

Dielectric Properties of Polyvinylpyrrolidone Doped with Copper Oxide Nanoparticle

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ABSTRACT: Synthesis, characterization and measurement of dielectric properties as a function frequency have been studied for the samples of polymer nanocomposites which are prepared from a polymer of Polyvinylpyrrolidone [PVP] and with copper oxide nanoparticles. The nanocomposites of PVP with copper oxide nanoparticles are prepared at different concentrations of PVP. The prepared samples were characterized using X-ray diffractometer to investigate their structure and crystallinity in nature. The XRD spectra show that PVP-CuO nanocomposites are crystalline in nature. The SEM images confirmed that the size of particles in nanocomposites of PVP with CuO is found to be in the range of 71.04 - 144.3 nm. The dielectric constant, dielectric loss and AC conductivity are studied as a function of frequency at room temperature. The dielectric constant and dielectric loss decreased as frequency increased up to 1 KHz and afterwards they remain almost constant. It is found that the dielectric constant of the nanocomposites increased as the concentration of the PVP increased but the dielectric loss decreased as the concentration increased. The AC conductivity increased as frequency increased after 1MHz.

KEYWORDS: PVP/CuO nanocomposites, XRD, SEM, FTIR, Dielectric Constant, Dielectric Loss and A C Conductivity.

I. INTRODUCTION

Biodegradable polymers have poor mechanical, thermal and water resistance properties compared to synthetic polymers. Therefore, in order to replace synthetic polymers with biodegradable polymers, the properties of biodegradable polymers have to be improved. The polymer substance of Poly vinyl pyrrolidone (PVP) is easily soluble in water and other polar solvents. The PVP substance is a hygroscopic powder, it easily gets wet due to absorbance of moisture in the atmosphere, during rain and winter seasons. The Pyrrolidone group of PVP prefers to complex with many inorganic salts resulting in fine dispersion and surface passivation for the composites. The substance of PVP which dissolves in water and organic solvents would be used for preparation of films and an additive to coatings. It is used as a binder in many pharmaceutical industries in drugs, that is, PVP binds to polar molecules exceptionally well, owing to its polarity. This has led to its application in coatings for photo-quality transparencies. Hence the water soluble polymers are important from industrial point of view. The PVP is highly soluble in polar solvents such as alcohol, so it is preferable to avoid phase separation in the reaction. The PVP is a cross linked polymer and hence it makes better thermal stability and high mechanical

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Vol. 5, Issue 2, February 2016

strength to the composites. Further, amorphous nature of PVP provides low scattering loss, which makes it an ideal polymer for composite materials for optical applications. The PVP polymer film is found to be easily accepts transition metal and rare earths as the dopant ions in technological importance [1-3]. The interactions between water soluble polymers and metal ions have significant influence on physical properties [4-6]. The PVP polymer film has a potential capacity to storage the charges and dopant dependent electrical and optical properties. It has a strong tendency for complex formation with a variety of molecules [7-10]. The metal oxides such as cupric oxide (CuO) is a transition metal oxide, is one of an important p-type semiconductor with band gap in the range of 1.8 - 2.5 eV [11, 12]. It has many potential applications in solar energy conversion, photo thermal, photoconductive, lithium ion batteries, solar cell photo catalytic, degradation of organic pollutants, antimicrobial, chemical and biological sensing etc. Now a day, preparation of nanocomposites plays major role in modification of materials properties.

In present work the nanoparticles of CuO were prepared without any additive like ionic liquids, capping agents by hydrothermal synthetic method using copper sulfatepentahydrate as base. The nanocomposites of CuO with PVP at different concentration were synthesized and characterized using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The morphological studies of CuO and its nanocomposites with PVP are observed by scanning electron microscopy (SEM). The properties such as dielectric permittivity, dielectric loss and AC conductivity of PVP/CuO nanocomposites have been studied as function of frequency in the range of 50 Hz to 50 MHz at room temperature.

