Dielectric Properties of PANI/CuO Nanocomposites

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Abstract. The combustion method is used to prepare the Copper Oxide (CuO) nanoparticles. The nanocomposites of Polyaniline (PANI) by doping with copper oxide nanoparticles have synthesized at 10, 20, 30, 40 and 50 different weight percentages during the in-situ polymerization. The samples of nanocomposite of PANI-CuO were characterized by using X-Ray diffraction (XRD) technique. The physical properties such as dielectric constant, dielectric loss and AC conductivity of the nanocomposites are studied as a function of frequency in the range 5Hz–35MHz at room temperature. It is found that the dielectric constant decreases as the frequency increases. The dielectric constant it remains constant at higher frequencies and it is also observed that in particular frequency both the dielectric constant and dielectric loss are decreased as a weight percentage of CuO increased. In case of AC conductivity it is found that as the frequency increases the AC conductivity remains constant up to 3.56MHz and afterwards it increases as frequency increases. This is due to the increase in charge carriers through the hopping mechanism in the polymer nanocomposites. It is also observed that as a weight percentage of CuO increased the AC conductivity is also increasing at a particular frequency.

1. Introduction
Copper oxide (CuO) nanoparticles are of special interest because of their applications in new materials. The Copper oxide can be easily mixed with polymers and it is relatively stable in terms of both chemical and physical properties [1, 5]. Copper oxide nanoparticles appear as a brownish-black powder. Copper oxide (CuO) is the transition metal oxides, attractive and interesting material because, it is a p-type semiconductor, anti-ferromagnetic and high temperature superconducting with low band gap energy of 1.2-1.9 eV. The CuO nanoparticles find potential applications in gas sensing, batteries, magnetic storage media and solar energy conversion [2, 6]. The variety of Conducting polymers such as Polyaniline (PANI), poly (3, 4-ethylenedioxythiophene) (PEDOT), polypyrrole (PPy) and its nanocomposites, have been used as electrode materials in batteries and super capacitors [1-5]. Polyaniline (PANI) is one of the most widely used conducting polymers due to its simple method to synthesize. PANI has excellent chemical and environmental stability and good electrical conductivity [6]. The present study consists of sample synthesis, characterization and measurement of dielectric properties as a function frequency of the samples of Polyaniline/copper oxide nanocomposites at 10, 20, 30, 40 and 50 weight percentages. The copper oxide nanoparticles were synthesized by low
temperature combustion method. The samples of nanocomposite of PANI-CuO were characterized by using X-Ray diffraction (XRD). The dielectric properties are studied as a function of frequency at room temperature. The value of dielectric constant decreased as frequency increases up to 64 Hz and afterwards they remain almost constant. It is found that the dielectric constant of the nanocomposites increased as the concentration of the Cu increased, whereas the dielectric loss decreased as the concentration increases up to a frequency of 38 Hz, afterwards it remains constant. The AC conductivity remains constant up to 3.5 MHz and afterwards it increases as frequency increases. Further, as a weight percentage of CuO increased the AC conductivity is also increased.

2. Experimental Measurements

2.1 Materials and Methods: Analytical grade Aniline, Ammonium peroxysulfate or Ammonium per sulphate, Methanol, Acetone, copper nitrate hexahydrate (Cu (NO₃)₂.6H₂O)) and fuel were used in the preparation of PANI and CuO Nanoparticles.

2.2. Preparation of CuO Nanoparticles:
The copper oxide Nanoparticles are synthesized by using a low temperature combustion method, copper nitrate (Cu (NO₃)₂.6H₂O)) and fuel is taken for synthesis. A copper nitrate of 2.14 gm was taken in Petri-dish and 10 ml of Ammonia as fuel was added to the Petri-dish and placed on a magnetic stirrer for 30 minutes. After obtaining a uniform solution, it is kept in a pre-heated muffle furnace at temperatures of 450°C. The mixture is boiled completely and left with a black coloured powder as a final yield to get the formation of CuO Nanoparticles. The average size of the CuO particle is about ~26 nm which is obtained using the Debye-Scherer formula from XRD spectra [7].

2.3. Preparation of Polyaniline/copper oxide Nanocomposites:
Aniline solution of 0.4M was dissolved in 100 ml of double distilled water. The HCl solution of 0.4 M was added to the aniline solution. This solution was taken in a beaker and placed on the magnetic stirrer and 0.8M Ammonium peroxysulfate (oxidizing agent) solution was added drop-wise to Aniline solution, then the solution colour changes to dark green. The mixture was stirred continuously for 5 hours at room temperature and left at rest to polymerize. After 24 hours the Precipitate was collected on a filter paper, the precipitate was washed repeatedly using acetone for the removal of residual impurities. The precipitate was firstly dried in the air for 30 minutes at room temperature and then in a hot air oven for 12 hours at 60°C and finally get a yield product of PANI [8]. The PANI/CuO nanocomposites were prepared using the same procedure as mentioned above where the copper oxide nanoparticles of 10 weight percent were added before adding the Ammonium peroxysulfate as an oxidizing agent to the aniline solution. A similar procedure is used for preparation of other nanocomposites of PANI/CuO at 20, 30, 40 and 50 weight percentages. The flow chart diagram for synthesis of the PANI and its composites is shown in Figure 1. The mixture of PANI/CuO nanocomposite of 250 mg was weighed using a single pan balance for preparation of a pellet. The pellet was prepared by applying 3-4 tons of pressure using a pellet making machine [Model-UTM]. Similarly the pellets of other weight percentages of PANI/CuO were prepared. A silver paste was coated on both sides of the surface of the pellet for providing electrical contacts. The prepared pellets of PANI/CuO nanocomposite were used for experimental measurements of capacitance, dissipation, impedance and phase angle to study the dielectric properties as a function of frequency at room temperature using computer interfaced LCR Q-meter [Model: HIOKI 3532-50].
3. Results and Discussions

