Dielectric and optical properties for (Poly vinyl alcohol-Carboxymethyl Cellulose –Copper Oxide) Nanocomposites and their Applications

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ABSTRACT

Nanocomposites are new materials important for several applications as humidity sensors, antibacterial etc. So, to fabricate a humidity sensor as application will make perpetration anew kind of (Poly vinyl alcohol - Carboxymethyl Cellulose –Copper Oxide) nanocomposites with different concentrations to test it’s for this purpose. From the results we note that the dielectric constant, dielectric loss and AC. Electrical conductivity of (PVA-CMC) blend increase with the increasing of the copper oxide nanoparticles concentrations at 100HZ. Whereas dielectric constant and dielectric loss decrease with increased frequency but AC. Electrical conductivity increases with increased frequency. The optical measurements are showed the absorbance of (PVA-CMC-Copper Oxide) nanocomposites is increased with increase of the concentrations of copper oxide nanoparticles. The indirect energy gap (Eg) of (PVA-CMC) blend decreases with the increase of the concentrations of copper oxide nanoparticles. All the optical constants as absorption coefficient, extinction coefficient, and refractive index, real and imaginary dielectric constants of nanocomposites are variation with the increase of the weight percentages of copper oxide nanoparticles. Surface resistance of (PVA-CMC-Copper Oxide) nanocomposites variation with increase relative humidity.

KEY WORDS: nanocomposites, AC. Electrical conductivity, copper oxide, humidity sensor, relative humidity.

1. INTRODUCTION

Day after day the need for new materials are necessary in most industries in our daily lives. So, polymer nanocomposites can be expressed as materials contain a tiny quantities of nanoparticles fillers are distributed in polymers homogenously by different concentrations. As compared with micro composites, the nanocomposites refer to nanometers in size usually less than 100 nm. Where different with nine orders in their number density while three orders of amount in length. So the distance in nanocomposites between neighboring additives as compared with micro composites are much smaller. Therefore, in nanocomposites the interaction of fillers with polymers is expected to be much more. Nanocomposites are a novel fabrication materials refers to a hopeful field in the area of nanoscience. Besides these properties, it shows the amazing advantages of structure, electrical, optical, biocompatibility and biodegradability in various industrial, medical, drug release packaging, and agricultural applications. Inside polymer blend the filler of nanoparticles interaction between them to form molecular bridges for nanocomposites. This is the origin for improved structural, electrical and optical properties of the nanocomposite as related to conventional micro composites.

Theoretical part: The dielectric constant ε can be gotten by using eq. (1)

\[ \varepsilon = \varepsilon_\infty \]  
Where C_p is parallel capacitance and C_0 is vacuum capacitor which can be calculated as eq. (2)

\[ C_0 = \varepsilon_0 \frac{a}{t} \]  
Where \( \varepsilon_0 \) is vacuum permittivity a: is the area of capacitance plate t: is the distance between two plates. Dielectric loss \( \varepsilon'' \) can be computed as follow:

\[ \varepsilon'' = \varepsilon D \]  
D: is dispersion factor.

The alternating conductivity is given by:

\[ \sigma_A = \varepsilon'' \varepsilon_0 \]  
Where \( \omega \) is the angular frequency.

Absorption coefficient (\( \alpha \)) is computed as the following equation:

\[ \alpha = 2.303 \left( \frac{A}{t} \right) \]  
A: is the absorbance. For amorphous polymers, indirect transition model can be computed as:

\[ A = \varepsilon D \left( \frac{E_g}{E_\infty} \right) \]  
Where D is a constant, \( E_\infty \) is the photon energy, \( E_g \) is the optical energy band gap, \( x = 3 \) for forbidden indirect transition and \( x = 2 \) for allowed indirect transition.

