

# Dielectric Spectroscopy of Polypyrrole-CeO<sub>2</sub> Nano Composites

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**Abstract:** Conducting Polypyrrole-Cerium Oxide (Polypyrrole-CeO<sub>2</sub>) composites were synthesized by in situ deposition technique by placing different weight percentages of CeO<sub>2</sub> powder (10, 20, 30, 40 and 50%) during the polymerisation of pyrrole. AC conductivity of Polypyrrole-CeO<sub>2</sub> composites was studied in the frequency range from 10<sup>2</sup>–10<sup>7</sup> Hz. It is found from these studies that, at low frequency AC conductivity remains constant and increases rapidly at higher frequency. This behavior is the characteristic of disordered materials. The dielectric behavior of these composites was also investigated in the frequency range 10<sup>2</sup>–10<sup>7</sup> Hz. From these studies it is observed that the dielectric constant and dielectric tangent loss decrease exponentially with frequency. At higher frequency the composites exhibit a low value of dielectric loss.

**Key words:** Polypyrrole, Composite, AC Conductivity, Oxide, Dielectric constant.

## 1. INTRODUCTION:

In the field of conducting polymers there has been explosive growth of present era research. As conducting polymers exhibit remarkable physical, thermal, electrical and magnetic properties, they have potential application in various fields [1]. Due to their significant levels of electrical conductivity, they are suitably used in electronic devices, batteries, functional electrodes, electrochromic devices, optical switching devices, sensors and so on [2]. To highly improve the applications of conducting polymers, many efforts have been taken by researchers to change their structure by using organic / inorganic dopants and oxidants [3].

Many investigated conducting polymers are available but among these Polypyrrole (PPy) has been used most widely because of its good electrical conductivity and appreciable environmental stability. Lot of potential applications of Polypyrrole such as sensors, solid electrolytes and electrodes, for capacitor and solid state batteries have been reported [4]. In addition to this, PPy is readily synthesized using a range of aqueous and non-aqueous solvents [5]. Recent investigations have shown that the synthesis of polymers in the presence of nanoparticles can increase the surface area of polymers [6, 7]. The incorporation of the conducting polymer as the shell in the core-shell structure can increase the surface area of the conducting polymers over that of the bulk polymer. This structure can be obtained from an in situ chemical oxidative polymerization in the presence of nanoparticles [8].

Among metal oxides, one of the most abundant rare earth metal oxides is Cerium Oxide. CeO<sub>2</sub> has received great attention because of its unique properties, including nontoxicity, biocompatibility, oxygen storage capability, electrocatalytic ability, optical, thermal properties, which have significant applications in solar cells, solid oxide fuel cells, gas sensors and biosensors [9]. Also, due to its unique properties such as high surface area to volume ratio compared with bulk material it has gained much attention in various research fields [10].

In the present study author reports synthesis, ac conductivity and dielectric spectroscopy of CeO<sub>2</sub> doped polypyrrole composites prepared by chemical oxidation method.

## 2. MATERIAL AND METHODS:

### 2.1 Materials:

Analytical-reagent-grade Pyrrole, Cerium Oxide and anhydrous Iron (III) Chloride (AR-grade) were obtained and used in the present study. Pyrrole monomer was purified by distillation under reduced pressure and stored in dark at 4°C before use.

### 2.2 Synthesis of Polypyrrole and Polypyrrole-CeO<sub>2</sub> composites:

For chemical polymerisation of pyrrole, FeCl<sub>3</sub> was used as an oxidant. Anhydrous ethanol was used as solvent for the polypyrrole synthesis.