3.1. XRD Analysis

To study the nature of crystalline or amorphous, we used the powder method of XRD for Pure PANI, Copper oxide (CuO) nanoparticle and for PANI/CuO nanocomposite. The XRD figures are given in Figures (2-4). The X-ray diffraction spectra in the present study is obtained using a Philips X-ray diffractometer with Coke α radiation (λ = 1.5406 Å). The diffractograms were recorded in terms of 2θ in the range 10 to 90 degrees with a scanning rate of 10 degrees per minute. The XRD spectra of synthesized pure PANI, CuO nanoparticles and PANI/CuO nanocomposites are given in Figures (2-4) respectively. In Figure 2, it shows the broad peak occurred at 2θ = 25.53° which says the amorphous nature of PANI and also mentioned in research articles [11, 13].
In Figure 3, it is observed that the sharp peaks are occurring at angles of 17, 32, 34, 38 and 53 degrees for CuO nanoparticles shown crystalline in nature. In Figure 4, it is observed that the sharp peaks are occurring at angles of 11, 21, 29, 31, 37, 44, 64 and 78 for PANI/CuO nanocomposites shown crystalline in nature. The peaks for the CuO are similar to that of PANI/CuO with the most number of intensive peaks occurred for PANI/CuO nanocomposites. The peaks are in good agreement with JCPDS file card No.41-0254. Further, it observed that PANI has no effect on the crystalline structure of CuO as shown in Figure 3; the particle size was determined by using the Debye Scherer formula given by equation [1]

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]

Where, D is the mean crystallite size of the powdered particles, \( \lambda = 1.54 \) Å is the wavelength of CuK\( \alpha \), \( \beta \) is full width at half maximum (FWHM) of intensity of major peak, \( \theta \) is the Bragg angle [9]. The crystallite size of the CuO nanoparticle is 26nm and that for nanocomposites of PANI/CuO are found to be 17nm. This clearly says that the formation of CuO dispersed in PANI nanocomposite.

4 Dielectric properties
The dielectric properties have been studied for all the nanocomposites of PANI-CuO.

4.1 Dielectric constants
The dielectric constant for PANI and nanocomposites of PANI with CuO at different weight percentages as function of frequency are shown in the Figure 5. The dielectric constant for PANI and all other nanocomposites of PANI/CuO are obtained, using the expression given in [2]

\[ \varepsilon' = \frac{cd}{\varepsilon A} \]

Where d is the thickness of the pellet, A is the area of the pellet, C is capacitance. The dielectric constant decreased as frequency increased up to 64 Hz for nanocomposites of PANI with CuO, which is shown in shown in Figure 5. The dielectric constant remains almost constant after frequency of 64 Hz and it shows independent of frequency because of electrical relaxation process. It is observed that the dielectric constant is high for PANI/CuO at 30 wt %. This is due to dipoles have align with the field before the field direction and the dielectric constant decreases due to shorter time available for the dipoles to align [12].
4.2 The dielectric loss factor

The Dielectric loss versus frequency for PANI nanocomposites are given in Figure 6. The dielectric loss are obtained using measured data of dissipation factor and dielectric values using the relation given below

\[ \varepsilon'' = \varepsilon'\tan\delta \]  

(3)

It is observed from Figure 6. The dielectric loss decreased gradually as frequency increased up to 38 Hz for all the nanocomposites. The dielectric loss \( \varepsilon'' \) decreases due to the migration of ions in the material [9].

**Figure 5.** The plot of dielectric constant with frequency for PANI/CuO Nanocomposites

**Figure 6.** The plot of Dielectric loss with frequency for PANI/CuO Nanocomposites
4.3 A.C conductivity
The A.C conductivity as a function of frequency for PANI and for the nanocomposites of PANI/CuO of different weight percentages at room temperature are shown in the Figure 7. The electrical property of AC conductivity ($\sigma$) as a function of frequency has been determined, using dielectric data using the following equation.

$$\sigma = \varepsilon''\varepsilon_0\omega \tan \delta$$  \hspace{1cm} (4)

Where $\varepsilon_0$ is the permittivity of free space = $8.85 \times 10^{-12}$ Fm$^{-1}$, $\omega$ is the angular frequency and $\varepsilon''$ is the dielectric constant.

![Figure 7. The plot of A.C Conductivity with frequency for PANI/CuO Nanocomposites.](image)

From Figure 7, it is observed that in all the cases, $\sigma$ (AC conductivity) remains constant up to 3.56 MHz afterwards it increased for higher frequencies. The nanocomposite of PANI/CuO at 40 wt % shows high conductivity due to interfacial polarization. But for the other wt% of PANI/CuO conductivity value is low because of dipole polarization. This behaviour of the nanocomposites may be due to the variation in the distribution of copper oxide nanoparticles in PANI [13].

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