Study the Structure, electrical and optical properties for (PVA-CMC-CuO) Bio nano composites

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ABSTRACT

Bio nano composites got the attention of the various industries, So. (PVA-CMC) blend have been prepared with different concentrations of CuO nanoparticles by using casting technique to obtain (PVA-CMC-CuO) bio nano composites. The optical microscope shows that copper oxide nanoparticles is aggregated as a clusters at lower concentrations but by increasing the concentrations of copper oxide nanoparticles, the path for nanoparticles begin form as a paths network inside the (PVA-CMC) blend. FTIR shows that there are no interactions between (PVA-CMC) blend and CuO nanoparticles. The results show that the volumetric electrical conductivity of (PVA-CMC) blend increases with the increasing of the copper oxide nanoparticles concentrations. The activation energies decrease with the increasing of copper oxide nanoparticles concentrations for bio nano composites. The absorbance (A) of bio nano composites is increased with increase of the concentrations of CuO nanoparticles. The electronic transitions for bio nano composites were indirect. The energy gap (Eg) of (PVA-CMC) blend decreases with the increase of the weight percentages of copper oxide nanoparticles. The optical constants (absorption coefficient (α), extinction coefficient (k), refractive index (n), real and imaginary dielectric constants (ε_r and ε_{im}) of bio nano composites are increased with the increasing of the weight percentages of CuO nanoparticles.

KEY WORDS: bio nano composites, DC. Electrical conductivity, copper oxide, FTIR, nanoparticles.

1. INTRODUCTION

In recent years bio nano composites have used much more in microelectronic industry especially sensor applications. Bio nano composites used in this purpose for several reasons as low cost, light-weight and good process ability. The unique properties of bio nano composites as electrical, optical, structural, electronic and mechanical properties, which got by corporation the polymers with metal nanoparticles or nano metal oxides that used in industry, economy and electronic applications as sensors, diodes and transistors. Where incorporation between polymers and additive lead to produce unique properties. Main physical features of PVA is water soluble, semi crystalline, nontoxic, biocompatible, eco-friendly, better film and fiber forming, good mechanical properties, excellent chemical resistance and biodegradable. It is produced by the polymerization of vinyl acetate to polyvinyl acetate (PVAc) and then hydrolysis to obtain PVA. It's a hydrophilic polymer which is serving special in application in medicine due to its excellent biocompatibility and biodegradable. Important property of (PVA) is semi crystalline nature which is the existence of both amorphous and crystalline areas causing interfacial effects which increases the physical features. So, these unique characterizes of poly vinyl alcohol makes it used in most commonly synthetic polymers.

Theoretical part: The volumetric electrical conductivity σ_V can be calculated for a regular body with a section has along the length (L), a constant area (A) and electrical resistance (R) using the relation:

The electrical conductivity of polymers increases exponentially with the increase of temperature according to the relation:

$$\sigma_{\rm v} = \sigma_{\rm o} \exp\left(-E_{\rm act}/K_{\rm B}T\right) \dots (2)$$

 σ_v : electrical volume conductivity at T temperature, σ_0 : conductivity at absolute zero of temperature, E_{act} activation energy and $K_B = Boltzmann$ constant.

Absorption coefficient (α) is defined by following equation:

$$\alpha = 2.303$$
 (A/t).....(3)

Where A: is the absorbance. The indirect transition model for amorphous semiconductors is: $\alpha h v = B$

$$B(hv-E_g)^m$$
.....(4)

Where B is a constant, hu is the photon energy, E_g is the optical energy band gap, m = 2 for allowed indirect transition and m = 3 for forbidden indirect transition. The Refractive index (n) is given by following equation:

 $n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}}....(5)$ Where R is the reflectance, can be obtained by:

R = 1 - A - T.....(6)

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The extinction coefficient (k) is calculated by using the following equation:

$$\mathbf{k} = \frac{\alpha \lambda}{4\pi}.$$
 (7)

 λ wavelength of incident light. The dielectric constant is divided into two parts real (ε_r), and imaginary (ε_{im}). The real and imaginary parts of dielectric constant (ε_r and ε_{im}) are calculated by using equations:

$$\begin{aligned} & \mathcal{E}_{r} = n^{2} - k^{2}.....(8) \\ & \mathcal{E}_{im} = 2nk....(9) \end{aligned}$$
Optical conductivity (σ_{op}) can be determines as:
 $\sigma_{op} = \frac{\alpha nc}{4\pi}....(10)$