II. EXPERIMENTAL MEASUREMENTS

Preparation of Samples: The Copper oxide nanoparticles and its nanocomposites with PVP at different concentration were prepared using chemicals of copper Sulfatepentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), aqueous ammonia, methanol (CH_3OH) and the polymer substance of Polyvinylpyrrolidone (K25). These chemical compounds were of analytical reagent (AR) grade procured from Sd fine Chemicals Mumbai. The Copper Sulfatepentahydrate of 0.05 mol% was dissolved in the combination of 1:1 ratio of distilled water and methanol results to a blue colour solution. Further, added 5 ml of aqueous ammonia solution drop wise while stirring. The solution was stirred continuously till to get a homogeneous mixture of precursors was formed. The resulting mixture was kept for 12 hours and then filtered the solution to get the precipitate. The resulting precipitate was washed repeatedly with deionised water and methanol to remove the impurities then it was dried in a hot air oven for 8 hours at temperature of 80 °C to get the powder of CuO nanoparticles.

SYNTHESIS OF PVP-CuO NANOCOMPOSITES: The copper sulfatepentahydrate of 0.05 mol% was dissolved in the combination of 1:1 ratio of distilled water and methanol results to a blue colour solution, while stirring, added 5 ml of aqueous ammonia solution drop wise. Further, 10 ml solution of 1N concentration of PVP was added to the above mixture with vigorous stirring. The mixture was kept for 12-16 hours to polymerize completely and then filtered the polymerized solution to get the precipitate. The resulting precipitate was washed repeatedly with deionised water and methanol to remove the impurities. Finally the resultant precipitate was dried in a hot air oven for 8 hrs at temperature of 80 °C to get mixture of PVP with CuO. Further, the synthesis process was repeated for preparation of CuO-PVP nanocomposite with 10 ml PVP solutions of 1.5N and 2.5N concentration separately one after the other. The mixture of 400 mg was taken by weighing through a single pan balance for preparation of a pellet. The pellet of CuO-PVP nanocomposite was prepared by applying 4-5 tons of pressure using a pellet making machine [Model-UTM]. Similarly the other pellets of the different concentration of PVP with CuO nanocomposites were prepared. A silver paste was coated on both sides of surface of the pellet for providing electrical contacts. The prepared pellets of CuO-PVP 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].

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 2, February 2016

III. RESULTS AND DISCUSSION

CHARACTERIZATION USING XRD: The prepared nanocomposites of CuO and its nanocomposites with PVP at different concentrations were used for characterization using powder X-ray method (Model: Regaku) of CuK_α radiation having a wavelength of 1.54060\AA . The XRD pattern with diffraction intensity versus 2θ was recorded over a range of 10 to 80 degrees. The XRD spectra of CuO nanoparticles is given in Fig.1 (a) and for the nanocomposites of CuO with PVP at different concentration are given in Fig.1 (b)-(d). The sharp peaks observed from these figures indicate that the samples are crystalline in nature. The positions of the peaks observed at angles of 2θ are 18, 24, 33, 36, 38, 42 and 63 degrees are nearly same for the CuO nanoparticles and its nanocomposites with PVP at different concentrations. The positions of peaks for the CuO nanoparticles observed at these angles were same and comparable to the others Asha and Ponnarasan [13,14] and hence its structure is monoclinic phase of CuO [13].