3.45ml (0.5M) of pyrrole was dissolved in 25ml of ethanol and stirred for 10 min. 25ml of FeCl<sub>3</sub>.6H<sub>2</sub>O was added drop wise to the ethanol solution of pyrrole. Cerium Oxide was varied in weight percentages (10, 20, 30, 40 and 50) and added to the polypyrrole solution. This reaction mixture was stirred for 3hr with magnetic stirrer in order to disperse

CeO<sub>2</sub> in the polymer solution. The obtained product was filtered and washed thoroughly with acetone and distilled water in order to remove the unreacted pyrrole and excess ferric chloride. The samples were vacuum dried for 1 hr at 60-70°C. The powders of polypyrrole and polypyrrole-CeO<sub>2</sub> composites obtained were crushed and finely ground using mortar pestle.

### 2.3 Measurements:

The composites so obtained were pressed in the form of circular pellets of 1cm diameter and thickness 2.5 to 3mm. The pellets were coated with silver paste on either side. The frequency dependent AC conductivity, dielectric constant and dielectric tangent loss of polypyrrole-CeO<sub>2</sub> composites are studied in the frequency range 10<sup>2</sup> Hz–10<sup>7</sup> Hz at room temperature using Hioki LCR Q meter.

## 3. RESULTS AND DISCUSSIONS:

### 3.1 AC Conductivity:

Figure 1 shows the variation of ac conductivity as a function of frequency for polypyrrole. The conductivity increases with increase in frequency. The ac conductivity exhibits two phases in the frequency range 10<sup>2</sup> Hz to 10<sup>7</sup> Hz. **Fig.1**

In frequency between 10<sup>2</sup> Hz to 10<sup>5</sup> Hz, the conductivity values are almost constant and beyond this increases suddenly. Lattice polarization around a charge in localized state may be responsible for multiple phases of conductivity in Polypyrrole.

Figure 2 shows the variation of ac conductivity as a function of frequency for different wt% of polypyrrole-CeO<sub>2</sub> composites. It is observed that all the composites show similar behaviour up to 10<sup>5</sup>Hz and beyond this frequency it increases steeply. This behaviour is the characteristic of disordered materials. [11].

In Figure 3, the values of  $\sigma_{ac}$  are plotted as a function of different weight percentage of CeO<sub>2</sub> in PPy at room temperature with three different frequencies (10 kHz, 100 kHz and 1000 kHz). It is observed that for all the frequencies, the value of  $\sigma_{ac}$  is found to decrease for 40wt% of CeO<sub>2</sub> in PPy and increases for 20 wt%, 30 wt% and 50 wt% of CeO<sub>2</sub> in PPy. The initial increase in the value of  $\sigma_{ac}$  is due to the extended chain length of PPy, where the localized charge carriers such as polarons undergo polarization leading to an increase in the further conductivity. However, the decrease in  $\sigma_{ac}$  for 40wt% is due to the partial blocking of charge carriers, which makes the polarization condition more difficult. **Fig. 2, Fig. 3**

### 3.2 Dielectric behaviour:

The frequency – dependent dielectric constant and dielectric losses of polypyrrole-CeO<sub>2</sub> composites at room temperature are plotted.

Figure 4 shows the variation of dielectric constant  $\epsilon'$  as a function of frequency for different wt% of polypyrrole-CeO<sub>2</sub> composites. It is found that dielectric constant decreases as frequency increases for different wt% of polypyrrole-CeO<sub>2</sub> composite. It is observed that Debye type relaxation mechanism is responsible for higher values of dielectric constant at low frequencies, which decreases as the applied frequency increases [12, 13]. Thus, above the frequencies of 100 kHz, the dielectric constants  $\epsilon'$  become independent of the applied frequency.

Figure 5 represents the variation of dielectric constant  $\epsilon'$  as a function of weight percentage of CeO<sub>2</sub> in Polypyrrole at room temperature at three different frequencies (10 kHz, 100 kHz and 1000 kHz). It is observed that for all the frequencies, the value of  $\epsilon'$  is found to increase tremendously for 40 wt% and decreases for 10 wt%, 20 wt%, 30wt% and 50 wt% of CeO<sub>2</sub> in polypyrrole, which is a characteristic of Debye type relaxation mechanism. This is also due to the additional contribution of hopping of polarons in the localized state. **Fig. 4, Fig. 5**

The variation of dielectric tangent loss ( $\tan\delta$ ) as a function of frequency for polypyrrole/ CeO<sub>2</sub> is shown in Figure 6 for different wt%. It is observed that the dielectric loss decreases as a function of frequency. The composite exhibit small value of dielectric loss at higher frequencies, which suggests that these materials are lossless materials at frequencies beyond 1MHz. The observed behaviour is consistent with the conductivity and dielectric constant results in these composites.

