoroughly washed with water. PANI-HCl, thus obtained, was stirred in 0.1M ammonia solution for 4–5 h and filtered. The product, PANI base, was dried at  $60^{\circ}\text{C}$  under vacuum for 24 h. Dried PANI base was mixed thoroughly with stoichiometric amount of CSA in pestle and mortar.

### Blending of PANI-CSA with PVC/NBR

PANI-CSA, tacifier (5 phr) and stearic acid (2 phr) were dispersed in PVC/NBR by passing through internal mixer (Brabender). The temperature was maintained at  $70^{\circ}\text{C}$  and speed at 30 rpm over a time period of 2 min, which has been standardized for various blends in our machine. The blend was placed in a steel mold, and compression molding was performed at  $170^{\circ}\text{C}$  at a pressure of 10 MPa for 2 min. The compressed sheet was taken out of the mold immediately and air cooled.

## Characterization

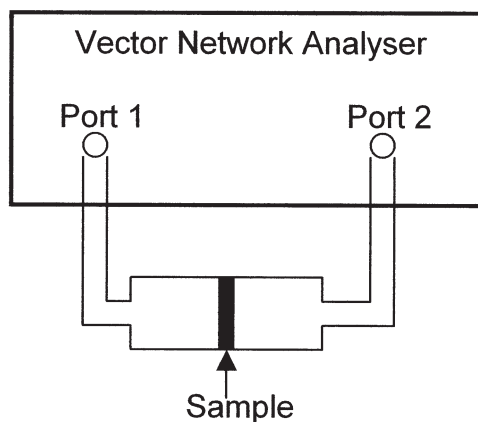
### FTIR spectra

FTIR spectra were recorded by using PerkinElmer (model 1650) spectrophotometer. PVC-NBR spectrum was recorded by exposing the film prepared by solution casting method. Spectrum of PANI-CSA sample was taken by dispersing in KBr (pellet). ATR probe was used for recording the spectrum of the blend.

Tensile properties of the blends were measured by using Universal testing machine (Hounsfield) at room temperature at a crosshead speed of 20 mm/min using dumbbell-shaped specimens, according to ASTM D 638. Dynamic mechanical analysis was performed by using dynamic mechanical thermal analyzer (DMTA) (Rheometric Scientific). The samples were cut to pieces (16 mm  $\times$  10 mm  $\times$  3 mm), and DMTA scans were done at 1 Hz frequency at a heating rate of  $5^{\circ}\text{C}/\text{min}$  in the temperature range of  $-50$  to  $130^{\circ}\text{C}$ . The study could not be conducted at higher temperature, as the sample loses its integrity beyond  $130^{\circ}\text{C}$ .

### Electrical conductivity

The sample films were checked for its electrical conductivity by using standard four-probe technique. The connectivity of the film with probe was maintained by



**Figure 1** Schematic representation of vector network analyzer test set-up.

using silver epoxy paint. The measurements were performed at ambient temperature.

### Microwave absorption properties

Evaluation of complex relative permittivity ( $\epsilon_r = \epsilon_r' - j\epsilon_r''$ ) was carried out from the measured s-parameters using a two-port vector network analyzer [Agilent, 8720ES]. Network analyzers measure the magnitude and phase response of device under test by comparing the incident signal transmitted by the device or reflected to its inputs. Samples were prepared in the form of rectangular film of thickness 0.025 cm. The sample holder with sample fixed on it was placed between two coaxial wave guides as shown in Figure 1. The measurements were performed in the frequency range of 8–12 GHz.