2. MATERIALS AND METHODS

In this paper the materials are used polymers (PVA (80 wt. %)), (CMC (20 wt. %)) as a polymer blend and the nano materials oxide as copper oxide (CuO) as additive. Magnetic stirrer is using in mixing process to get homogeneous solution when the polymers (PVA+CMC) are dissolved in distill water. The copper oxide nanoparticles (NPs) were added to solution with concentrations are (0, 3, 6, 9 and 12) wt. %. The casting technique was used to preparation the (PVA-CMC-CuO) bio nano composites. Optical microscope has been used to known the homogeneity between polymer blend and nanoparticles. To diagnosis the interaction between the polymers and the additive FTIR has been used. D.C electrical properties of (PVA-CMC-CuO) bio nano composites have been measured by determining the D.C electrical resistance for different temperature range (50-80)⁰C by using the Keithley electrometer type 2400 source mater. The UV/1800/ Shimadzu spectrophotometer it's used to measure the optical properties of (PVA-CMC-CuO) bio nano composites in range of wavelength (200-800) nm.

3. RESULTS AND DISCUSSION

Figure.1, shows the distribution of copper oxide nanoparticles in (PVA-CMC) polymer blend at magnification power (20x). The CuO nanoparticles are aggregates as a cluster at lower percentages as figure below. But by increasing the concentrations of CuO nanoparticles, the nanoparticles form a paths network inside the (PVA-CMC) blend especially at (9 and 12 % wt.) copper oxide nanoparticles have highest diffusivity in (PVA-CMC) blend.



Fig.1. Photomicrographs (x20) for (PVA-CMC-CuO) bio nano composites: (A) for pure, (B) for 3 wt.% CuO nanoparticles, (C) for 6 wt.% CuO nanoparticles, (D) for 9 wt.% CuO nanoparticles, (E) for 12 wt.% CuO nanoparticles

Figure 2, shows the FTIR spectra of (PVA-CMC-CuO) bio nano composites. The interactions in bio nano composites can be studies by Fourier transform infrared radiation device (FTIR). For all samples of bio nano composites show broad bands at around 3255.41 cm⁻¹ and 3288.3 cm⁻¹ are observed because of OH groups in the polymers matrix chain. The other bonds as (C-O-C) group can be noted in the bands at (1084.2-1416.21) cm⁻¹ were attributed to the PVA film was not so transparent. The peaks at 1647-1681 cm⁻¹ due to the presence of such free C=O groups due to deformation vibration of the absorbed water molecules. C-N group of CMC due to the overlapping by (C=O) group. The (C-O) groups of polymers matrix can be assigned at the peaks at (1417-1421) cm⁻¹. Peaks at (2900-2908) cm⁻¹ were due to the presence of C-H groups. The C=C stretching mode appear in the bands at (1708-1655) cm⁻¹. The peak at (1089-1096) cm⁻¹, the band be strong for all samples of bio nano composites this is due to the stretching mode of C-O group. The two strong bands observed at around 1418 cm⁻¹ and 842 cm⁻¹ are due to the stretching and bending modes of CH₂ group respectively. The change in spectral of (PVA-CMC) involves shifting in some bonds and change in the intensities due to CuO nanoparticles. The interaction between nanoparticles and polymer blend causes these changes. From the FTIR studies note that there are no interactions between (PVA-CMC) blend and CuO nanoparticles. From figures noted the transmittance decreases slightly with the increasing of copper oxide nanoparticles concentrations because of the increasing in density of nano composites. These are consistent with the results of researchers.



Fig.2. FTIR spectra for (PVA-CMC-CuO) bio nano composites; A- (PVA-CMC) blend, B- 3 wt.% CuO nano particles, C- 6 wt.% CuO nanoparticles, D- 9 wt.% CuO nanoparticles

Fig.3, shows the plot of D.C volumetric electrical conductivity of (PVA-CMC-CuO) bio nano composites conductivity vs. the content of copper oxide nanoparticles at 323K. The plot shows that D.C electrical conductivity of (PVA-CMC) blend increases with the increasing of the CuO nanoparticles concentrations. Especially remarkably after insertion of CuO nanoparticles (9%) in the (PVA-CMC) blend. Hence, as the concentration of copper oxide nanoparticles increases the number of free charge carriers also increases, all together electrons from polar O⁻² terminated CuO nanoparticles surfaces and from the (PVA-CMC) blend chains, resulting in the improvement in the conductivity of (PVA–CMC-CuO) bio nano composites. In addition to; When the concentration of nanoparticles for (PVA-CMC-CuO) bio nano composites reach to (9 and 12 wt. %), the copper oxide nanoparticles form conductive paths network (conducting particles) in the bio nano composites as shown in figures.2.



