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Investigation on CuO Dispersed PVA Polymer Films

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Abstract

Addition of inorganic nanoparticles to polymers allows the modification of physical properties of polymers as well as the implementation of new features in polymer matrix. In the present work, we have made an attempt to disperse CuO nanoparticles in the polyvinyl alcohol (PVA) and to understand the change in structural, optical and electrical properties of the polymer film. CuO nanoparticles were added in four different concentrations, viz. 2.5, 5.0, 7.5 and 10 wt%. A total of 5 films were prepared (including the pure PVA film, for comparison).The prepared films were subjected to XRD, FESEM, UV-Vis spectral, PL spectral and electrical analyses. The results obtained are reported.

Keywords: Polymer thin films; Inorganic nanoparticles; Structural properties; Optical properties; Electrical properties

I. INTRODUCTION

Fabrication of inorganic nanoparticles in polymer matrices has attracted much attention, because the combination of inorganic nanoparticles and a polymer provides a simple route to stable and processable composite materials, integrating the promising properties of both components [1]. It is well known that the electrical and optical properties of polymers can be improved to a desired limit through suitable doping [2]. Also the optical and electrical properties of nanocomposites films can be adjusted by varying the composition. Over the years, Polyvinyl alcohol (PVA) polymer has attracted attention due to its high dielectric strength, good charge storage capacity and dopant dependent electrical and optical properties [3].

PVA is a water soluble synthetic polymer which has a melting point of 230 °C and density 1.36 g/cm^3. Also, PVA has carbon chain backbone with hydroxyl groups attached to methane carbons; these OH groups can be a source of hydrogen bonding and hence assist the formation of polymer composite [4]. However, the retention of homogenous dispersion of nano-sized particle in the preparation process of nanocomposites is very difficult, because of strong tendency for nanoparticles to agglomerate [5]. To prevent the formation of agglomeration of nanoparticles in polymers, the combination of inorganic particles with polymers is usually accomplished by surface modification. CuO is the simplest member in the family of Cu compounds and exhibit a range of potential physical properties, such as high temperature superconductivity, electron correlation effects and spin dynamics [6,7]. It possesses useful photovoltaic and photoconductive properties because CuO crystal structure has a narrow band gap [8]. CuO nanoparticles have been applied in different areas including gas sensors [9], catalysis [10], batteries [11], solar energy conversion [12], etc. CuO is much cheaper than silver oxide and can be mixed with polymer more easily to obtain composites with unique chemical and physical properties, because they can reduce friction and mend worn surface [13,14].

The crucial factors for the use of a semiconducting material as an active layer in the solar cells are the band gap and optical absorption of the material. The relatively large band gap of polymer such as PVA limits the absorption of near-infrared light and thus lowers the light harvesting and therefore cannot be used as an active layer in organic solar cells. The control over the band gap is necessary while designing new materials for organic solar cells. The band gap engineering allows one to design and synthesize new materials with maximum overlap of absorption spectrum with the solar emission spectrum. It is often found that the synthesis of low band gap polymer is not only the solution to address this problem but also the position of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) limits the open-circuit voltage (Voc) of the photovoltaic cell. These two properties of organic materials can be controlled by introducing nano-inorganic salts or introducing alternative electron rich and electron-deficient units in the polymer backbone [15,16]. Recently, synthesis and design of several important low band gap polymers with enhanced absorption abilities have been reported and researchers have made a breakthrough in fabricating polymer solar cells with conversion efficiency up to 5-7 % based on the II-VI compounds filled polymers [17].

Keeping this in view, in order to find new polymer composites with tuned properties for photonic and electronic applications, we have made an attempt to prepare CuO dispersed PVA polymer films with different concentrations of CuO by a simple chemical method. The results obtained in the present study are reported herein.

II. MATERIALS AND METHODS

Polyvinyl alchocol, dimethyl sulphoxide (DMSO), demineralised water, copper acetate and urea were purchased from Aldrich. Pure PVA thin film was prepared by dissolving 2.5 g of PVA in a mixed solvent of DMSO and water at 40 ^{o}C and stirred continuously for about 1 hour. The thin film was made by evaporating the excess solvent by pouring the solution in petri dish and dried it in sunlight. For CuO dispersed PVA films, the above prepared PVA solution was modified by adding 2.5 wt% of copper acetate and urea solution. The same procedure was followed for the remaining concentrations (5.0, 7.5 and 10 wt%) also. Pure and CuO dispersed PVA thin films were characterized by X-ray diffraction (XRD), field effect scanning electron microscopic (FESEM), thickness and refractive index, UV-Vis spectral, photoluminescence (PL) spectral and electrical (both DC and AC) measurements by using the standard available procedures. The polymer films prepared in the present study are represented as: Pure PVA for the pure PVA polymer film and 2.5 % CuO, 5.0 % CuO, 7.5 % CuO and 10 % CuO respectively for the 2.5 wt%, 5.0 wt%, 7.5 wt% and 10 wt% CuO dispersed PVA polymer films.

