



# Dielectric Constant Study of Polyaniline – CeO<sub>2</sub> Composites

## KEYWORDS

Dielectric constant, Polyaniline, CeO<sub>2</sub>

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**ABSTRACT** *In situ* polymerization of aniline was carried out in the presence of CeO<sub>2</sub> to synthesize Polyaniline - CeO<sub>2</sub> composites by chemical oxidation method. The PANI/ CeO<sub>2</sub> composites have been synthesized with various compositions viz., 10, 20, 30, 40 and 50 Wt. % of CeO<sub>2</sub> in PANI. The Dielectric constant was studied in the frequency range 10<sup>2</sup>–10<sup>7</sup> Hz at room temperature. It is observed that, Dielectric constant is maximum for 40wt% of CeO<sub>2</sub> in PANI. The dimensions of CeO<sub>2</sub> particles in the matrix have a greater influence on the Dielectric constant values.

## 1. Introduction

Polymers have traditionally been considered as a good electrical insulators and a variety of their applications have relied on their insulating property [1]. However more than a decade now, researchers have shown that certain class of polymers which are conjugated, exhibit semiconducting behavior [2]. The discovery of doping has led to a further dramatic increase in the conductivity of such conjugated polymers to values as high as 10<sup>5</sup> S/cm. The presence of an extended  $\pi$  conjugation in polymers, however, confers the required mobility to charges that are created on the polymer backbone (by the process of doping) and make them electrically conducting [3]. Conducting polymers have become the foci of much research in materials science and among all; polyaniline and polypyrrole have received greater attraction due to their favorable economics, easy synthesis, environmental stability and unique chemistry [4]. The electrical conductivities of the intrinsically and conducting polymer systems range from those insulators (<10<sup>-5</sup> and 10<sup>-10</sup> S/cm) to those of typical semiconductors such as silicon ( $\approx$ 10<sup>-5</sup> S/cm) and to those greater than 10<sup>4</sup> S/cm (nearly to that of a good metal such as copper  $\approx$ 5 $\times$ 10<sup>5</sup> S/cm) [5]. Applications of these polymers have begun to emerge a new era. These include coating and blends for electrostatic dissipation and electromagnetic interference (EMI) shielding [6, 7]. Electromagnetic radiation absorbs for welding (joining) of plastics, conductive layers for light emitting polymer devices and anti corrosion for iron and steel [8]. Many attempts in the preparation of polypyrrole composites with inorganic particles were also performed, such as with montmorillonite and  $\gamma$ -zeolite [9]. Polypyrrole inorganic particles were also investigated for their applications in electroheological (ER) fluid and high-density information storage [10].

## 2. Experimental

### Materials and Methods

Ammonium persulphate (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, Hydrochloric acid (HCl) and Cerium oxide (CeO<sub>2</sub>) used were of AR grade. Doubly distilled water and aniline is used as a solvent and a monomer. Polyaniline is prepared by oxidative method and Polyaniline composites were prepared by *in situ* polymerization method with dispersion of CeO<sub>2</sub> in polyaniline.

### Synthesis of Polyaniline/ CeO<sub>2</sub> Composites

Aniline was dissolved in 1M HCl to form polyaniline (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 [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], which acts as an oxidant, was added slowly with continuous stirring for 4-6 hours at 0-5°C. The precipitated powder recover was vacuum-filtered and washed with deionizer water. Finally, the resultant precipitate was dried in an oven for 24 hours to achieve a constant weight. In the similar

manner pure PANI is prepared without adding Cerium oxide. PANI/ CeO<sub>2</sub> composites were prepared in weight percent ratio in which the concentration of Cerium oxide (10, 20, 30, 40 and 50%) was varied. The test samples to be used were prepared in pellet form of diameter 10mm and thickness 3mm by applying pressure of 7t using Pye-Unicam dye. The contacts for these composites were made using silver paste as electrodes on both sides.

Dielectric constant measurements were carried out at room temperature over the frequency range 10<sup>2</sup>-10<sup>7</sup>Hz using the Hiokie LCR Q meter.

## 3. Results and Discussion

Figure 1. shows the X-ray diffraction pattern of Polyaniline – CeO<sub>2</sub> composite with 50 wt % of CeO<sub>2</sub> in polyaniline. It is seen from figure 1 that the cubic peaks of CeO<sub>2</sub> indicates the crystalline nature of the composite. By comparing the XRD pattern of composite with that of CeO<sub>2</sub> (JCPDS No. 34-0394), the prominent peaks corresponding to  $2\theta = 26.52^\circ$ ,  $33.51^\circ$  and  $59.58^\circ$ , are due to (111), (200), and (222) planes of CeO<sub>2</sub>. By comparing the XRD patterns of the composite and CeO<sub>2</sub>, it is confirmed that CeO<sub>2</sub> has retained its structure even though it is dispersed in PANI during polymerization reaction. The peaks of CeO<sub>2</sub> after doping in PANI, are shifted slightly to higher values and also the peak of PANI at 27<sup>o</sup> has broadened this is due to dispersion of CeO<sub>2</sub> in PANI.