### Measurement procedure

The measurements were carried out in sweeper and s-parameter test set. For higher accuracy of the measurement of  $S_{11}(\omega)$  and  $S_{21}(\omega)$ , full calibration with step sweep mode and averaging had been done. The s-parameters were first transformed to reflection coefficient  $R$  and transmission coefficient  $T$  using the following relations:

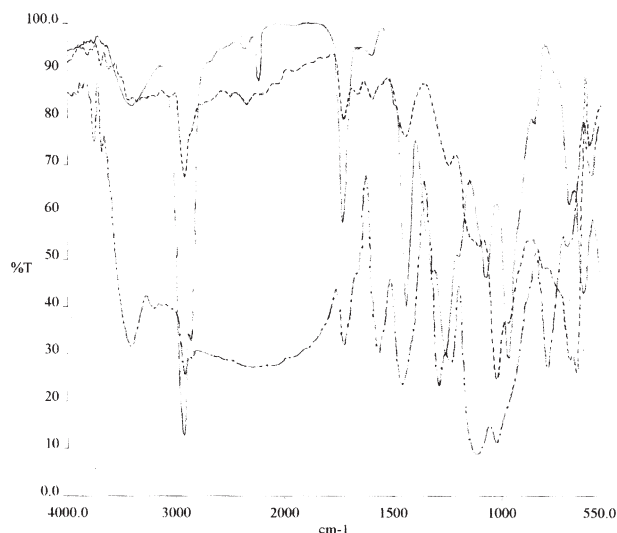
$$R = K \pm (K^2 - 1)^{1/2}$$

where

$$K = \frac{[S_{11}^2(\omega) - S_{21}^2(\omega)] + 1}{2S_{11}(\omega)}$$

and

$$T = \frac{[S_{11}(\omega) + S_{21}(\omega)] - R}{1 - [S_{11}(\omega) + S_{21}(\omega)]R}$$



**Figure 2** FTIR spectra of PVC-NBR/PANI-CSA: (----) PVC-NBR; (-•-) PANI-CSA; (—) PVC-NBR/PANI-CSA.

Relative permittivity and permeability were calculated from  $T$  and  $R$  using the following relations:

$$\mu_r = \frac{1 + R}{\Lambda(1 - R) \left[ \frac{1}{\lambda_0^2} - \frac{1}{\lambda_c^2} \right]^{1/2}}$$

$$\varepsilon_r = \frac{\left[ \frac{1}{\Lambda^2} - \frac{1}{\lambda_c^2} \right] \lambda_0^2}{\mu_r}$$

where

$$\frac{1}{\Lambda^2} = - \left[ \frac{1}{2\pi d} \ln(1/T) \right]^2$$

### Scanning electron microscopy

Blend samples were fractured after cooling in liquid nitrogen. The fractured samples were used for SEM study. Micrographs were taken by employing scanning electron microscope (Philips, XL-30).

## RESULTS AND DISCUSSION

In the present work, attempt has been made to make a conducting polymer blend, which will have appreciable conductivity as well as sufficient mechanical strength. PVC/NBR blend is thermoplastic in nature. Our approach was to make conducting blend using environment friendly technique. No solvent was used in the method. Usually, for solvent-free processing, the samples are exposed to high temperature for a long period.<sup>24–27</sup> The processing at high temperature for long period is associated with degradation of

PANI-CSA. In the present method, the samples were exposed to high temperature for only 2 min. This ensured minimum degradation of PANI-CSA. Further, the strength of the blend is quite appreciable for application. Because of the conducting nature of the blend, it is expected to have microwave absorption properties. These studies were also incorporated in the report. A simple approach was made to blend doped PANI (PANI-CSA) with PVA-NBR. The processing at 170°C for a short period does not affect the stability to appreciable extent. Further, the material remains thermoplastic in nature. This method adds to various techniques in the direction of making blends/composites of PANI. This is one of the simplest approaches in making conducting blend.