III. RESULTS AND DISCUSSION

3.1 XRD Analysis

The X-ray diffraction measurements were carried out on all the five films prepared in the present study using X-ray powder diffractometer (PANalytical X-ray diffractometer) with Cu Kα radiation of wavelength 1.54056 Å. The XRD patterns of as-prepared pure and CuO dispersed PVA polymer composites observed in the present study are shown in Figure 1. Figure shows clearly that the broad peak around 20 ^{o} is the characteristic peak of PVA [18]. As the concentration of CuO was increased , new sharp peaks have appeared around 42 ^{o} , 61 ^{o} and 74 ^{o} indicating clearly the inclusion of CuO in the PVA host matrix. Also the position of new peaks are well matched with the cubic structure of CuO [JCPDS File No: 780428].

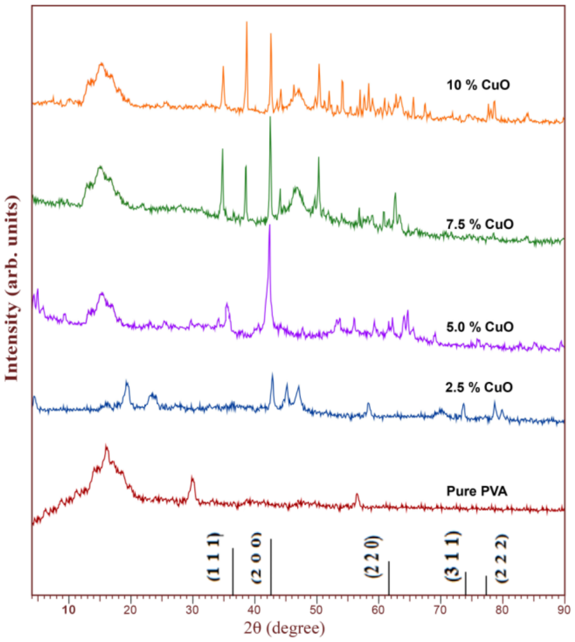
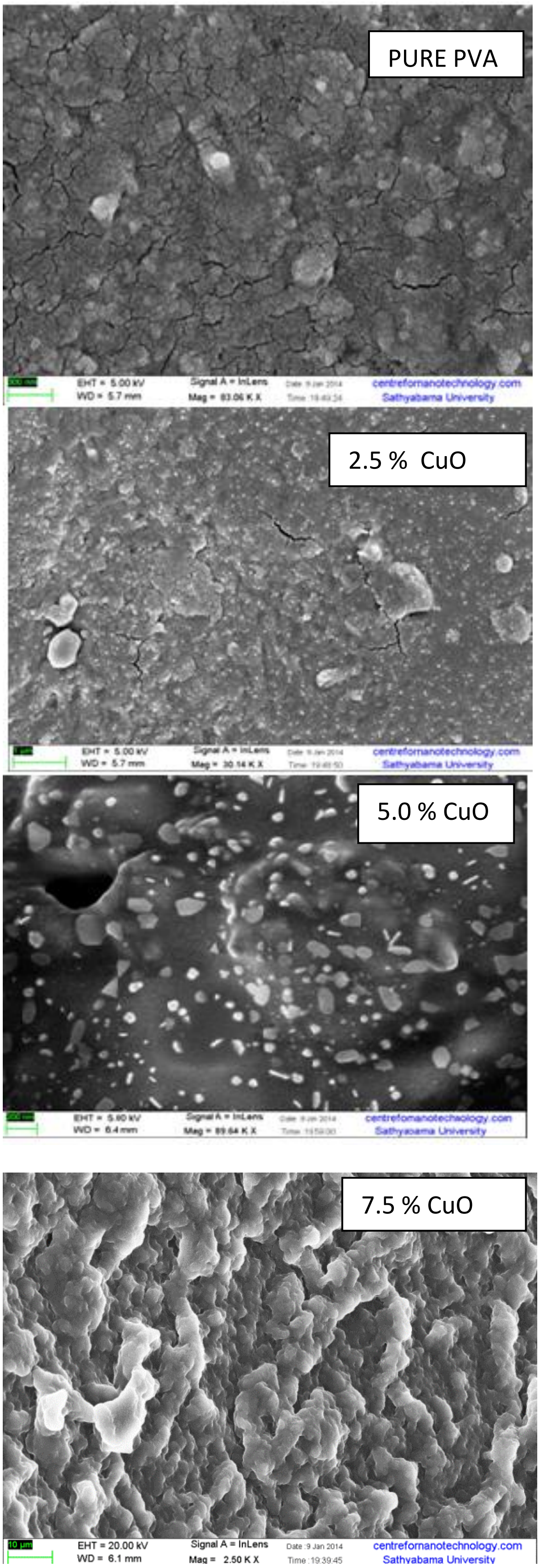