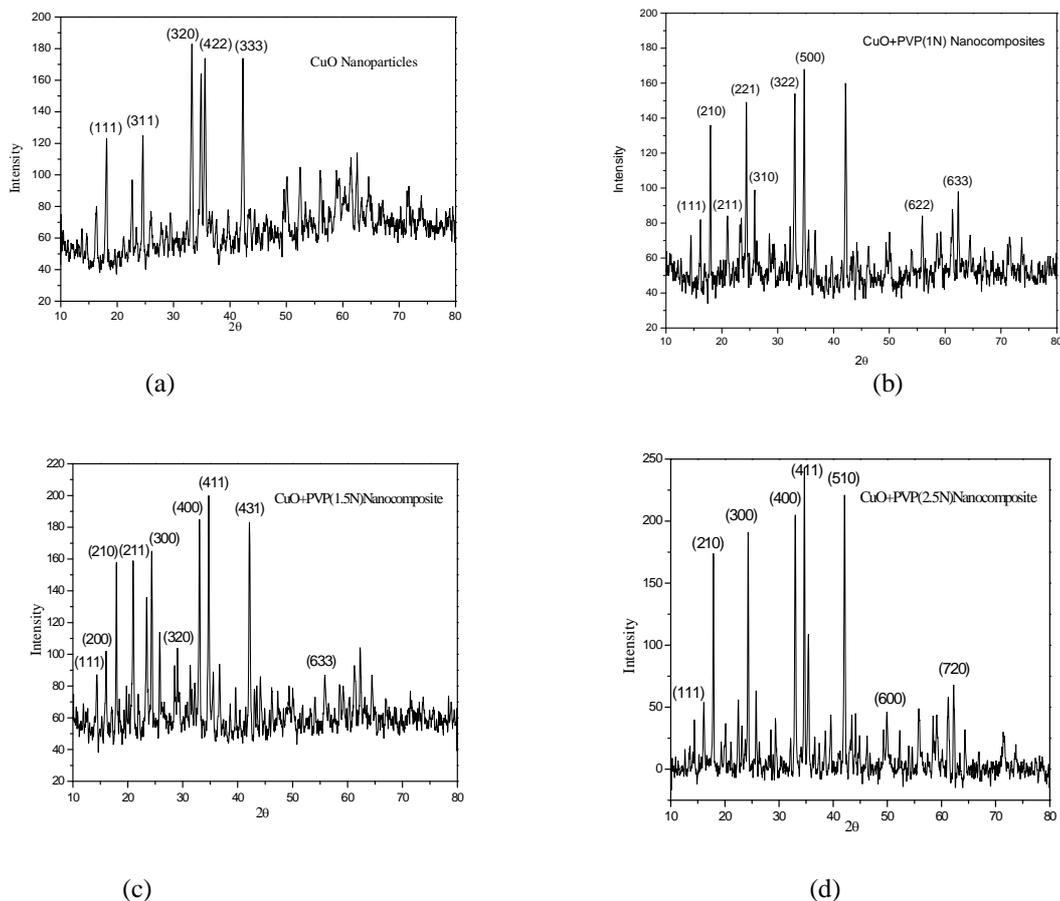


Fig.1: XRD spectra of (a) CuO nanoparticle and (b)-(d) PVP-CuO nanocomposites.

International Journal of Innovative Research in Science, Engineering and Technology

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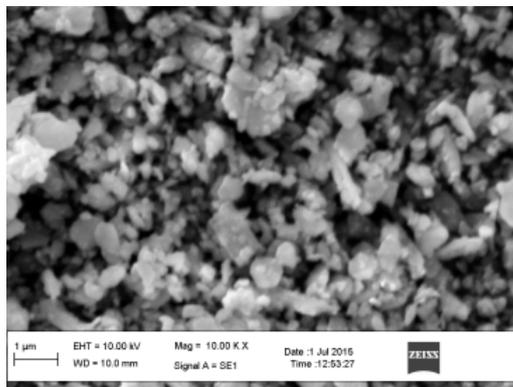
Vol. 5, Issue 2, February 2016

The crystallite size is calculated using the Debye Scherrer equation given by

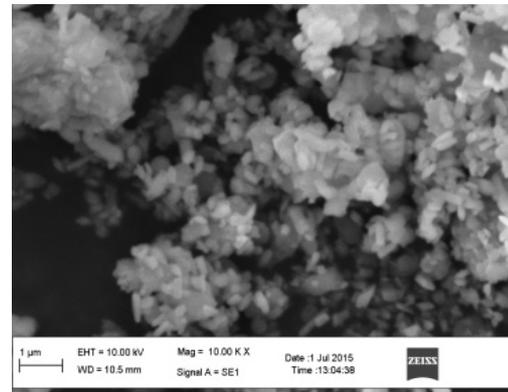
$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

where D is the crystallite size, β is FWHM of strong intensive peak, λ is the wavelength of the X-ray and θ is the Bragg angle. The average crystallite size of the synthesized CuO nanoparticles is 58 nm. In case of 1N concentration of PVP with CuO nanocomposites, the particle size is 70 nm, for 1.5N concentration of PVP with CuO the particle size is 65nm and for 2.5N concentration of PVP with CuO the particle size is 69nm. It is observed that the particle sizes in the composites are increased compared to the CuO nanoparticles, hence the particles size should be in the nanometre range.