Refractive index (n) is determined by following equation:

\[ n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \]
Where \( R \) is the reflectance, can be gotby:
\[
R = 1 - A \cdot T \quad \text{(8)}
\]
The extinction coefficient \( (k) \) is determined by the following equation:
\[
k = \frac{\alpha \lambda}{4\pi} \quad \text{(9)}
\]
Where \( \lambda \) is the wavelength of incident light. The dielectric constant is classified into two parts real \( (\varepsilon_r) \), and imaginary \( (\varepsilon_{im}) \). It can be computed each of the real and imaginary parts of dielectric constant \( (\varepsilon_r \text{ and } \varepsilon_{im}) \) as the following equations:
\[
\varepsilon_r = n^2 - k^2 \quad \text{(10)}
\]
\[
\varepsilon_{im} = 2nk \quad \text{(11)}
\]
Optical conductivity \( (\sigma_{op}) \) can be determines as:
\[
\sigma_{op} = \frac{\alpha n c}{4\pi} \quad \text{(12)}
\]

2. MATERIALS AND METHODS

In this paper the materials used are polymers (Poly vinyl alcohol (80 wt. %)), (Carboxymethyl Cellulose (20 wt. %)) as a polymer blend and the nanoparticles as copper oxide as fillers. To get homogeneous solution for (PVA-CMC) blend has been used magnetic stirrer in mixing process when each of the (PVA and CMC) polymers are dissolved in distill water. The (CuO) nanoparticles (NPs) were added to solution with concentrations are \( (0, 3, 6, 9 \text{ and } 12) \) wt. %. To prepare the (PVA-CMC-CuO) nanocomposites, the casting method has been used. A.C. electrical properties of (PVA-CMC-CuO) nanocomposites have been measured by determining the dielectric constant, dielectric loss and A.C. electrical conductivity for different frequencies range \( (100-5 \times 10^6) \) Hz by using LCR meter type (HIOKI 3532-50 LCR Hi TESTER). To measure the optical properties of (PVA-CMC-CuO) nanocomposites in range of wavelength \( (200-800) \) nm, The UV/1800/ Shimadzu spectrophotometer device has been used.

3-1 Fabrication of humidity sensors: The application of humidity sensor for (PVA-CMC-CuO) nanocomposites were prepared by precipitated the solution of these nanocomposites on glass slides dimensions \( (2 \times 2) \text{cm}^2 \) by using spin coating method after cleaning by ethanol and distilled water and left to dry mix for two days. Aluminum electrodes were deposition on the surface of the samples of (PVA-CMC-CuO) nanocomposites by using the vacuum evaporation system (Edwards Coating System -C) type. To examine the sample place in box and the water vapor was used as a source of humidity. The control network monitored and controlled variations in humidity. The electrical resistance for different humidity range \( (30-90) \% \) was measured by using the Keithley electrometer type 2400 source mater, system locally manufactured.

3. RESULTS AND DISCUSSION

Fig.1, shows the plot of the variation of dielectric constant vs. the content of CuO nanoparticles in the (PVA-CMC-CuO) nanocomposites at 100Hz. The dielectric constant of them can be computed by equation 1. With increase of copper oxide nanoparticles (CuONPs), the increase in dielectric constant for (PVA-CMC-CuO) nanocomposites is seen at lower frequency. This is not only due to the atomic, ionic and electronic influence but also due to the space charge influence.

![Effect of CuO nanoparticles concentrations on dielectric constant for (PVA-CMC) blend at 100Hz](image)

The plot of the variation of dielectric constant of (PVA-CMC-CuO) nanocomposites vs. frequency are shown in figure 2, with increasing frequency, the dielectric constant (PVA-CMC-CuO) nanocomposites decreases very fast due to control of the atomic and electronic influence in the (PVA-CMC) blend and space charge reduces gradually. At higher frequency, the dielectric constant for (PVA-CMC-CuO) nanocomposites becomes almost frequency independent representing the rotational motion of the polar molecules of the dielectric is not enough rapid for the achievement of equilibrium with the field. In other word, because of the electric dipoles cannot continue the frequency of the applied electric field and so, it stops.
Figure 2. Variation of dielectric constant for (PVA-CMC-CuO) nanocomposites with frequency at room temperature

The dielectric loss of nanocomposites can be computed by equation 3. Fig 3, shows the plot of the effect of concentrations for CuO nanoparticles vs. dielectric loss of (PVA-CMC) blends at 100 Hz. The dielectric loss of (PVA-CMC-CuO) nanocomposites increases with the increasing of the concentrations for nanoparticles of copper oxides. These increases due to the increases of the charge carriers number as shown in figure. For (PVA-CMC-CuO) nanocomposites, CuO nanoparticles forms as a clusters when the low concentrations. But its forms a path network in the (PVA-CMC-CuO) nanocomposite when the concentration of nanoparticles exceeds 9 wt. %, as fig 4.