Figure 7 shows the dielectric tangent loss ( $\tan\delta$ ) as a function of wt% of CeO<sub>2</sub> in polypyrrole at three different frequencies (10 kHz, 100 kHz and 1000 kHz). It is observed that at all frequencies  $\tan\delta$  decreases for 20 wt%, 30 wt% and 50 wt% and increases for 10 wt% and 40 wt%. The behavior of change in wt% is observed due to the high relaxation time. At this stage the charge carriers will reorient with respect to field. Once the reorientation completes, relaxation time decreases, hence  $\tan\delta$  decreases. **Fig. 6, Fig. 7**

## 4. CONCLUSION:

Polypyrrole-CeO<sub>2</sub> composites have been synthesized by in situ polymerization method. The AC conductivity is studied in the frequency range 10<sup>2</sup> – 10<sup>7</sup> Hz. The results of AC conductivity and dielectric constant show a strong dependence on weight percentage of CeO<sub>2</sub> in polypyrrole. The dielectric constant and dielectric loss response as a function of frequency shows Debye – type relaxation mechanism in Polypyrrole and its composites. Even though CeO<sub>2</sub> is added up to 50 wt% in Polypyrrole, the behavior of dielectric loss with respect to frequency follows same trend as that of pure Polypyrrole. At higher frequencies these composites exhibit almost zero dielectric loss, which suggests that these composites are lossless materials at frequencies beyond 1 MHz.

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## FIGURE CAPTIONS:

- Fig. 1** Variation of ac conductivity ( $\sigma_{ac}$ ) as a function of frequency for pure PPy  
**Fig. 2** Variation of ac conductivity ( $\sigma_{ac}$ ) as a function of frequency for Polypyrrole-CeO<sub>2</sub> composites.  
**Fig. 3** Variation of ac conductivity ( $\sigma_{ac}$ ) as a function of wt% of CeO<sub>2</sub> at different frequencies.  
**Fig. 4** Variation of dielectric constant ( $\epsilon'$ ) as a function of frequency for Polypyrrole- CeO<sub>2</sub> composites.  
**Fig. 5** Variation of dielectric constant ( $\epsilon'$ ) as a function of wt% of CeO<sub>2</sub> at different frequencies.  
**Fig. 6** Variation of dielectric tangent loss ( $\tan\delta$ ) as a function of frequency for Polypyrrole- CeO<sub>2</sub> composites.  
**Fig. 7** Variation of dielectric tangent loss ( $\tan\delta$ ) as a function of wt% of CeO<sub>2</sub> at different frequencies.