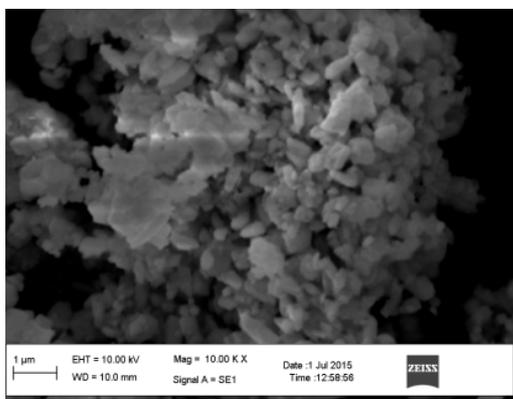
SEM IMAGES: The surface studies are also observed using SEM images for PVP-CuO nanocomposites at doping of different concentrations of PVP. The SEM images of CuO nanoparticles is shown in Fig.2(a) and for nanocomposite of PVP/CuO are shown in Fig. 2(b)-(d). It is observed from these figures that the size of particles is obtained in nanometre range. The size of particles in CuO is in the range of 58-71nm and in nanocomposite of PVP/CuO is in the range of 71.04-220 nm. The SEM image reveals that the distribution of CuO in PVP polymer matrix. It is observed that as concentration of PVP increased the particles size increased and agglomeration taken placed.



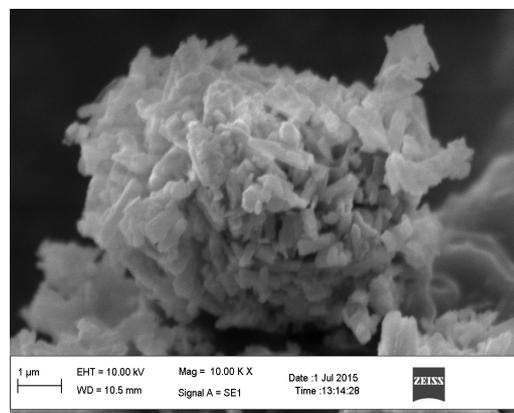
(a) CuO Nanoparticle



(b) CuO+PVP (1N)



(c) CuO+PVP (1.5N)



(d) CuO+PVP (2.5N)

Fig.2: SEM images of (a) CuO nanoparticles and (b) - (d) PVP-CuO nanocomposites.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 2, February 2016

DIELECTRIC CONSTANT: The dielectric constant as function of frequency for CuO nanoparticles and for the nanocomposites of PVP/CuO, that is, for 1N, 1.5N and 2.5N concentration of PVP with CuO at room temperature is obtained using the experimental measured data of capacitance with the help of equation given by

$$\epsilon' = \frac{Cd}{\epsilon_0 A} \tag{2}$$

Where C is capacitance of the sample, d is thickness of the sample, A is area of the sample and ϵ_0 is the permittivity of free space. The variation of dielectric constant with frequency for CuO nanoparticles and for the nanocomposites of PVP with CuO at different concentration of PVP is shown in Fig.3. The dielectric constant of nanocomposites of PVP with CuO decreased exponentially as frequency increased up to 200 Hz and afterwards it shows independent of frequency because of electrical relaxation process. The decrease in dielectric constant at lower frequency may be due to the concentration of PVP. The distance between the CuO nanoparticles is reduced, thereby increasing the interaction between nanoparticles, could reduce the dipole-dipole interaction, leads to reduction in the dielectric constant [15,16]. The dielectric constant shown almost independent of frequency for CuO nanoparticles compared to its nanocomposites with PVP.

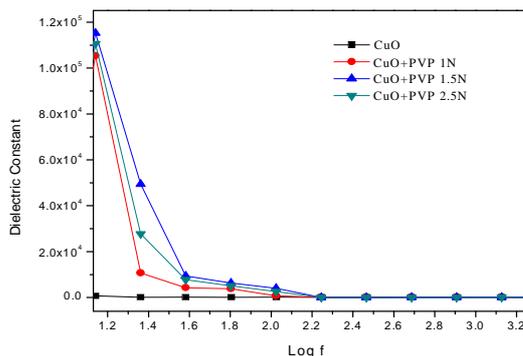


Fig.3: Plot of dielectric constant with frequency for CuO and PVP/CuO nanocomposites.

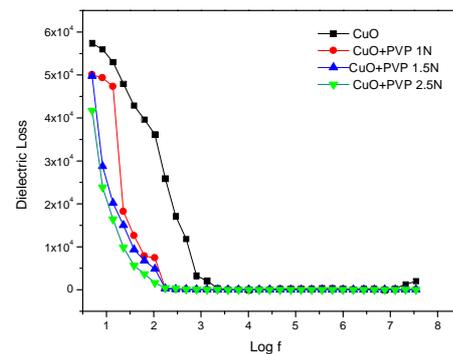


Fig.4: Plot of dielectric loss with frequency for CuO and PVP/CuO nanocomposites.