Figure 3. Effect of CuO nanoparticles concentrations on dielectric loss for (PVA-CMC) blend at 100Hz

Figure 4. Photomicrographs (x20) for (PVA-CMC-CuO) nanocomposites: (A) for 0.5 wt.% CuO nanoparticles (B) for 3 wt.% CuO nanoparticles (C) for 6 wt.% CuO nanoparticles (D) for 9wt.% CuO nanoparticles (E) for 12wt.% CuO nanoparticles

Figure 5, shows the plot of the variation of dielectric loss of (PVA-CMC-CuO) nanocomposites vs. frequency. For all samples of nanocomposites the dielectric loss decreases with the increasing of the frequency of applied electric field, this manner attributed to the decreases of the space charge polarization contribution and associated to the inability of dipoles to rotate quickly leading to a gap between frequency of oscillating dipole and that of the applied field. But the dielectric loss becomes very large for (PVA-CMC-CuO) nanocomposites at lower frequencies, due to free charge motion within the material in addition to; the enough time for electric dipoles to align with applied electric field before it variation electric dipoles direction; so the dielectric constant of those nanocomposites is high. These are similar with the results of researchers.
The A.C electrical conductivity of nanocomposites can be computed by equation.4, figure.6, shows the plots the variation of A.C electrical conductivity for (PVA-CMC-CuO) nanocomposites vs. concentrations of CuO nanoparticles at 100 Hz. From the figure noted increases the CuO nanoparticles concentrations, the A.C electrical conductivity of nanocomposites increases. This is increases of the conductivity attributed to the increase in the number of charge carriers due to dopant nanoparticles composition which reduces the resistance of nanocomposite gradually and increases the A.C electrical conductivity.in addition to; the CuO nanoparticles forms a path network in the nanocomposites especially at concentrations of nanoparticles (9 wt. % and 12 wt. %) for (PVA-CMC-CuO) nanocomposites, as fig.4.

![Figure 6](image6.png)

**Figure 6. Effect of CuO nanoparticles concentrations on A.C electrical conductivity for (PVA-CMC) blend at 100Hz**

Fig.7, shows the plot of the variation of A.C electrical conductivity of (PVA-CMC-CuO) nanocomposites vs. frequency respectively at room temperature. The A.C electrical conductivity increases with increasing of the frequency of electric field for all samples of nanocomposites, where the frequency acts as a pumping force, pushing the charge carriers between the different conduction states. Indicates the conduction is may be due to one of the following two donor ionization processes: Cu$^+$→Cu$^{2+} + e^-$ for copper interstitial (Cu) or, VO→VO$^+$ + e$^-$ for oxygen vacancy (VO) (PVA-CMC) blend which forms localized levels below the conduction band. This means the mobility of charge carriers and the hopping of ions from the cluster. In the low frequency, more charge accumulation occurred at the electrode and electrolyte interface, leading to a decrease in the number of the ionization processes for CuO nanoparticles and oxygen vacancy for (PVA-CMC) blend. The mobility of charge carriers was higher in the high-frequency region; hence the electrical conductivity increases with frequency for (PVA-CMC-CuO) nanocomposites. This is similar to the results of the researchers.

![Figure 7](image7.png)

**Figure 7. Variation of A.C electrical conductivity for (PVA-CMC-CuO) nanocomposites with frequency at room temperature**

To know the effects of copper oxide filler on the optical properties of (PVA-CMC) blend, UV-visible absorption spectra for (PVA-CMC-CuO) nanocomposites was measured. Fig.8, shows the absorbance for (PVA-CMC-CuO) nanocomposites. It’s indicated that intensity of the peak increase with increases copper oxide filler. The absorption band shifts due to the formation of intermolecular hydrogen bonding existing between Cu ions with the adjacent OH groups of the PVA and CMC main chain. The increase in copper oxide nanoparticles leads to the increase in absorption for (PVA-CMC-CuO) nanocomposites.