Fig 1: XRD patterns of pure and CuO dispersed PVA films

3.2 FESEM Analysis

The FESEM images for all the five films prepared were obtained using FESEM-SUPRA 55) - CARL ZEISS, GERMANY**.** FESEM images of pure and CuO dispersed PVA films observed in the present study are shown in Figure 2. The images give the information about the surface of the grown films. Depending on the concentration of CuO presence in the PVA matrix, the morphology of CuO-PVA composite varies and greatly influences the properties. Pure PVA shows smooth surface whereas dispersion of CuO with different concentrations shows remarkable changes in the surface. This indicates the incorporation of CuO nanoparticles in the PVA polymer (host) matrix endorsing the results of XRD measurements. Moreover, homogeneity is maintained with the increase in concentration of CuO. The XRD and FESEM analyses indicate the formation of proper CuO-PVA nanocomposites. Thus, it is understood that the simple chemical method adopted in the present study along with copper acetate, urea and PVA as the precursors favours the formation of films of proper CuO-PVA nanocomposites.



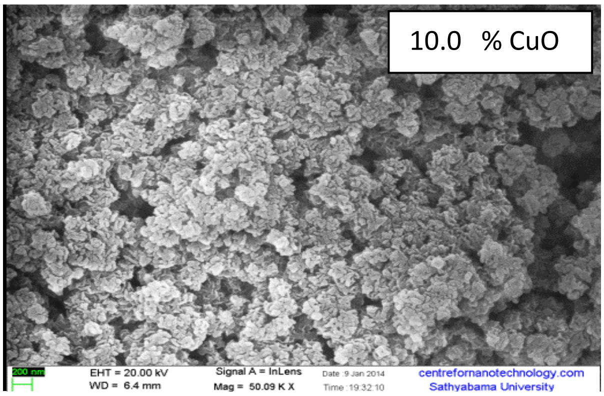


Fig 2: FESEM images of pure and CuO dispersed PVA films

3.3 Thickness and Refractive Index Measurements

Spectroscopic reflectometry involves illuminating samples with a white light (typically tungsten halogen or deuterium- halogen) at an incident angle which is normal to the sample and then measuring the reflectance and interference from the same geometry. Depending upon the nature of the coating or film ultra-violet, visible or near infrared wavelength measurements may be necessary to obtain an optimum fitting of the measured curve relative to the theoretical reflectance curve. The theoretical curve is developed from a database of optical constants (n and k). The "n" value is the refractive index and "k" is the extinction coefficient. The sampling process initially involves measuring a reference uncoated substrate followed by the sample measurement using the same conditions. The thickness and refractive index of the films prepared in the present study were measured using a US Mprobe VIS spectroscopic reflectometer. The thickness and refractive index were measured at different places in every film and the average values were determined.

Table 1: The average thicknesses and refractive indices of pure and CuO dispersed PVA thin films

Sample Name	Thickness (x 10^{-10} m)	Refractive index
Pure PVA	1758	1.428
2.5 wt % CuO	1821	1.521
5.0 wt % CuO	1836	1.633
7.5 wt % CuO	1796	1.697
10 wt % CuO	1795	1.752

It is interesting to note that the thickness does not vary significantly from one place to another in the film. This indicates that the films formed in the present study are of uniform thickness. The average thickness and refractive index values observed for the pure and CuO dispersed thin films are given in Table 1. The increase in refractive index observed due to

CuO dispersion proves the presence of CuO in the PVA matrix, because CuO has higher refractive index (n >2). Moreover, it can be seen that the refractive index increases almost in proportion with the increase in CuO concentration considered for the preparation of films. Also, the measured value of n for maximum CuO concentrated film well matches with the reported one for CuO doped PVA thin films **(** n=1.78) [19].