Fig.3. Effect of CuO nanoparticles concentrations for (PVA-CMC) blend on D.C electrical conductivity at 323k

Figure.4, shows the plot of D.C volumetric electrical conductivity (σ_v) of (PVA-CMC-CuO) bio nano composites conductivity vs. the temperature. This figure explains as temperature increases, D.C volume electrical conductivity (σ_v) of (PVA-CMC-CuO) bio nano composites increases. The performance of electrical conductivity of bio nano composites with temperature attributed to break the bonds of molecules of (PVA-CMC) blend and the liberalization of charge carries to the conduction bond of (PVA-CMC-CuO) bio nano composites and mobility in polymer blend chains which moving impurity, which leads to increase the conductivity. copper oxide nanoparticles in addition to (PVA-CMC) polymer blend chains is operated as traps for the moving charge carriers by hopping process.

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Fig.4. Variation of D.C electrical conductivity for (PVA-CMC-CuO) bio nano composites with temperature

Figure.5, shows the plot of the variation of $(\ln \sigma_v)$ vs. (1000/T) for (PVA-CMC-CuO) bio nano composites to compute the activation energy of bio nano composites by equation (2). Due to increase in temperature, free volume and mobility which increases. These two blend and filler then permits free charges to jump from one to another site thus increase conductivity of (PVA-CMC-CuO) bio nano composites. The conductivity increases so as temperature indicates more ions gained kinetic energy by thermally activated hopping of charge carriers between trapped sites, which is temperature dependence. The sharp increases of D.C conductivity between 323K° to 353K° can be attributed to large heat energy absorbed by the samples and thus induce mobility of electrons.



Fig.5. Variation of ln (σ) and inverted absolute temperature for (PVA-CMC-CuO) bio nano composites

Figure.6, shows the plot of concentration of copper oxide nanoparticles vs. activation energy. The activation energies will decreases with the increasing of the nanoparticles concentrations for bio nano composites, this behavior attributed to creation local energy levels in the energy gap which acts as traps for charge carriers. At high concentrations of CuO nanoparticles, the activation energy has lower values which attributed to formation a continuous network of nanoparticles in the bio nano composite, where a concentration of copper oxide nanoparticles increase the number of conductive paths increase and the distance between the conductive particles becomes smaller.





Now we measured the UV-visible absorption spectra for (PVA-CMC-CuO) bio nano composites to known the effect of (CuO) additive on the optical properties of (PVA-CMC) blend.

Figure.7, shows UV-visible absorption spectra for (PVA-CMC-CuO) bio nano composites. It indicates that intensity of the peak increase with increasing CuO additive, this is because of the added CuO nanoparticles have been absorbed the incident radiation by its free electrons. The absorption band shifts give an idea of the formation of inter-intermolecular hydrogen bonding existing between Cu ions with the adjacent OH groups of the PVA main chain. The increasing in absorption for (PVA-CMC-CuO) bio nano composites are mainly due to the increase in CuO nanoparticles.





Figure.8, shows the plot of absorption coefficient vs. function of incident photon energy for (PVA-CMC) blend with different percentage of copper oxide nanoparticles. It shows the absorption low when the low energy, this means the probability of electrons transition low. But in the high energy, absorption becomes large this indicate the high probability for electrons transitions. From the figure; we notice an increasing in absorption coefficient for (PVA-CMC-CuO) bio nano composites when increase of additive CuO nanoparticles. These increases attributed to increasing the number of carries charges of CuO nanoparticles which cause to increase the absorbance. The conduction band of copper oxide filled of free electrons because of Oxygen Vacancies which due to from non-stoichiometry. Absorption coefficient helps to conclusion the transition electrons. Photons and electrons play important role in the energy and momentum conservation, but when the value of absorption coefficient low (less than 10⁴cm⁻¹) in the low energy expected indirect transition of electrons. The momentum conservation is by phonons only. From the results it's indicated absorption coefficient for (PVA-CMC-CuO) bio nano composites has values are less than (10⁴ cm⁻¹) which mean it's have indirect energy band gap as shown in figure.9.



