

Research Article

Dielectric Spectroscopy of Nanostructured Polypyrrole-NiO Composites

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Conducting polypyrrole-nickel oxide (polypyrrole-NiO) composites were synthesized by in situ deposition technique by placing different weight percentages of NiO powder (10, 20, 30, 40, and 50%) during the polymerisation of pyrrole. The polypyrrole-NiO composites were later characterised with Fourier transform infrared spectroscopy (FTIR) which confirms the presence of polypyrrole in the composite. AC conductivity was studied in the frequency range from 10^2 to 10^7 Hz. From these studies it is found that AC conductivity remains constant at low frequency and increases rapidly at higher frequency, which is the characteristic behavior of disordered materials. The dielectric behavior of these composites was also investigated in the frequency range 10^2 – 10^7 Hz. It is observed from these studies that the dielectric constant and dielectric tangent loss decrease exponentially with frequency. The composites exhibit a low value of dielectric loss at higher frequency.

1. Introduction

Polymers have been considered as insulators as they found many applications due to their insulating properties. So far, any electrical conduction in polymers which is generally due to loosely bounded ions was mostly regarded as an undesirable phenomenon [1]. However, emerging as one of the most important materials in the twentieth century, the use of polymers moves from primarily passive materials such as coatings and containers to active materials with useful electronic, optical, energy storage, and mechanical properties. Although conducting polymers are known as new materials in terms of their properties, the first work describing the synthesis of a conducting polymer was published in the nineteenth century. In 1862, Henry Letheby prepared polyaniline by anodic oxidation of aniline, which was conductive, and showed electrochromic behavior. For more than three decades, conjugated organic polymers were known as the best candidates because of their unique electrical transport properties as well as their potential utility in the emerging technology [2, 3].

Electrically conducting polymers are synthesized either by reduction or by oxidation reaction, which is called doping process, giving materials with electrical conductivities up to

10^5 S/cm. As conducting polymers exhibit significant levels of electrical conductivity, they are suitably used in electronic devices, batteries, functional electrodes, electrochromic devices, optical switching devices, sensors, and so on [4].

Among the conducting polymers, polypyrrole has drawn considerable attention due to its high conductivity, simple preparation, stability, and good mechanical and electrochemical properties. It exhibits a wide range of surface conductivities ($10^{-3} \text{ Scm}^{-1} < \sigma < 100 \text{ Scm}^{-1}$) depending on the functionality and substitution pattern of the monomer and the nature of the counterion or dopant [5].

There are many potential applications in the electronic and electrochromic devices [6, 7], secondary batteries [8–10], capacitors [11, 12], light emitting diodes [13, 14], and enzyme electrodes [15–17]. There are other potential application areas of polypyrrole such as chip-in-chip connector, microwave shielding, and corrosion protection [18]. Apart from these, polypyrrole is widely used in sensor applications because they provide stable and porous matrix for the gas component and also facilitates the e-transfer process [19]. Also, polypyrrole offers a new class of materials in biological and biomedical applications including biosensors [20]. These composites can also be used in the low k -dielectric materials above 10^3 Hz.