3.4 UV-Vis-NIR Spectral Analysis

The optical absorption is an important tool to obtain optical energy band gap of crystalline and amorphous materials. The fundamental absorption corresponds to the electron excitation from the valence band to the conduction band can be used to determine the nature and value of the optical band gap. UV-Vis-NIR spectral analysis was carried out for all the five films prepared in the present study in the wavelength range 190 – 900 nm using Jasco V – 630 spectrophotometer **.** Figure 3 shows the optical absorption spectra (A) and the corresponding Tauc plots (B) of pure and CuO dispersed PVA films observed in the present study. The absorption spectra reveal that the increase in concentration of CuO produces red shift in the absorption peak and results in low band gap.

The pure PVA nanocrystalline film has no remarkable absorption in the visible light region with a wavelength above 400 nm whereas the CuO dispersed nanocrystalline film extends the absorption spectrum obviously into the visible region. The result indicates the ability of doped CuO crystalline films to harvest the visible component of solar radiation. Thus, the CuO dispersed PVA crystalline films could be promising photocatalysts under visible light. Also the optical band gap of the synthesized films were determined from Tauc plot by taking energy along x-axis and $(\alpha h\nu)^2$ along y-axis . CuO addition decreases the band gap from 3.47 to 1. 63 eV with increasing concentration which is similar to that observed for PVA-CuI composite films [3]. This may be attributed to salt complexation with polymer matrix besides the expected nanaoparticle aggregation. Increase in absorption and decrease in band gap may be due to charge transfer transitions. Thus, the present study indicates that CuO dispersion tunes the optical absorption property of PVA significantly and consequently makes the PVA film more useful.

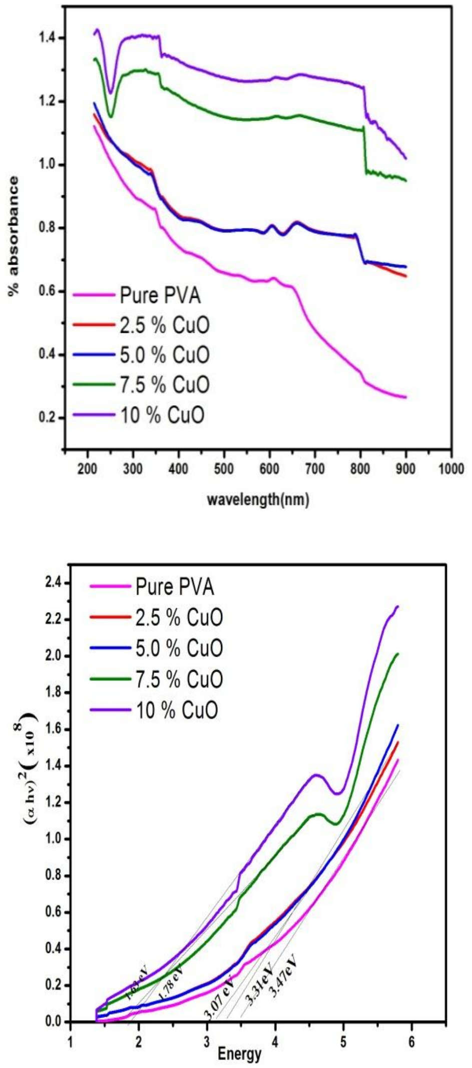


Fig 3: (A) UV-Vis-NIR absorption spectra and (B) Tauc plots of pure and CuO dispersed PVA films

3.5 PL Analysis

PL spectra were recorded for all the five films prepared in the present study using Perkin Elmer model: LS45 spectrophotometer **.** The PL spectra of the prepared films with the excitation wavelength of 280 nm are shown in Figure 4. Though bulk CuO could not emit light, the nano structures can emit visible and UV light [20]. PL emission is mainly attributed to the presence of vacancies or impurities. Vacancies may be copper or oxygen vacancies while the defects may be interstitial copper or anti-oxygen sites [20]. Vacancies present in the material induces the formation of new energy levels in the band gap and as a result emissions will arise from these trap levels while exciting the sample. Emission occurs due to radiative recombination of a photo-excited hole with an electron and the emission peaks are commonly referred to as deep level or trap site emission due to oxygen vacancies [21]. The observed PL spectra show clearly the violet emission. The CuO dispersion in PVA matrix increases the wavelength of light emitted almost in proportion with the concentration of CuO.