### FTIR spectra

Figure 2 shows the FTIR spectra of PVC-NBR, PANI-CSA, and the blend, respectively. PVC-NBR exhibits peaks at 2242  $\text{cm}^{-1}$ , which can be assigned to —CN group, and one at 632  $\text{cm}^{-1}$  signifying the presence of aliphatic C—Cl. Benzenoid and quinonoid rings are represented by 1465 and 1568  $\text{cm}^{-1}$  peaks, respectively. In the spectra of NBR-PVC/PANI-CSA, the peaks at 1465 and 1568  $\text{cm}^{-1}$  appears without much shifting. The peak assigned to —CN shifts to around 2260  $\text{cm}^{-1}$ , and the peak due to C—Cl shifts to 663  $\text{cm}^{-1}$ . The shifting may be due to possible hydrogen bonding with amine group of PANI.

### Mechanical properties

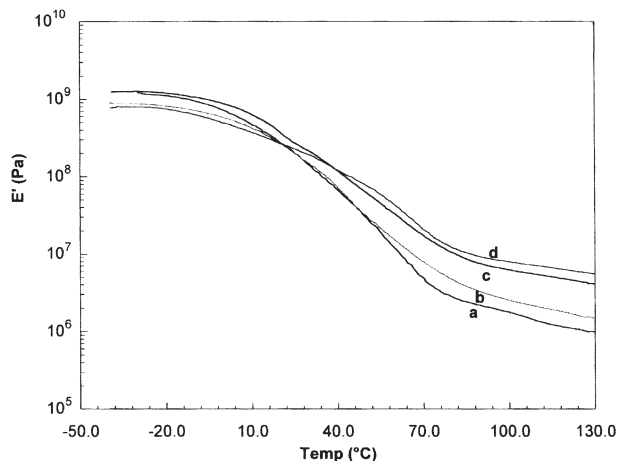
Table I shows the variation of tensile strength and elongation of PVC-NBR/PANI-CSA blends. There is reduction in tensile strength as PANI loading is increased. However, the reduction is not appreciable. There is definite decrease in percentage elongation as the loading of PANI is increased. It decreases from 218 in the case of PVC-NBR to 9.3 for PVC-NBR/PANI (100/75). This may be due to incorporation of PANI hard segments in soft PVC-NBR matrix.

### Dynamic mechanical properties

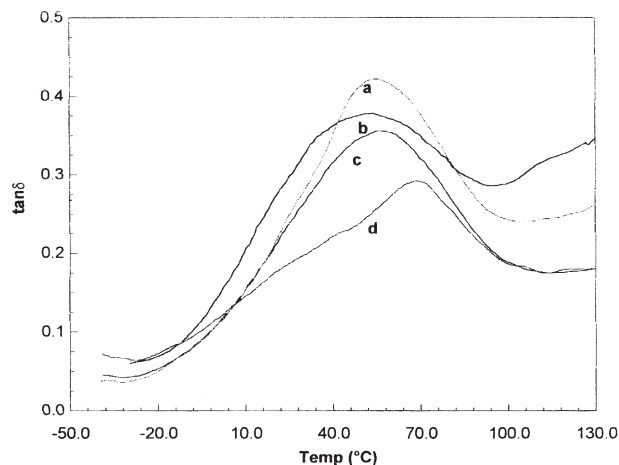
Figure 3 shows the storage modulus ( $E'$ ) of PVC-NBR/PANI-CSA blend as a function of temperature.

**TABLE I**  
Tensile Properties of PVC-NBR/PANI-CSA Blend

Composition of PVC-NBR/PANI	Tensile strength (MPa)	% Elongation
100/0	13.00	218
100/25	11.36	89
100/50	11.20	40
100/75	10.5	09



**Figure 3** Plot of storage modulus ( $E'$ ) versus temperature for PVC-NBR/PANI-CSA blend; (a) 100/0 (w/w); (b) 100/25; (c) 100/50; (d) 100/75.



**Figure 4** Plot of  $\tan \delta$  versus temperature for PVC-NBR/PANI-CSA blend; (a) 100/0 (w/w); (b) 100/25 (w/w); (c) 100/50 (w/w); (d) 100/75 (w/w).