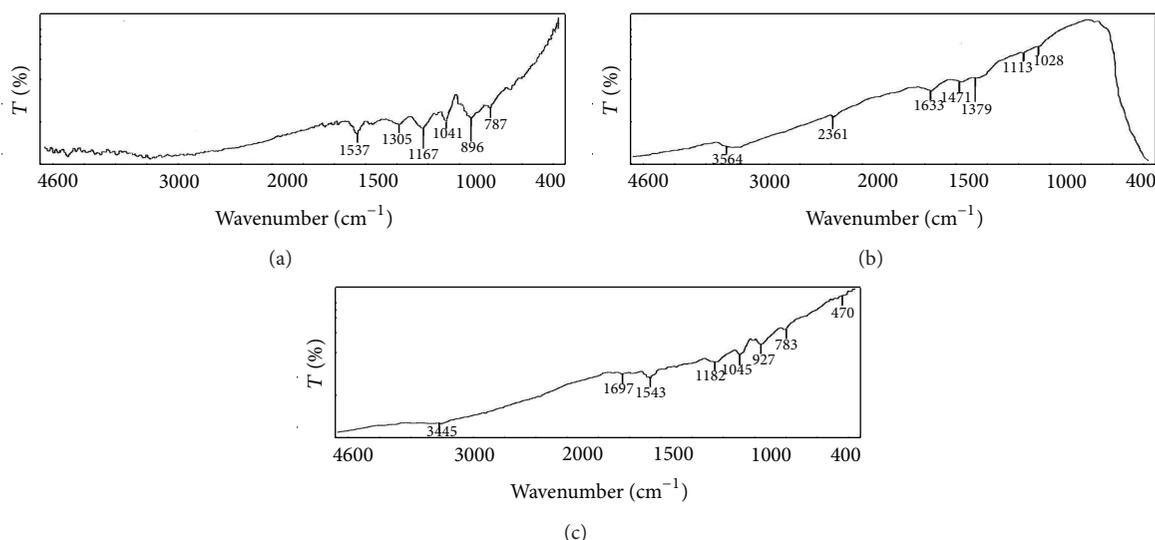


FIGURE 1: FTIR spectra of (a) pure polypyrrole, (b) pure NiO, and (c) polypyrrole-NiO (50%).

Polypyrrole can be synthesized either by oxidative chemical polymerisation [21, 22] or by electrochemical oxidation in aqueous or organic solutions [23].

In the present study author reports synthesis, AC conductivity, and dielectric spectroscopy of NiO doped polypyrrole composites prepared by chemical oxidation method.

2. Material and Methods

2.1. Materials. Analytical-reagent-grade pyrrole, nickel 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.

2.2. Synthesis of Polypyrrole and Polypyrrole-NiO Composites. For chemical polymerisation of pyrrole, FeCl_3 was used as an oxidant. Anhydrous ethanol was used as solvent for the polypyrrole synthesis.

3.4 mL of pyrrole was dissolved in 25 mL of ethanol and stirred for 10 min. 25 mL of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added dropwise to the ethanol solution of pyrrole. Nickel oxide was varied in weight percentages (10, 20, 30, 40, and 50) and added to the polypyrrole solution. This reaction mixture was stirred for 3 hr with magnetic stirrer in order to disperse NiO 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-NiO composites obtained were crushed and finely ground in agate mortar.

2.3. Measurements. The composites so obtained were pressed in the form of circular pellets of 1 cm diameter and thickness of 2.5 to 3 mm. The pellets were coated with silver paste on either side. The FTIR spectra of all the samples were recorded

on Perkin Elmer (model 783) IR spectrometer in KBr medium at room temperature in the region 4600–400 cm^{-1} . The frequency-dependent AC conductivity, dielectric constant, and dielectric tangent loss of polypyrrole-NiO composites are studied in the frequency range 10^2 Hz– 10^7 Hz at room temperature using Hioki LCR Q meter.

3. Results and Discussions

3.1. FTIR Spectra. The infrared spectrum of pure polypyrrole is shown in Figure 1(a). The absorption peak at 1537 cm^{-1} is due to intraring C=C and interring C–C vibration. The bands at 1305 and 1167 cm^{-1} may correspond to =C–H in-plane vibration. The band located at 1041 cm^{-1} is for the in-plane deformation of C–H bond of pyrrole ring, while the peaks at 896 and 787 cm^{-1} are attributable to =C–H out-of-plane vibrations. These bands are also called bipolaron bands.

Figure 1(b) indicates the IR spectrum of pure NiO which shows several significant absorption peaks. The band at 3564 cm^{-1} originates due to amine vibrations. The peak at 1633 cm^{-1} occurs due to C=N stretching originating from amine vibrations within the pyrrole ring. The band at 1113 cm^{-1} appears due to C–O–C stretching.

Figure 1(c) shows the IR spectrum of polypyrrole-NiO (with 50 weight%) composite which exhibits absorption peaks at 1543, 1189, and 1045 cm^{-1} . The peak at 1543 cm^{-1} is comparatively lower than the peak 1547 cm^{-1} in pure polypyrrole. This is due to the shifting of bands towards a lower wavelength after composite formation. The band at 1189 cm^{-1} may be due to C–H in-plane vibration and the peak at 1045 cm^{-1} may be attributed to the C–H vibration of 2,5-substituted pyrrole which indicates the presence of polymerized (or oxidized) pyrrole in the composite. The band at 470 cm^{-1} may be due to the metal oxygen stretching which in turn implies the presence of a metal oxygen bond.

