

# Frequency-Dependent Conductivity and Dielectric Permittivity of Polyaniline/CeO<sub>2</sub> Composites

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**ABSTRACT:** The PANI/CeO<sub>2</sub> composites were synthesized using *in situ* deposition technique by placing fine graded CeO<sub>2</sub> in polymerization mixture of aniline. This is the single step polymerization process for the direct synthesis of emeraldine salt phase of polymer. Low frequency dielectric studies were carried out on pressed pellets of PANI/CeO<sub>2</sub> with various concentrations of cerium oxide (10, 20, 30, 40, and 50 wt % of CeO<sub>2</sub> in PANI). The results are interpreted in terms of polarons and bipolarons, which are responsible for the dielectric relaxation mechanism and frequency dependence of conductivity. It is found that a.c.

measurements at room temperature may well serve as a parallel way to the time consuming d.c. conductivity versus temperature technique, to detect the thermal degradation of the transport properties in conducting polymers. It is observed that the charge motion via creation/annihilation of polarons and bipolarons increases as the weight percentage of the composite is increased. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1403–1405, 2006

**Key words:** conducting polymers; polyaniline; cerium oxide; dielectric permittivity

## INTRODUCTION

The organic conducting polymer polyaniline (PANI) and its composites, PANI/CeO<sub>2</sub>, have recently been the subject of intense investigation to understand the conduction mechanisms present in these systems and to study the effects of localization introduced by disorder.<sup>1–7</sup> The insulating emeraldine base form of polyaniline (PANIEB) consists of equal number of reduced [–(C<sub>6</sub>H<sub>4</sub>)–N(H)–(C<sub>6</sub>H<sub>4</sub>)–N(H)–] and oxidized [–(C<sub>6</sub>H<sub>4</sub>)–N(H)=C<sub>6</sub>H<sub>4</sub>=N–] repeat units. The conducting emeraldine salt form (PANIES) is achieved by doping with aqueous protonic acids like HCl where protons are added to the –N= sites, while maintaining the number of electrons in the polymer chain constant. This leads to an increase in conductivity by more than 10 orders of magnitude depending on the strength of the acid.<sup>8</sup> The conductivity in PANI and PANI/CeO<sub>2</sub> is governed by hopping of charge carrier between polymer chains and is more one dimensional in character. With higher composition of CeO<sub>2</sub> in PANI, magnetic susceptibility measurements indicate that the regions of the bulk polymer are more conducting than others, yielding an overall structure consisting of “metallic islands” dispersed in amorphous insulating matrix.<sup>9</sup> Even though the conductiv-

ity within the metallic islands is rather high (about 250 S/cm), the overall bulk conductivity is governed by charge transport within the amorphous regions of the polymer<sup>1</sup> and is much lower.

Investigations on PANI/CeO<sub>2</sub> composites have focused in particular on the localization effect of electrons along the polymer chain because of the disorder introduced by the presence of the methyl group placed at random on one of the two “ortho” positions of the benzene ring in PANI. Many studies have been performed to investigate the conductivity and localization effects as a function of temperature in these systems<sup>2–4, 7</sup> at higher concentration levels of CeO<sub>2</sub>. However, there have been no studies on the frequency dependence of the conductivity and dielectric response in PANI/CeO<sub>2</sub> composites, especially at lower concentrations of CeO<sub>2</sub>. Dielectric measurement is a powerful method of studying motion of charge and its delocalization within the amorphous regions of the polymer, making it a suitable tool to investigate the PANI/CeO<sub>2</sub> composites.

In the present study, the frequency dependence of conductivity and dielectric permittivity of PANI/CeO<sub>2</sub> composites with various concentrations of CeO<sub>2</sub> in PANI has been investigated. The results are interpreted in terms of polarons and bipolarons formed during synthesis and various concentrations of CeO<sub>2</sub> in PANI of these materials, their localization along the chain being due to the disorder and their subsequent diffusion via creation and annihilation. Our results are consistent in that the transport of charge is signifi-

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cantly affected as the substituent group of main chain polymer backbone gets larger.

## EXPERIMENTAL

### Materials and methods

All Chemicals used were of analytical reagent grade. The monomer aniline was doubly distilled prior to use. Ammonium persulphate  $((\text{NH}_4)_2\text{S}_2\text{O}_8)$ , hydrochloric acid (HCl), and cerium oxide ( $\text{CeO}_2$ ) (Sigma, India) were used as received.

Aniline (0.1 mol) was dissolved in 1M HCl to form PANI. Cerium oxide was added to PANI solution with vigorous stirring to keep the cerium oxide suspended in the solution. To this reaction mixture, 0.1M of ammonium persulphate  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ , which acts as the oxidant, was added slowly with continuous stirring for 4–6 h at 0–5°C. The precipitated powder recover was vacuum-filtered and washed with deionized water. Finally, the resultant precipitate was dried in an oven for 24 h to achieve a constant weight.