Results of optical (UV-Vis-NIR and PL spectral) measurements indicate that the CuO dispersed PVA polymer films prepared in the present study are expected to be more useful in photonics applications.

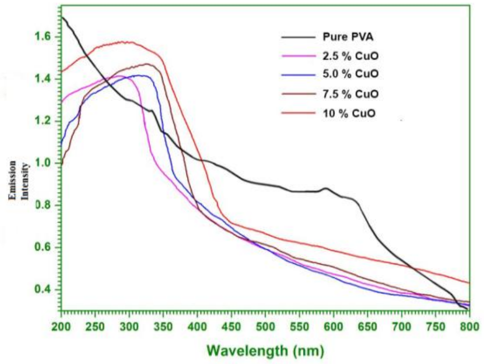


Fig 4: PL spectra of pure and CuO dispersed PVA thin films

3.6 Electrical Properties

3.6.1DC electrical measurements

DC electrical conductivity measurements were carried out on all the five films prepared in the present study by using the conventional two-probe technique in the temperature range 30 – 90 °C. The DC electrical conductivities observed in the present study are shown in Figure 5. It is found that the DC conductivity increases with the increase in temperature as well as with the increase in CuO concentration. This indicates that the electronic conduction is increased significantly by dispersing CuO in the PVA matrix indicating that the space charge contribution may play an important role in the charge transport process [22,23].

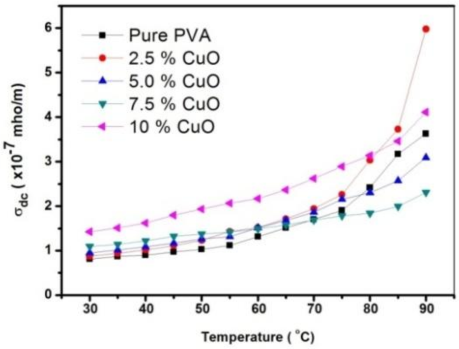


Fig 5: DC electrical conductivities of pure and CuO dispersed PVA films

3.6.2 AC electrical measurements

Dielectric spectroscopy is sensitive to the heterogeneous system and can provide insights into the structures and electrical properties of the materials at molecular and macroscopic levels [24]. The dielectric constant and dissipation (dielectric loss) factor are crucial parameters required in the design of electronic and other related electrical devices and furthermore, as a function of temperature or frequency, they reveal much information on the chemical or physical state of the polymer [25].

The dielectric measurements were performed using an impedance analyzer (Agilent 4284 A LCR meter) covering a frequency range from 20 to 1×10^6 Hz. The film samples were cut into circular pieces of diameter 13 mm and coated with silver paste and mounted between the electrodes of the parallel plate capacitor. Capacitance (C) and dielectric loss factor (tan δ) were measured for various frequencies at room temperature. The real part of the dielectric constant was calculated using the relation

$$\varepsilon' = \frac{C}{C_0}$$

where C and Co are the capacitance values with and without sample, respectively; Co = [(0.08854 A)/d] pF, where A (cm^2) is the area of the electrode and d (cm) is the thickness of the film sample. The imaginary part of the dielectric constant was calculated using the relation

$$\varepsilon'' = \varepsilon' \tan\delta$$

The AC electrical conductivity was calculated by using the relation

$$\sigma_{ac} = \varepsilon_0\, \varepsilon' \tan\delta\, \omega$$

where ω is the angular frequency which is equal to 2πf (where f is the frequency of the applied field).

Variations of ε', ε'' , tan δ and σ_{ac} with frequency are shown in Figures 6 to 8 for all the 5 film samples considered in the present study. It can be seen that the dielectric constant (both real and imaginary parts) and dielectric loss factor decrease while the AC electrical conductivity increases with increasing frequency. Moreover, CuO dispersion nearly decreases the real part of dielectric constant and increases the imaginary part of dielectric constant, dielectric loss factor and AC electrical conductivity significantly. However, all the dielectric parameters (except the real part of dielectric constant) considered are found to vary nonlinearly with the CuO concentration. This may be due to the complexity involved in the charge transport and polarization processes.

The rapid decrease in the dielectric constant noticed over the low frequency range 1 -100 kHz may be attributed to the tendency of dipoles in macromolecules to orient themselves in the direction of the applied field in the low frequency range. However, in the high frequency range the dipoles will hardly be able to orient themselves in the direction of the applied field, and hence the value of the dielectric constant decreases [26]. Also, CuO dispersion in

PVA matrix nearly decreases the value of ε' with increasing CuO concentration.