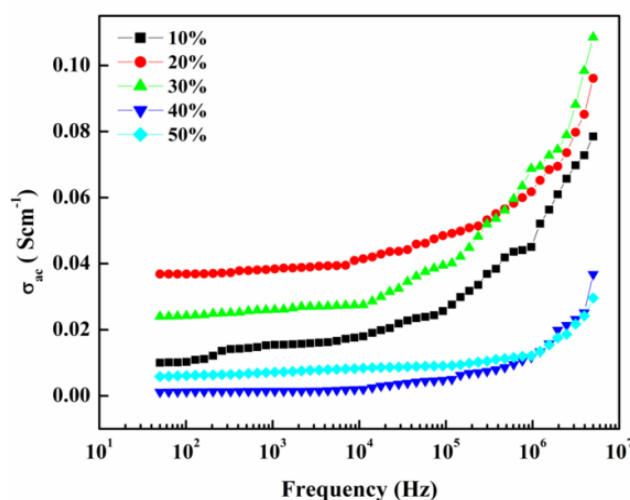


Fig. 1

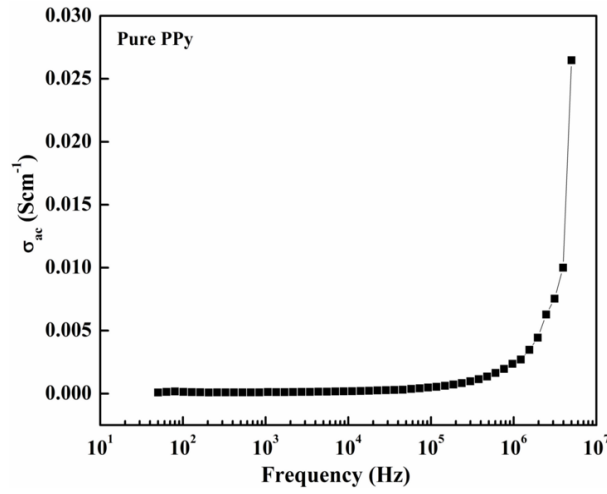


Fig. 2

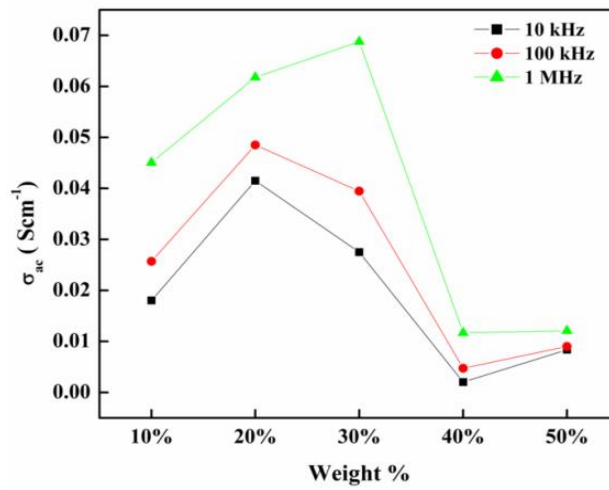


Fig. 3

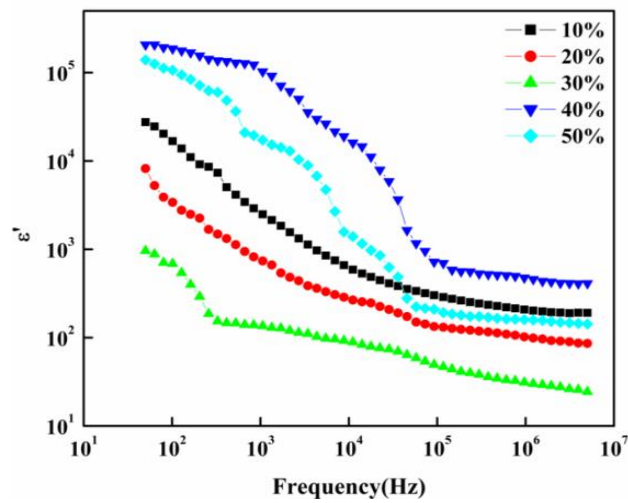