PANI/ $\text{CeO}_2$  composites were prepared in weight percent ratio in which the concentration of cerium oxide (10, 20, 30, 40, and 50 wt %) was varied. The test samples to be used were prepared in pellet form of diameter 10 mm and thickness 3 mm by applying pressure of 7 t using Pye–Unicam dye. The contacts for these composites were made using silver paste as electrodes on both sides.

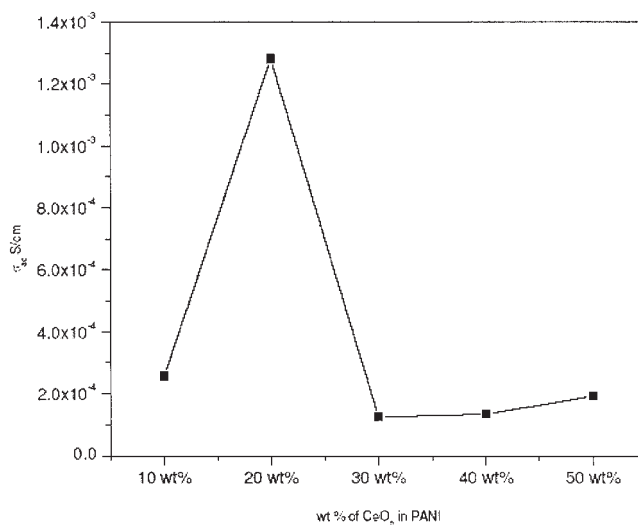
Dielectric measurements of PANI/ $\text{CeO}_2$  composites were carried using Hioki impedance analyzer 3532–50 (Japan) in the frequency range  $10^2$ – $10^6$  Hz at room temperature.

## RESULTS AND DISCUSSION

Figure 1 shows the electrical conductivity ( $\sigma$ ) of PANI/ $\text{CeO}_2$  composites for different weight percentage (10, 20, 30, 40, and 50 wt % of  $\text{CeO}_2$  in PANI) at room temperature. This conductivity was extracted from the measured real and imaginary parts of the complex dielectric permittivity  $\varepsilon^*$  ( $=\varepsilon' - i\varepsilon''$ ) using the following relation:

$$\sigma = \sigma' - i\sigma'' = i2\pi f\varepsilon_0 (\varepsilon^* - 1) \quad (1)$$

where  $f$  is the frequency,  $i = \sqrt{-1}$ , and  $\varepsilon_0$  is the permittivity of vacuum. This procedure was applied for all samples. It is clear from the figure that conductivity ( $\sigma_{ac}$ ) values showed a slight change for composites having low concentration of  $\text{CeO}_2$ . A sudden increase in  $\sigma$  value is found for a particular concentration of  $\text{CeO}_2$  (i.e., 20 wt %). This is the critical concentration for which conductivity has maximum value and on further increasing the concentration, we find a decrease in  $\sigma$  value. The decrease in conductiv-



**Figure 1** The Conductivity of PANI/ $\text{CeO}_2$  composites for different weight percent of  $\text{CeO}_2$  in PANI at a frequency of 10 KHz.

ity by increase in weight percent of  $\text{CeO}_2$  in PANI may be due to particle blockage conduction path by  $\text{CeO}_2$  embedded in PANI matrix.<sup>10</sup> Also, increase in weight percent of  $\text{CeO}_2$  leads to a larger number of polarons where the interpolaron coupling gets progressively stronger even though disorder present, leading to severe pinning of polarons, thus restricting their contribution at higher frequencies, hence in the reduction of conductivity.<sup>11</sup>

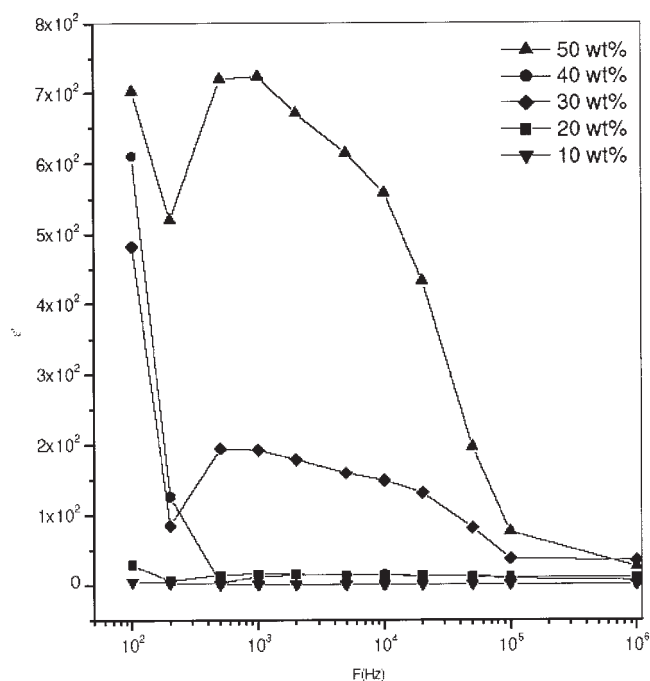
Figure 2 shows the real part of the dielectric permittivity ( $\varepsilon'$ ) as a function of frequency of PANI/ $\text{CeO}_2$  composites (10, 20, 30, 40, and 50 wt % of  $\text{CeO}_2$  in PANI). The increasing dielectric permittivity with increase in concentration of  $\text{CeO}_2$  as seen from Figure 2 is a result of contributions from the backbone PANI and the polarons and bipolarons formed.<sup>2</sup> At frequencies below 100 Hz, the dielectric permittivity is seen to increase much more rapidly, suggesting stronger coupling between the polarons ( $\varepsilon' = 7.07 \times 10^2$ ,  $6.13 \times 10^2$ ,  $4.82 \times 10^2$ , 29, 4.55 for 10, 20, 30, 40 and 50 wt % of  $\text{CeO}_2$  respectively).  $\varepsilon'$  exhibits a low frequency plateau corresponding to the bulk static dielectric constant  $\varepsilon_0$  and then decreases with increasing frequency, finally forming low-value plateau around  $10^6$  Hz. For all the composites,  $\varepsilon'$  is relatively constant except 50 wt % representing these additional contributions to the dielectric response with an almost Debye-like relaxation mechanism.<sup>12,13</sup>