DIELECTRIC LOSS: The dielectric loss as function of frequency for CuO nanoparticles and nanocomposite of PVP/CuO, that is, CuO with PVP at 1N, 1.5N and 2.5N concentration are obtained with help of experimentally measured data of dissipation and the values of dielectric constant using the relation given by

$$\epsilon'' = \epsilon' \tan \delta \tag{3}$$

Where ϵ' is the dielectric constant of CuO nanoparticles and its nanocomposites with PVP and $\tan \delta$ is dissipation factor at the respective frequency. The variation of dielectric loss as a function of frequency at room temperature is shown in Fig.4. It is observed from Fig.4 that the dielectric loss decreased exponentially as frequency increased up to 200Hz and afterwards it is shown independent of frequency for both CuO nanoparticles and for its nanocomposites. The decrease of dielectric loss with frequency can be attributed to the fact that at low frequencies the value of loss is due to the migration of ions in the material. At medium frequencies, loss is due to the contribution of ions jump, conduction loss of ions and ions polarization loss. At higher frequencies ions vibrations may only be source of dielectric loss and hence has the minimum value. It is also observed that the dielectric loss in nanocomposites of PVP-CuO is lesser compared to CuO nanoparticles in

the region of lower frequency. Further it is noticed that the concentration of PVP with CuO increased then the dielectric loss decreased at any given value of frequency in the lower frequency region.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 2, February 2016

AC Conductivity: The electrical property of AC conductivity (σ_{ac}) as function of frequency are obtained for CuO nanoparticles and for its nanocomposites with polymer of PVP at different concentrations using the measured values of the dielectric constant and dielectric loss through the relation given by

$$\sigma_{ac} = \epsilon' \epsilon_0 \omega \tan \delta \tag{4}$$

Where ϵ_0 is the permittivity of free space, ω is angular frequency and ϵ' is the dielectric constant. The variation of AC conductivity as a function of frequency at room temperature is given in Fig.5. It is observed from Fig.5 that A C conductivity remains constant up to 1.6 MHz after that the conductivity increased exponentially. It is also observed that as doping of PVP with CuO nanoparticles increased the AC conductivity decreased but the conductivity is found to be higher for CuO nanoparticles compared to its nanocomposites with PVP. The exponential increase in AC conductivity at higher frequency is due to various factors that may influence the conductivity. The increase in conductivity may be due to available number of charge carriers for conduction and all the dipoles are aligned in one particular direction and also the extension of chain length of PVP where the polarons get sufficient energy to hop between favourable localized sites.

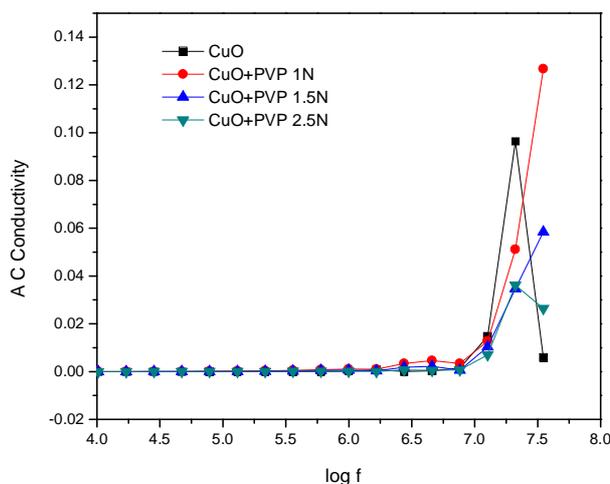


Fig.5: Variation of AC conductivity with frequency for PVP/CuO nanocomposites

FTIR ANALYSIS: Fourier Transform Infrared spectroscopy is used to measure the vibrational frequencies of bonds in the molecule. The FTIR spectra of CuO nano particles and its nanocomposites are shown in Fig.6(a)-(d). The strong intensity peak at 3573 cm^{-1} assigned to alkyl (O-H) stretching for the deformation of diethylamine, 3483 cm^{-1} assigned to (NH) vibration of amine group, weak band at 2352 cm^{-1} assigned to carboxylic group (COO-) vibration. Peak at 1626 cm^{-1} assigned to amide (COO-) while the very intense peak positioned at 1149 cm^{-1} revealed the presence of (O-H) stretching for alkyl. The characteristic peaks of CuO positioned from 985 cm^{-1} to 425 cm^{-1} . The peaks positioned at around 606 and 523 cm^{-1} observed due to Cu-O stretching in one direction and 421 cm^{-1} from Cu-O stretching in opposite direction [17-18].