Fig.8. Variation of absorption coefficient (α) for (PVA-CMC-CuO) bio nano composites with photon energy

Figure.9, and figure.10, show the relationship between absorbance edge $(\alpha hv)^{1/2}$ and $(\alpha hv)^{1/3}$ for (PVA-CMA-CuO) bio nano composites as a function of photon energy respectively , by take straight line from the upper part of the curve in direction axis (X) in value $((\alpha hv)^{1/2} =0)$ and $((\alpha hv)^{1/3} =0)$ we get to indirect forbidden energy gap transition (allowed and prevent) respectively[17] .it indicates that the value of forbidden energy gap(allowed and prevent) of (PVA-CMA-CuO) bio nano composites decrease with increasing 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 bio nano composites type 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 increasing the additive.



Figure.11, shows the variations of extinction coefficient (k) with wavelength for (PVA-CMC-CuO) and bio nano composites. By using eq. (8) shows an increasing in extinction coefficient with increasing of CuO nanoparticles July - September 2017 1124 JCPS Volume 10 Issue 3

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for (PVA-CMC) blend. The behavior of (k) can be attributed to high absorption coefficient.in addition to; loss in incident photon energy due to the interaction between the carries energy in the samples and the incident light, which leads to polarize of the medium charges. This result indicates that the CuO nanoparticles will modify the structure of the host (PVA-CMC) blend. In the visible region, when the concentration of CuO nanoparticles increases the absorbance increases.



Fig.11. Variation of extinction coefficient for (PVA-CMC-CuO) bio nano composites with wavelength

Fig.12, shows the plot of the variations of refractive index (n) vs wavelength for (PVA-CMC-CuO) bio nano composites. This figure shows the index of (PVA-CMC) blend increases with increase of the CuO nanoparticles which attributed to increase the scattering of incident photon which causes to increase the reflectance.in addition to; further addition of CuO nanoparticles causes increasing the intensity for (PVA-CMC-CuO) bio nano composites. When the incident light interacts with (PVA-CMC) blend has further addition of nanoparticles of copper oxide, the reflection will be high hence the reflectivity for (PVA-CMC-CuO) bio nano composites will be increased.



Fig.12. Variation of refractive index for (PVA-CMC-CuO) bio nano composites with wavelength

Figure.13, and figure.14, show the variations of real and imaginary part ($\mathcal{E}_r, \mathcal{E}_{im}$) respectively with wavelength for (PVA-CMC-CuO) bio nano composites. It can be indicated that \mathcal{E}_r is greater than \mathcal{E}_{im} because it mainly proportional with n² as shown in equation (9) 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 (10) because the refractive index value is very small. From the figures note that real and imaginary parts of (PVA-CMC) blend increases 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.15, shows the plot of optical conductivity vs. wavelength for (PVA-CMC-CuO) bio nano composites. The behavior for (PVA-CMC) blend is different from the (PVA-CMC-CuO) bio nano composites. 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) nano composites. This behavior is attributed to absorption coefficient because the proportional on it as indicated.

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Fig.15. Variation of optical conductivity for (PVA-CMC-CuO) bio nano composites with wavelength 4. CONCLUSION

The nanoparticles form a paths network inside the (PVA-CMC) blend especially at (9 and 12 % wt.). From the FTIR studies note that there are no interactions between (PVA-CMC) blend and CuO nanoparticles.

By increasing the temperature and concentration of copper oxide nanoparticles, volumetric electrical conductivity of (PVA-CMC-CuO) bio nano composites increases.

By increasing concentration of CuO nanoparticles, activation energy of (PVA-CMC-CuO) bio nano composites decreases.

Absorption coefficient of (PVA-CMC-CuO) bio nano composites was less than (10⁴) so, the transition electronic indirect.

With increasing weight percentage of copper oxide nanoparticles for (PVA-CMC-CuO) bio nano composites, each of (extinction coefficient, refractive index, real and imaginary part) increases.

Optical conductivity for (PVA-CMC-CuO) bio nano composites increase with higher photon energy and decrease with low photon energy.

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