In the glassy region,  $E'$  value lies around 1 GPa, and not much variation is observed for different blend ratios. Table II shows the  $E'$  values at 35°C.  $E'$  values of pure PVC-NBR and PVC-NBR/PANI-CSA (100/25) are almost identical. However, beyond 25 parts loading of PANI-CSA there is certain increase in  $E'$  value. The increase can be explained in terms of increase in rigidity due to the presence of hard segments of PANI coupled with compatibility of the two systems. This high value around 160 MPa at ambient temperature ensures potential application for practical purposes. Further, a fairly high modulus around 10 MPa is maintained in rubbery phase.

Figure 4 shows the  $\tan \delta$  plot for the blends. Single  $\tan \delta$  peak indicates the miscibility of PANI-CSA and PVC-NBR to produce a compatible blend. When hard segments of PANI were incorporated in soft PVC-NBR matrix, there is increase in temperature for  $\tan \delta_{\max}$ . Further, it is expected that polar interaction will be very high between resin and PANI-CSA. Temperature for  $\tan \delta_{\max}$  increases from 53°C for PVC-NBR to 70°C for PVC-NBR/PANI-CSA (100/75). As expected,  $\tan \delta_{\max}$  value reduces from 0.42 to 0.29, while the loading of PANI-CSA is increased to 75 parts. The  $\tan \delta_{\max}$  value of 0.29 in the blend is quite good in respect of application where the matrix has to sustain mechanical vibration.

#### Electrical conductivity

The blend samples have hardness in the range of 48–53 shore D. Therefore, four-probe method was conveniently used for the measurement. The electrical conductivity of PANI-HCl and PANI-CSA are 1.2 and 40 S/cm, respectively. Figure 5 shows the variation of electrical conductivity of PVC-NBR/PANI-CSA blends with variation of PANI-CSA content. It can be observed that there is monotonous increase of conductivity with PANI-CSA content. There is no clear percolation threshold in the plot. However, percolation threshold for melt blending of PANI-*p*-toluene sulfonic acid with polystyrene and copolyamide, was reported to be lying around 10 wt %.<sup>25</sup> In the present study, minimum PANI-CSA concentration is 25 phr. It is therefore obvious that the percolation threshold does not appear in the plot.

#### Microwave absorption properties

Figure 6 shows the plot of relative permittivity ( $\epsilon'$ ; real component) versus frequency.  $\epsilon'$  is the capacitive component, which indicates the charge storage capacity of the matrix. The value increases with the incorporation of PANI-CSA. The plot shows monotonous increase of  $\epsilon'$  with PANI-CSA loading. At 75 parts

**TABLE II**  
Storage Modulus and  $\tan \delta$  Values of NBR-PVC/PANI-CSA Blends

Composition of PVC-NBR/PANI-CSA blends	Storage modulus $E'$ at 35°C (MPa)	Temperature for $\tan \delta_{\max}$ (°C)	$\tan \delta_{\max}$
100/0	100	53.02	0.42
100/25	102	54.53	0.38
100/50	165	57.02	0.36
100/75	169	69.67	0.29



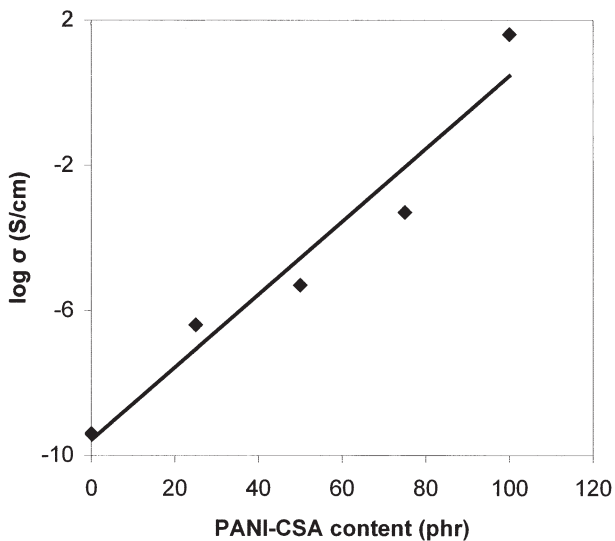


Figure 5 Plot of conductivity ( $\sigma$ ) versus PANI-CSA content in PVC-NBR/PANI-CSA blend.