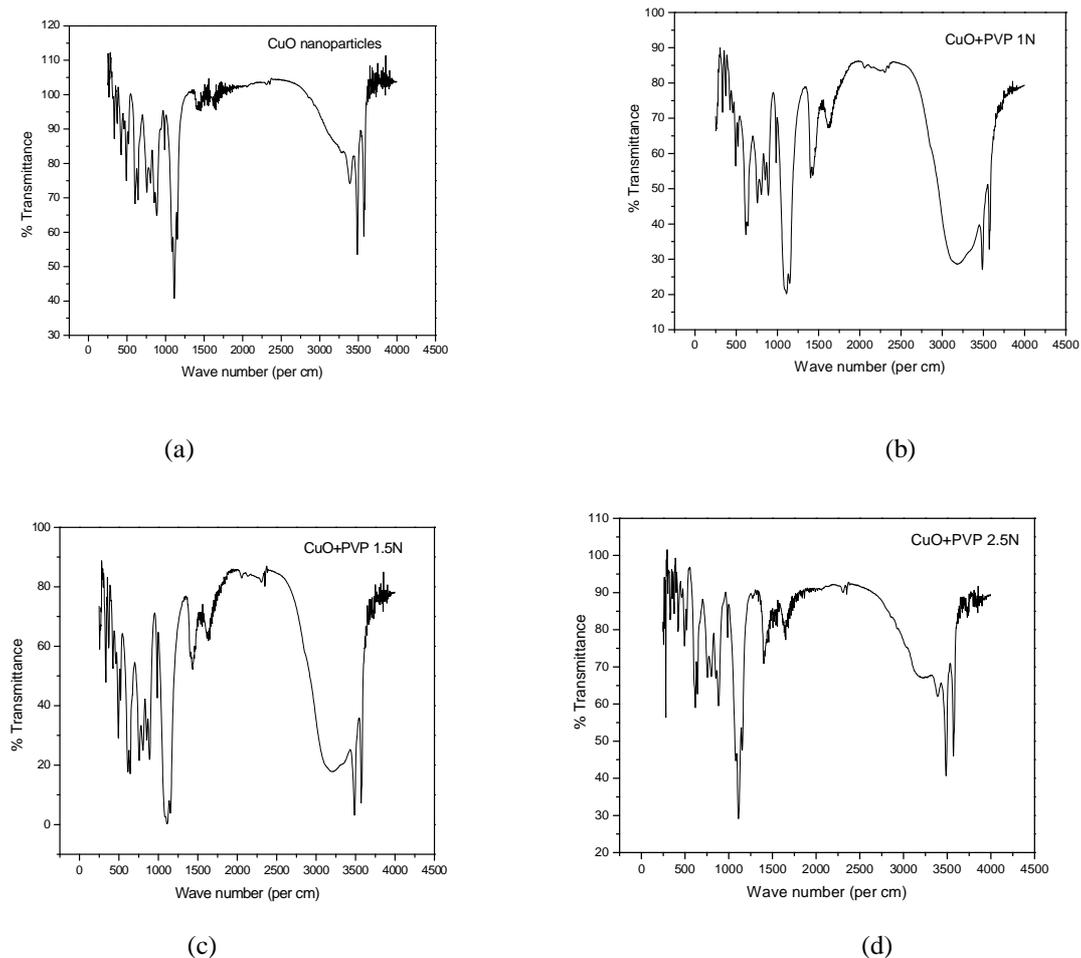


Fig.6: FTIR spectra of (a) CuO nanoparticles and (b)-(d) PVP/CuO nanocomposites.

IV. CONCLUSION

CuO and its nanocomposites with PVP at different concentration have been synthesized by hydrothermal synthetic polymerization method. The XRD spectrum for the nanocomposites of PVP with CuO reveals that the PVP/CuO nanocomposites are crystalline in nature. The sizes of the particles in nanocomposites are in nanometre range which can found by the SEM images and XRD. The values of dielectric constant have been increased at different concentration of PVP and dielectric loss decreased at lower frequency region as concentration increased. A remarkable increase is observed in AC conductivity after the doping of PVP.

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Vol. 5, Issue 2, February 2016

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