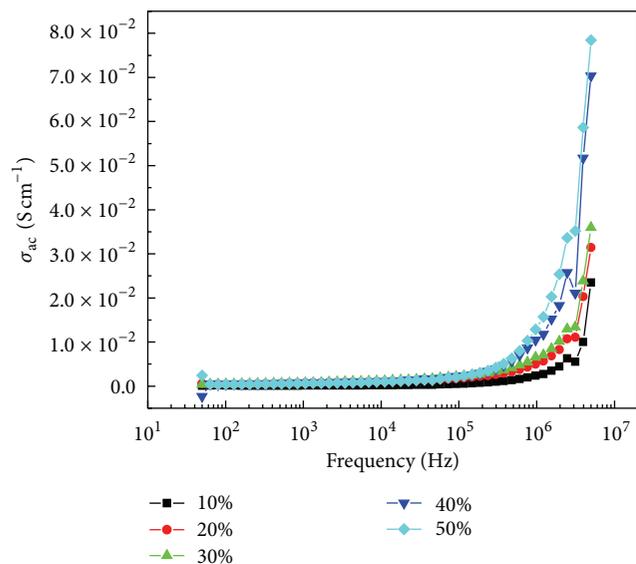


FIGURE 2: Variation of AC conductivity (σ_{ac}) as a function of frequency for polypyrrole-NiO composites.

The IR spectra of other composites (polypyrrole with 10, 20, 40, and 50% of NiO) show similar absorption peaks without many variations in their stretching frequencies.

3.2. AC Conductivity. Figure 2 shows the variation of AC conductivity as a function of frequency for different wt% of polypyrrole-NiO composites. It is observed that all the composites show similar behaviour up to 10^5 Hz and beyond this frequency it increases suddenly. This behaviour is the characteristic of disordered materials. At higher frequencies, conductivity increases with frequency according to the hopping model of charge transport in disordered materials can be approximated by a power law given by [24] $\sigma(\omega) = \sigma_0 + A\omega^s$, where σ_0 is the DC conductivity (frequency-independent plateau in the low frequency region), A is the preexponential factor, and s is the fractional exponent between 0 and 1. The values of σ_0 , A , and s were obtained by fitting the $\sigma(\omega)$ to $\sigma(\omega) = \sigma_0 + A\omega^s$. The overall behaviour of σ_{ac} follows the universal dynamic response [25] which has widely been seen in disordered materials.

Figure 3 shows the variation of AC conductivity as a function of wt% of NiO in polypyrrole at three different frequencies (10 kHz, 100 kHz, and 1000 kHz). It is observed that for all the frequencies the value of σ_{ac} is found to increase for increasing weight percentages. This is due to the improvement in the weak links between the polymer and the oxide particles which results in a stronger coupling through the grain boundary [26]. Pure polypyrrole is very light with poor compactness since microparticles are randomly oriented and the linkage among the polymer particles is very weak, resulting in relatively lower conductivity [27], but the presence of NiO in the composites helps the formation of granular shaped particles, which leads to an increase in the compactness. As the wt% of NiO in the composites increases, the change in the compactness becomes more significant due to the

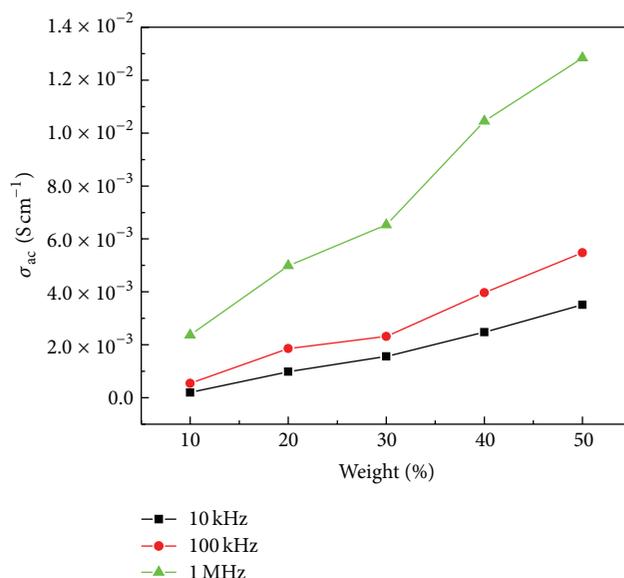


FIGURE 3: Variation of AC conductivity (σ_{ac}) as a function of wt% of NiO at different frequencies.