loading of PANI-CSA, the value reaches around 18. As the loading increases, sudden decrease in  $\epsilon'$  is expected as the PANI-CSA particles come very close so that the discharge becomes easier. However, in the present study, the loading was restricted to 75 parts, as the film quality deteriorates on further increase in loading. In the case of pure PANI-CSA, as expected,  $\epsilon'$  reduces to around 9, which reflects a large drop in charge storage capacity of the matrix. At this state, all PANI-CSA particles remain interconnected.

Figure 7 shows the plot of relative permittivity ( $\epsilon''$ ; loss component) versus frequency. It can be seen that with increase of PANI-CSA loading the loss component increases as the connectivity of PANI particles are increased. At 75 parts loading of PANI-CSA, the value reaches to around 8. Pure PANI-CSA shows a value ranging from 94 to 66. As the connectivity is

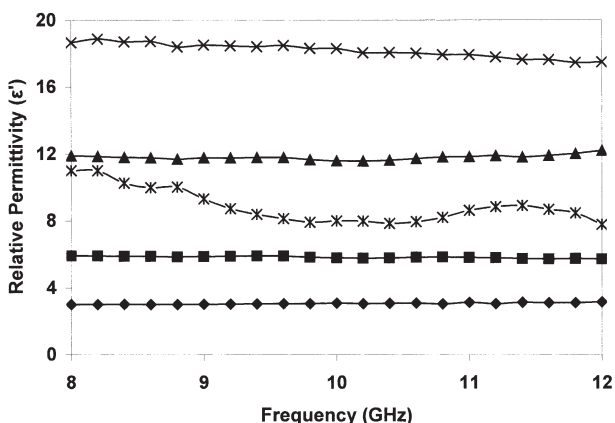


Figure 6 Plot of real part of relative permittivity ( $\epsilon'$ ) as a function of frequency for PVC-NBR/PANI-CSA blend; (♦), 100/0 (w/w); (■), 100/25 (w/w); (▲), 100/50 (w/w); (×), 100/75 (w/w); (\*), 0/100 (w/w).

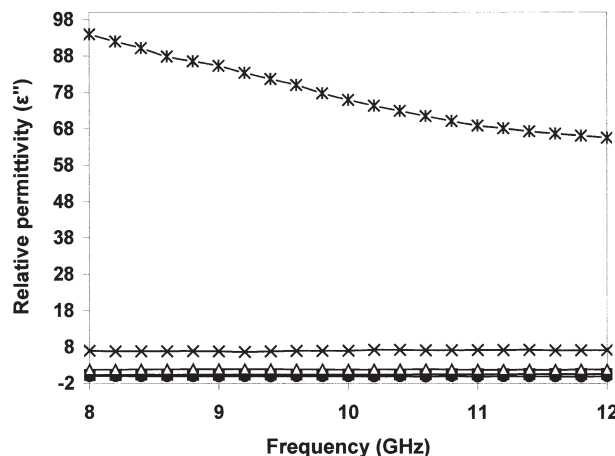


Figure 7 Plot of imaginary part of relative permittivity ( $\epsilon''$ ) as a function of frequency for PVC-NBR/PANI-CSA blend; (♦), 100/0 (w/w); (■), 100/25(w/w); (▲), 100/50 (w/w); (×), 100/75 (w/w); (\*), 0/100 (w/w).