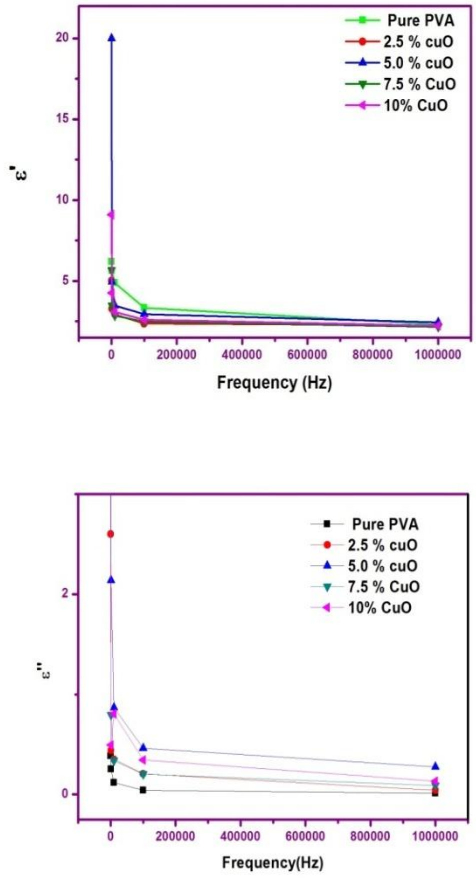


Fig 6 : Variations of ε' and ε'' with frequency for pure and CuO dispersed films

The tan δ spectrum shows relaxation process for all the film samples considered, and as the degree of cross-linking increases, the magnitude of the relaxation peak decreases [27] and the breadth increases [28]. The observed tan δ values are below 1.0 which indicates that the dielectric phenomenon is predominant in all the film samples considered.

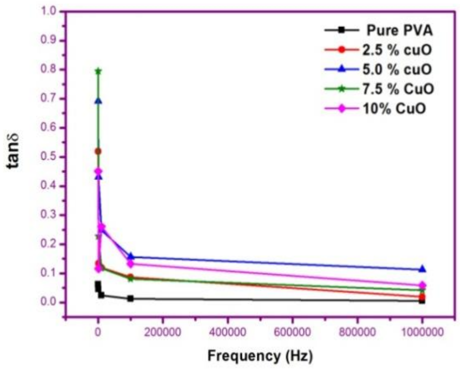


Fig 7: Variation of tan δ with frequency for pure and CuO dispersed PVA films

The increase of AC electrical conductivity with frequency is common for polymeric and semiconductor samples [29]. As the filler concentration is increased, the inorganic filler molecules start bridging the gap separating the two localized states and lowering the potential barrier between them, thereby facilitating the transfer of charge carrier between two localized states [30]. The frequency and temperature dependent conductivity is caused by the hopping of charge carriers in the localized state and also due to the excitation of charge carriers to the states in the conduction band [31]. The term hopping refers to the sudden displacement of charge carriers from one position to another neighboring site and, in general, includes both jumps over a potential barrier and quantum mechanical tunneling [32,33].

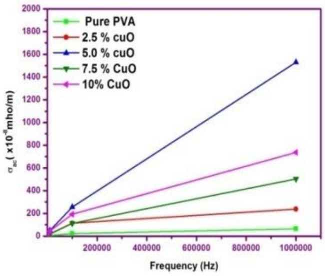


Fig 8: Variation of σ_{ac} with frequency for pure and CuO dispersed PVA films

Results of electrical (both DC and AC) measurements observed in the present study indicate an increase of electronic conductivity and decrease of the real part of dielectric constant with the increase in concentration of CuO dispersion in the PVA polymer matrix. This leads to an expectation that the CuO dispersed PVA polymer films prepared in the present study will find more utility in electronic and other related electrical devices.

IV. Conclusions

Pure and CuO dispersed PVA polymer films have been prepared successfully by a simple chemical method and characterized structurally, optically and electrically. The XRD and FESEM analyses and thickness measurement indicate that the simple chemical method adopted in the present study favour the formation of good quality films of proper CuO-PVA nanocomposites. Results of optical and electrical measurements indicate respectively a decrease of band gap and an increase of electronic conductivity with CuO dispersion making the CuO-PVA nanocomposites (films) prepared in the present study expected to be more useful in photonic and electronic device applications.

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