![Figure 8](image8.png)

**Figure 8. Variation of absorbance for (PVA-CMC-CuO) nanocomposites with wavelength**

Fig.9, shows the plot of absorption coefficient vs. incident photon energy for (PVA-CMC) blend with different concentrations of copper oxide nanoparticles (CuONPs). It shows the absorption low when energy is low, this means the electrons transitions are low. In the high energy, absorption becomes large this indicate the high probability for electrons transitions. Absorption coefficient for (PVA-CMC-CuO) nanocomposites is increased by increase of CuO nanoparticles additive. The advantage of the absorption coefficient to conclude the transition
electrons nature, when the value of absorption coefficient is high in the higher energy expected direct transition of electrons. The energy and momentum conservation can by electrons and photons, when the value of absorption coefficient low expected indirect transition of electrons. The momentum conservation is by phonons only. From the results it’s indicated absorption coefficient for (PVA-CMC-CuO) nanocomposites has values are less than \((10^4 \text{ cm}^{-1})\) which mean it’s have indirect energy band gap as shown in figure.9.

![Figure 9](image1.png)

**Figure.9. Variation of absorption coefficient \((\alpha)\) for (PVA-CMC-CuO) nanocomposites with photon energy**

Fig.10 and fig.11, show the relationship between absorbance edge \((\alpha h\nu)^{1/2}\) and \((\alpha h\nu)^{1/3}\) for (PVA-CMA-CuO) nanocomposites as a function of photon energy respectively, by take straight line from the upper part of the curve in direction axis (X) in value \((\alpha h\nu)^{1/2} = 0\) and \((\alpha h\nu)^{1/3} = 0\) we get to indirect forbidden energy gap transition (allowed and prevent) respectively. Its indicate that the values of forbidden energy gap (allowed and prevent) of (PVA-CMA-CuO) nanocomposites decrease with increase CuO nanoparticles concentration this attribute to great localize levels in the forbidden energy gap, and the transition of electrons by two stage: the first transition of electron from valence band to localize levels and the second from localize levels to the conduction band in the allowed indirect transition. But in prevent indirect transition, the transition of electrons between the tails of localize of the levels made by the additive. And these nanocomposites types heterogeneous in other word; the electrons conduction depend on defects and additive impurity, where increasing in the CuO additive make several passes of electrons in the (PVA-CMC) blend, therefor passes easy from valence to conduction band. This is explaining the decrease of energy gap by increase the additive.

![Figure 10](image2.png)

**Figure.10. Variation of \((\alpha h\nu)^{1/2}\) for (PVA-CMC-CuO) nanocomposites with photon energy**

![Figure 11](image3.png)

**Figure.11. Variation of \((\alpha h\nu)^{1/2}\) for (PVA-CMC-CuO nanocomposites with photon energy**

Fig.12, shows the variations of extinction coefficient \((k)\) against wavelength for (PVA-CMC-CuO) nanocomposites. It shows an increase in extinction coefficient with increasing of copper oxide nanoparticles for (PVA-CMC) blend. The increasing of extinction coefficient \((k)\) is attributed to high absorption coefficient. Where copper oxide nanoparticles will modify the structure of the host (PVA-CMC) blend. An interesting result that when the concentration of CuONPs increases the absorbance in the visible region increases.

![Figure 12](image4.png)

**Figure.12. Variation of extinction coefficient for (PVA-CMC-CuO) nanocomposites with wavelength**

![Figure 13](image5.png)

**Figure.13. Variation of refractive index for (PVA-CMC-CuO) nanocomposites with wavelength**

Fig.13, illustrates the plot of the variations of refractive index \((n)\) with wavelength for (PVA-CMC-CuO) nanocomposites. The index of (PVA-CMC) blend increases with increasing the copper oxide nanoparticles which attributed to increase the scattering of incident photon which causes to increase the reflectance in addition to; further addition of copper oxide nanoparticles causes increasing the intensity for (PVA-CMC-CuO) nanocomposites. When the incident light interacts with (PVA-CMC) blend has further addition of CuO nanoparticles, the reflection will be high hence the reflectivity for (PVA-CMC-CuO) nanocomposites will be increased.
Fig.14 and fig.15, shows the variations of real and imaginary part ($\varepsilon_r$, $\varepsilon_{im}$) respectively with wavelength for (PVA-CMC-CuO) nanocomposites. It can be indicated that $\varepsilon_r$ is greater than $\varepsilon_{im}$ because its mainly proportional with $n^2$ as shown in equation (10) because the effect of extinction coefficient is very small and could be neglected. It is indicated from this figure that the imaginary part proportional with extinction coefficient by equation (11) because the refractive index value is very small. From the figures are noted that real and imaginary parts of (PVA-CMC) blend increase with increasing of the copper oxide nanoparticles which indicates that the samples have no same structure. Hence, the change in the additive of CuO nanoparticles gave change in the chemical composition of the (PVA-CMC) blend.