The IR spectra of polyaniline – CeO<sub>2</sub> composite (50 wt % of CeO<sub>2</sub> in PANI) is shown in Fig. 2. The prominent peaks that are observed in polyaniline – CeO<sub>2</sub> composite are 3437 cm<sup>-1</sup>, 2918 cm<sup>-1</sup>, 2844 cm<sup>-1</sup>, 1578 cm<sup>-1</sup>, 1486 cm<sup>-1</sup>, 1300 cm<sup>-1</sup>, 1134 cm<sup>-1</sup>, 899 cm<sup>-1</sup>, 831 cm<sup>-1</sup>, 707 cm<sup>-1</sup>, 646 cm<sup>-1</sup>, and 504 cm<sup>-1</sup>. By careful observation of IR the characteristic stretching frequencies are considerably shifted towards higher frequency side. The typical peaks are observed at 899 cm<sup>-1</sup>, 831 cm<sup>-1</sup>, 646 cm<sup>-1</sup> and 504 cm<sup>-1</sup>. The data suggest that, there is a Vander walls kind of interaction between the polymer chain and CeO<sub>2</sub>. This is further supported by the FTIR spectra of polyaniline / CeO<sub>2</sub> under reference.

The SEM micrograph of polyaniline & polyaniline – CeO<sub>2</sub> composite with 50 wt % of CeO<sub>2</sub> in polyaniline is shown in figure 3. High magnification SEM image reveals the presence of CeO<sub>2</sub> particles uniformly distributed throughout the composite sample. A small variation in the particle dimensions of CeO<sub>2</sub> so dispersed in polyaniline has been observed. Also fibrillar morphology is observed in the composite. The contrast in the image is due to the difference in scattering from different surface areas as a result of geometrical differences between polyaniline and CeO<sub>2</sub>.

Since structure property correlation plays a significant role, a

correlation between dimension of CeO<sub>2</sub> used for composite preparation and its effect on electrical properties.

Figure 4. shows the variation of  $\epsilon'$  as a function of frequency for polyaniline – CeO<sub>2</sub> composites (different wt %). In all the cases it is observed that, the dielectric constant is quite high at low frequency and decreases with increase in applied frequency. The observed behavior may be due to Debye like relaxation mechanism taking place in these materials [11].

Figure 5 represents the variation of  $\epsilon'$  as a function of wt% of CeO<sub>2</sub> at room temperature and at three different frequencies. It is observed that the values of dielectric constant decreases up to 20wt% and then increases up to 40 wt%, further increase of wt% of CeO<sub>2</sub> it decreases. Again, all these results go in accordance with the conductivity behavior. The observed change in conductivity is mainly responsible for the anomaly in dielectric constant behavior.

**4. Conclusion**

Efforts have been made to synthesize PANI/ CeO<sub>2</sub> composites to tailor make their properties. The results of dielectric constant show a strong dependence on the wt. % of CeO<sub>2</sub> in PANI.

**5. Acknowledgement**

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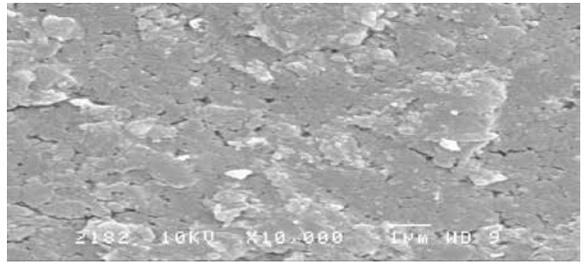


Figure: 3 SEM Micrograph of Polyaniline CeO<sub>2</sub> (50 wt %)

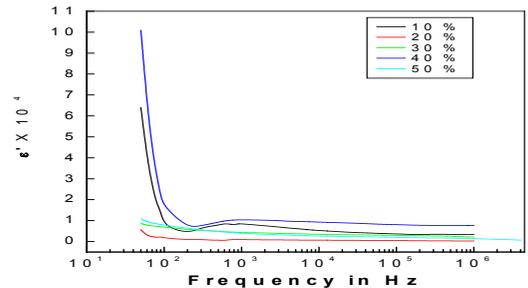


Figure 4. Variation of dielectric constant as a function of frequency for Polyaniline CeO<sub>2</sub>

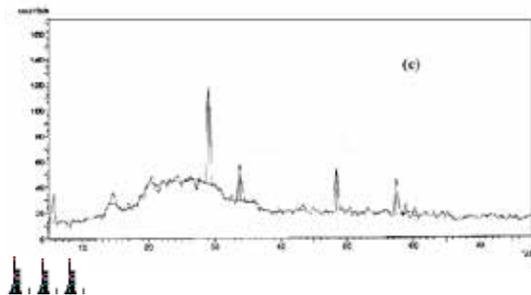


Figure.1 X – Ray diffraction pattern of Polyaniline – CeO<sub>2</sub> composite (50 wt %)

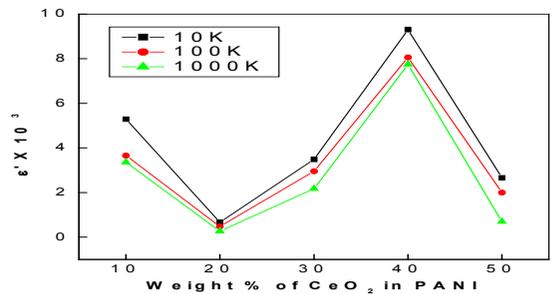


Figure 5 Variation of  $\epsilon'$  as a function of wt% of CeO<sub>2</sub> at different frequencies



Figure : 2 FTIR spectra of PANI – CeO<sub>2</sub> composite (50 wt%)

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