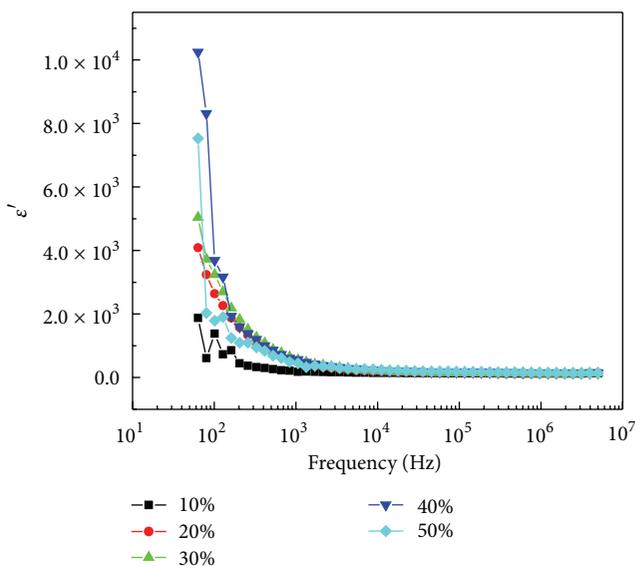


FIGURE 4: Variation of dielectric constant (ϵ') as a function of frequency for polypyrrole-NiO composites.

encapsulation of polymer on the salt. This ultimately leads to an increase in macroscopic conductivity of the composites.

3.3. Dielectric Behaviour. The frequency-dependent dielectric constant and dielectric losses of polypyrrole-NiO composites at room temperature are plotted.

Figure 4 shows the variation of dielectric constant ϵ' as a function of frequency for different wt% of polypyrrole-NiO composites. It is found that dielectric constant decreases as frequency increases for different wt% of polypyrrole-NiO composite. It is observed that Debye-type relaxation mechanism is responsible for higher values of dielectric constant

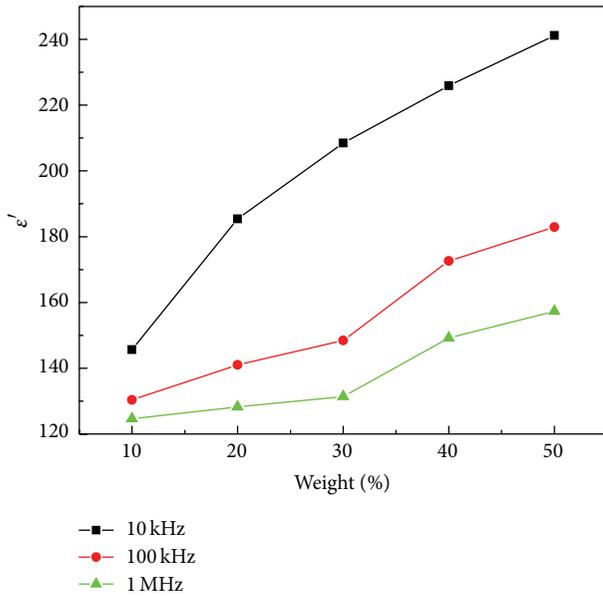


FIGURE 5: Variation of dielectric constant (ϵ') as a function of wt% of NiO at different frequencies.