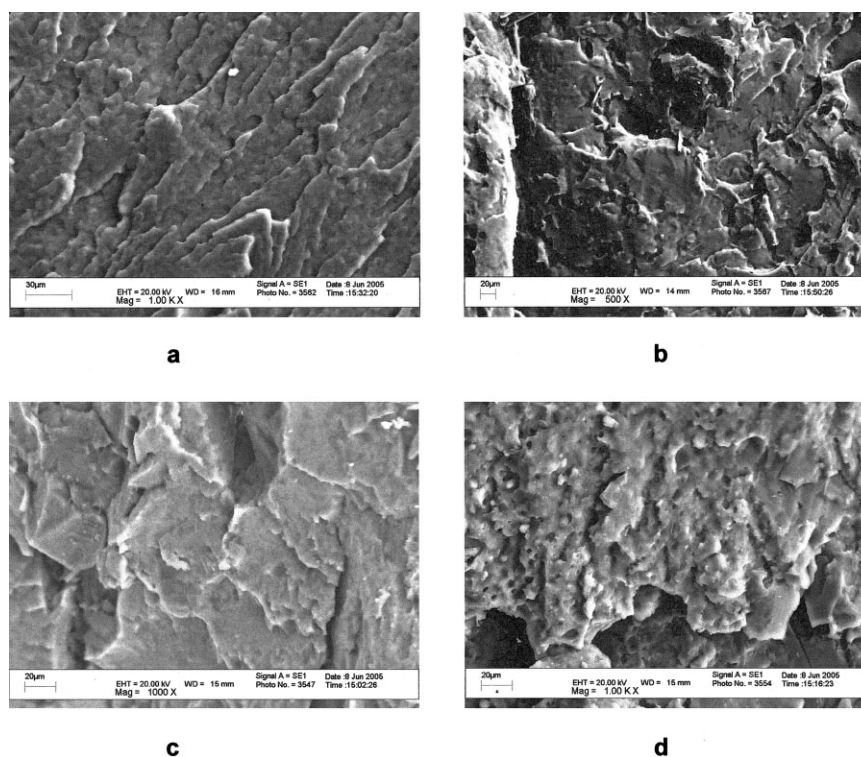
maximum, the energy transfer also becomes maximum. Obviously, the dissipation reaches maximum value, and the  $\epsilon''$  value shoots up to a very high value.

Scanning electron microscopy

Figure 8 shows the SEM pictures of PVC-NBR/PANI-CSA blends. It can be seen that the fracture morphology changes with loading of PANI-CSA. The blend without PANI-CSA (Fig. 8(a)) shows typical single phase morphology. After incorporation of PANI-CSA, the micrograph shows homogeneity in the blend. In all the other micrographs (Fig. 8(b)–8(d)), the homogeneity is maintained. However, in Fig. 8(b) (100/50), small globular morphology also appears. It increases in size with further increase of PANI-CSA. This may be due to the formation of conducting islands, as PANI-CSA content is very high. The presence of conducting islands along with homogenous morphology accounts for rapid increase of conductivity as observed in our study.

CONCLUSIONS

A convenient and environment friendly method was followed for blending ( $\pm$ )-camphor sulfonic acid doped polyaniline with polyvinyl chloride/nitrile rubber. The conductivity of the blend was found to be in increasing order, as the loading of PANI-CSA was increased. Tensile strength did not change much with loading of PANI-CSA; however, elongation shows constant decrease. Storage modulus increased at higher PANI-CSA loading, whereas  $\tan \delta$  value decreased. There is shift in  $\tan \delta_{max}$  temperature with loading. Loss component of relative permittivity was found to increase with polyaniline content. SEM pic-



**Figure 8** Scanning electron micrograph of PVC-NBR/PANI-CSA blend; (a) 100/0 (w/w); (b) 100/25 (w/w); (c) 100/50 (w/w); (d) 100/75 (w/w).

tures shows homogeneity of PVC-NBR and PANI-CSA phases.

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