Figure 3 shows the imaginary part of dielectric permittivity ( $\varepsilon''$ ) of PANI/ $\text{CeO}_2$  composites (10, 20, 30, 40, and 50 wt % of  $\text{CeO}_2$  in PANI).  $\varepsilon''$  shows a loss characterized by a relaxation frequency for all the samples. The peak maximum frequency  $f_{\text{max}}$  of all the composites seem to occur concomitantly with a sudden decreasing of  $\varepsilon'$  values, which are not masked by a.c.

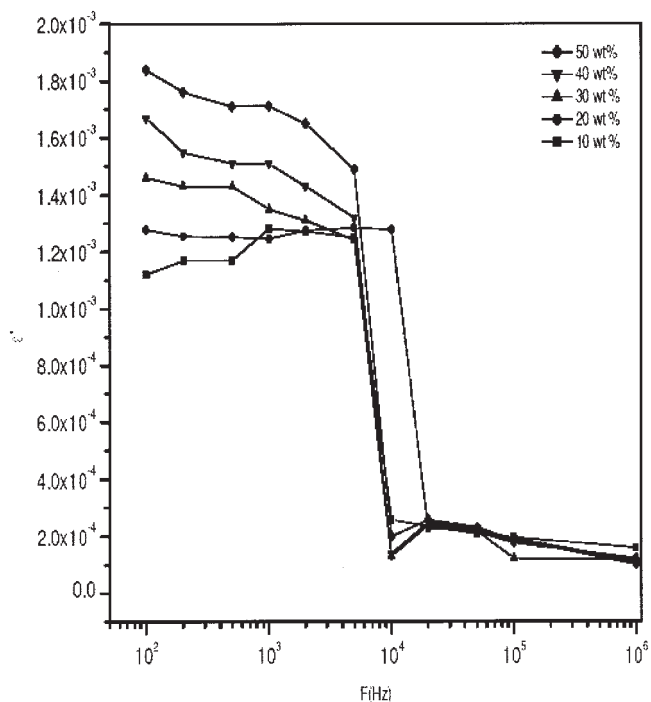
conduction. After the loss factor reaches  $f_{max}$ , it decreases almost linearly in all the composites. At high frequency region beyond  $10^4$  Hz,  $\epsilon''$  exhibits low value plateau. The difference in the dielectric relaxation times with changing concentration may be due to the electric charges being displaced inside the polymer (stronger localization) and/or their lower concentration.<sup>14</sup> Two possible causes can exist. The first is that the increase in the counteranion size led to an increasing interchain distance, which makes hopping between chains more difficult and hence resulting in reduction in the conductivity. Another possible assumption depends on the changing concentration of CeO<sub>2</sub>.

### CONCLUSIONS

The PANI/CeO<sub>2</sub> composites were synthesized using *in situ* deposition technique by placing fine graded CeO<sub>2</sub> in polymerization mixture of aniline. Low frequency dielectric studies were carried out on pressed pellets of PANI/CeO<sub>2</sub> with various concentrations of cerium oxide (10, 20, 30, 40, and 50 wt % of CeO<sub>2</sub> in PANI). The results on PANI/CeO<sub>2</sub> composites are interpreted in terms of polarons and bipolarons and their contribution towards conductivity and dielectric relaxation. Increase in concentration of CeO<sub>2</sub> leads to an increase in polarons formed and is responsible for the spread as the polymer is made more conducting.



**Figure 2** Frequency dependence of the real part of the dielectric permittivity ( $\epsilon'$ ) of PANI/CeO<sub>2</sub> composites.



**Figure 3** Frequency dependence of imaginary part of dielectric permittivity ( $\epsilon''$ ) of PANI/CeO<sub>2</sub> composites.

Higher and lower concentration of the PANI/CeO<sub>2</sub> composites have similar conductivities, which reflects the severe pinning effects on the motion of polarons because of the extreme disorder introduced by the larger pendant groups on the main chain PANI.

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