Fig. 4

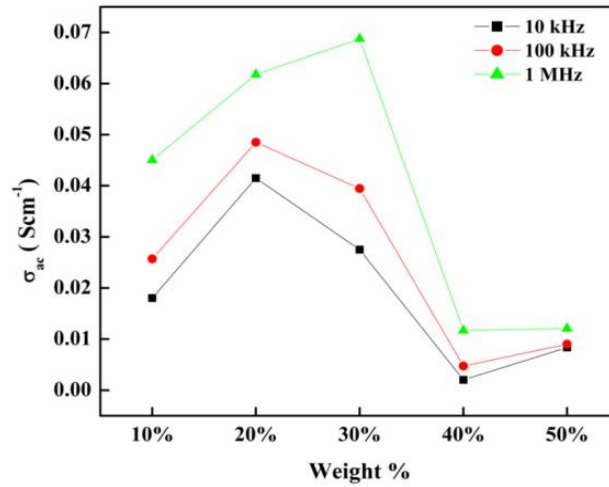


Fig. 5

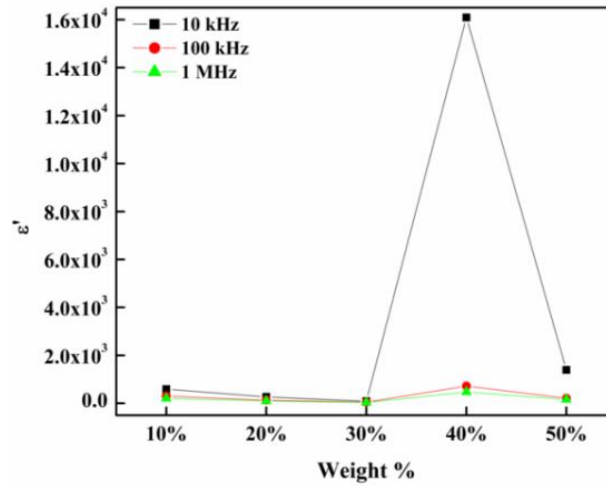


Fig. 6

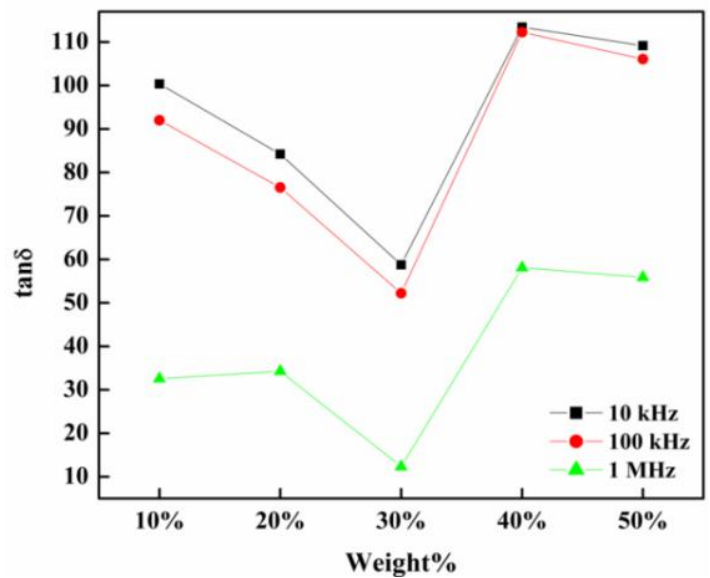
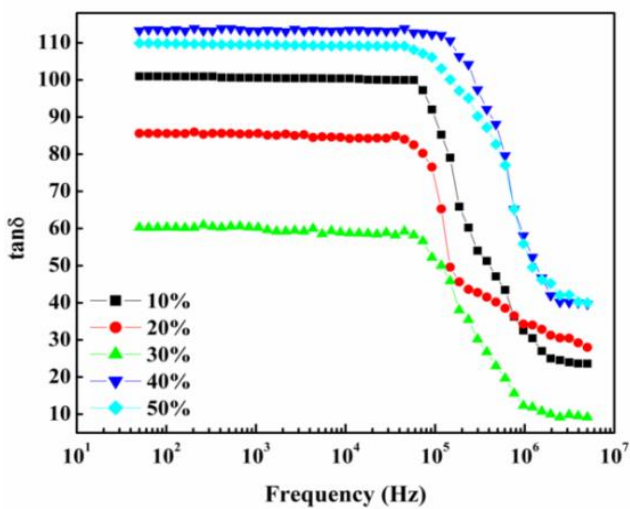


Fig. 7