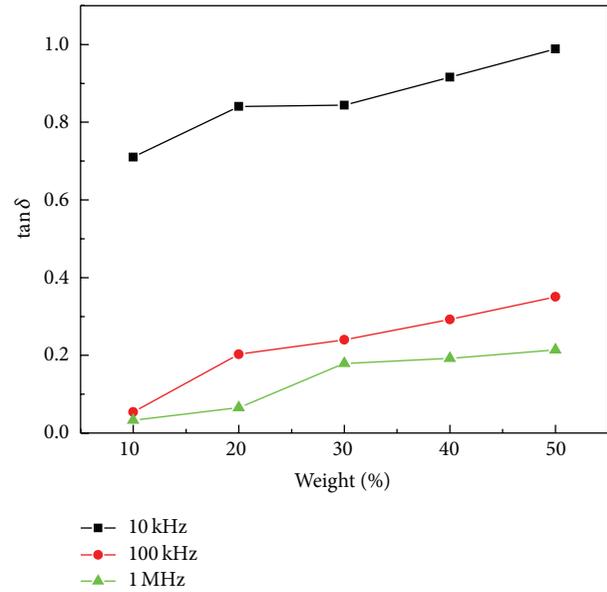


FIGURE 7: Variation of dielectric tangent loss ($\tan\delta$) as a function of wt% of NiO at different frequencies.

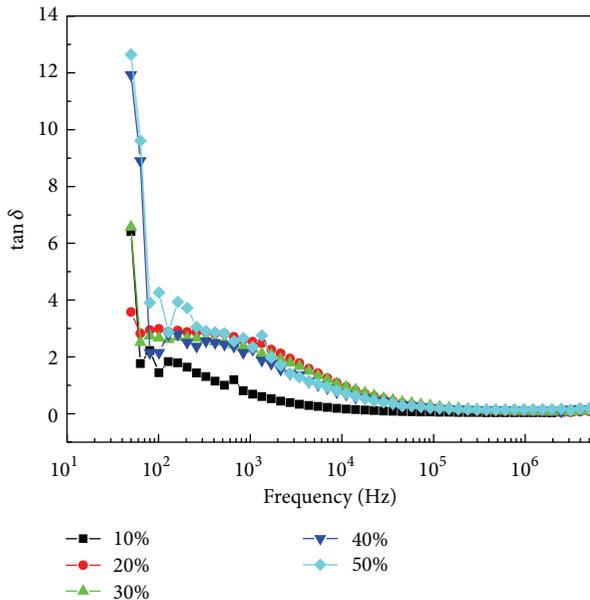


FIGURE 6: Variation of dielectric tangent loss ($\tan\delta$) as a function of frequency for polypyrrole-NiO composites.

at low frequencies, which decreases as the applied frequency increases [28, 29].

Figure 5 represents the variation of dielectric constant ϵ' as a function of weight percentage of NiO in polypyrrole. It is observed that the value of dielectric constant is smaller for the composites with lower content of NiO; however, further increase in NiO content increases the dielectric constant of the composite.

The dielectric tangent loss ($\tan\delta$) as a function of frequency for polypyrrole-NiO is shown in Figure 6 for different

wt%. It is observed that the dielectric loss decreases as a function of frequency. The composites exhibit small value of dielectric loss at higher frequencies, which suggests that these materials are lossless materials at frequencies beyond 1 MHz. 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 NiO in polypyrrole at three different frequencies (10 kHz, 100 kHz, and 1000 kHz). It is observed that the dielectric loss values are higher for higher content of the oxide in the composite.

Higher dielectric constant and higher dielectric loss for higher content of oxide can be interpreted by an increase in crystallinity due to clustering of NiO particles in the polymer matrix. The resulting orderliness in these composites increases the interfacial interactions between the polymer and NiO, leading to maximum space charge (Maxwell Wagner) polarization [30].

4. Conclusion

Polypyrrole-NiO composites have been synthesized by in situ polymerization method. A detailed characterization of the composites has been carried out with IR technique. FTIR studies confirm the presence of PPy in the composite. The AC conductivity is studied in the frequency range 10^2 – 10^7 Hz. The results of AC conductivity and dielectric constant show a strong dependence on weight percentage of NiO in polypyrrole. The increase in the conductivity of polypyrrole-NiO composites over pure polypyrrole is due to macroscopic conductivity. Polypyrrole-NiO composites with higher wt% of NiO show higher conductivity than pure polypyrrole due to increased orderliness in the composites. The frequency-dependent dielectric constant is based on the dielectric

mechanism. The dielectric loss arises due to the localized motion of charge carriers.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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