![Figure 14. Variation of real part of dielectric constant for (PVA-CMC-CuO) nanocomposites with wavelength](image)

![Figure 15. Variation of imaginary part of dielectric constant for (PVA-CMC-CuO) nanocomposites with wavelength](image)

Fig.16, shows the plot of optical conductivity vs. wavelength for (PVA-CMC-CuO) nanocomposites. The behavior for (PVA-CMC) blend is different from the (PVA-CMC-CuO) nanocomposites. The optical conductivity increases in higher photon energies and then at lower photon energies it decreases, in furthermore the additive of CuO nanoparticles increase the optical conductivity of the (PVA-CMC-CuO) nanocomposites. This behavior is attributed to absorption coefficient because the proportional on it as indicated in equation.12.

![Figure 16. Variation of optical conductivity for (PVA-CMC-CuO) nanocomposites with wavelength](image)

Fig.17, shows the plot of variation of surface resistance for (PVA-CMC-CuO) nanocomposites. Content of copper oxide nanoparticles at low humidity (35%RH). It shows that surface resistance decreases slowly due to Cu' restricted and the water absorbed is low.in addition to; contact chance between (PVA-CMC-CuO) nanocomposites and water molecules is lower, in other word, the H-H bond form is difficult where water molecules could not reach to the surface of samples hence, a continuous water layer not formed. So, the transfer of H' or H$_3$O$^+$ on the discontinuous water layer is so difficult.

![Figure 17. Effect of CuO nanoparticles concentrations for (PVA-CMC) blend on resistance at 35 RH%](image)

For high humidity (95%RH), as fig.18, surface resistance decreases sharply due to the interaction between the samples and molecules of water absorbed increases. As a result a continuous water layer is formed this is lead to the H-H bond is easy formed.

![Figure 18. Effect of CuO nanoparticles concentrations for (PVA-CMC) blend on resistance at 95 RH%](image)
Fig.19, shows the plot of variation of resistance for (PVA-CMC-CuO) nanocomposites vs. the relative humidity (%RH). The resistance decreases with increase humidity, because of $\text{CuO} + \text{H}_2\text{O} \rightarrow \text{Cu}^+ + \text{H}_2\text{O}_2$.

The decrease in the resistance of (PVA-CMC-CuO) nanocomposites with increasing humidity can be attributed to the mobility of the CuO ion (charge carries) which is binding force between it and polymer blend chains is weak in general; van der Walls forces of attraction. Where the ions released increase by increase humidity which leads to increase absorbed water layer on the surface of nanocomposites which it leads to the dissociation of hydrogen ions H-H.

![Figure.19. Variation of resistance for (PVA-CMC-CuO) nanocomposites with relative humidity (RH%)](Image)

4. CONCLUSION
- Volumetric electrical conductivity of (PVA-CMC-CuO) nanocomposites increases with increasing the temperature and concentration of copper oxide nanoparticles.
- Activation energy of (PVA-CMC-CuO) nanocomposites decreases with increases concentration of copper oxide nanoparticles.
- The transition electronic of (PVA-CMC-CuO) nanocomposites was indirect. Because of the absorption coefficient of less than (10$^4$).
- Each of (extinction coefficient, refractive index, real and imaginary part) increases with increase weight percentage of copper oxide nanoparticles for (PVA-CMC-CuO) nanocomposites.
- With higher photon energy, optical conductivity for (PVA-CMC-CuO) nanocomposites is increased and decrease with low photon energy.
- For humidity sensor application, surface resistance for (PVA-CMC-CuO) nanocomposites decrease with increase copper oxide nanoparticles.
- Surface resistance for (PVA-CMC-CuO) nanocomposites decrease with increase relative humidity (RH%)

REFERENCES


