



Investigation on Nanosized CuO Incorporated Hydroxypropyl Methylcellulose Polymer Nanocomposite Films

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ABSTRACT

Addition of metal-oxide nanoparticles (NPs) to polymers allows the modification of physical properties of polymers as well as the implementation of new features in the polymer matrix. In this work, we have made an attempt to disperse CuO NPs in the hydroxypropyl methylcellulose (HPMC) and to understand the changes in structural, optical and thermal properties of the polymer films. CuO NPs were added in four different concentrations, viz., 0.1, 0.2, 0.3 and 0.4 wt.%. A total of five films were prepared (including the pure HPMC film, for comparison). The prepared films were subjected to X-ray diffractometer, scanning electron microscope, Fourier transform infrared, differential scanning calorimeter, and ultraviolet-visible spectral analyses. The obtained results are reported.

Key words: Polymer nanocomposite films, Metal-oxide nanoparticles, Structural properties.

1. INTRODUCTION

Fabrication of polymer nanocomposites, with metal-oxide nanoparticles (NPs) dispersed in the polymer matrix has paying much attention, recently as advanced technological materials. Because the combination of metal-oxide NPs and a polymer offers simple processing steps, low cost and can be integrating the promising properties of both components [1]. It is well known that the addition of nano-sized inorganic particles into the polymeric matrices, the new composite material will show changed - mechanical, thermal, optical, and effective bactericidal function - which is very much differ from those of conventional materials [2]. By suitable doping, the properties of polymers can be improved to a desired limit [3]. We have investigated the effect of the addition of CuO NPs on the mechanical, thermal, optical and structural properties of hydroxypropyl methylcellulose (HPMC) polymer films. Hence, in this paper, we have reported tensile strength (TS), elongation break (E in %), and Young's modulus (Y), thermal transitions, optical band gap and morphological studies of HPMC polymer films with and without incorporated of CuO NPs at different concentrations.

2. EXPERIMENTAL

2.1. Synthesis of CuO Nanopowder

An analytical grade of cupric sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and sodium hydroxide (NaOH) were

purchased and used as precursors and stabilizing agent respectively. Double distilled water was used as solvent throughout the experiment. In a typical reaction, a mixture of 0.5 M sodium hydroxide and 0.1 M of copper sulfate aqueous solution is prepared in the ratio of 1:3 and stirred for 15 min. The resulting solution is kept in a domestic microwave oven (operated with frequency 2.45 GHz and power 800 W) for 10 min. The obtained colloidal precipitate was separated by centrifugation, washed with distilled water and absolute ethanol several times. In the end, acetone washing is used to remove the organic impurities and then dried at 40°C for 24 h.

2.2. Preparation of HPMC/CuO Nanocomposite Films

To study the effect of prepared CuO nanomaterials on properties of HPMC polymer, HPMC/CuO nanocomposites were prepared with five different percentage (i.e., 0.1, 0.2, 0.3, and 0.4) weights of CuO in the 5% - HPMC matrix film. This was denoted as HC1, HC2, HC3, and HC4, respectively. Where, H stands for HPMC (with average molecular weight approximately 25,000 Daltons) and C1 to C4 indicates CuO nanomaterials of different % weight. The prepared films were free from air bubbles. Thicknesses of the produced films were in the range of 0.09-0.21 mm and they were cut into pieces suitable for measurements. The thicknesses of the films were

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measured by Mitutoyo instrument, Model (2050F) made in Japan.

3. RESULTS AND DISCUSSIONS

3.1. X-ray Diffraction (XRD) Analysis

The XRD measurements were performed to examine the nanostructured feature and crystallinity of pure CuO, neat HPMC, and HPMC-CuO polymer nanocomposites. The crystalline nature of pure nano-CuO was observed by various sharp peaks shown by XRD patterns in Figure 1. XRD of HPMC/CuO NP nanocomposite films are given in Figure 2. For the pure HPMC, the main diffraction peak was observed at $2\theta = 20.88^\circ$, which represents its partial crystallinity structure [4]. From Figure 1, it was clear that the synthesized CuO showed the main characteristic peaks, which are sharper and stronger at $2\theta = 35.4^\circ$ and 38.6° confirming the monoclinic structure of CuO NPs as reported earlier [5]. 10 distinct diffraction peaks can be seen at the 2θ values of 32.77, 35.41, 38.61, 48.66, 53.34, 58.13, 61.43, 67.90, 72.23 and 75.04° for the nano-sized crystalline structure of CuO

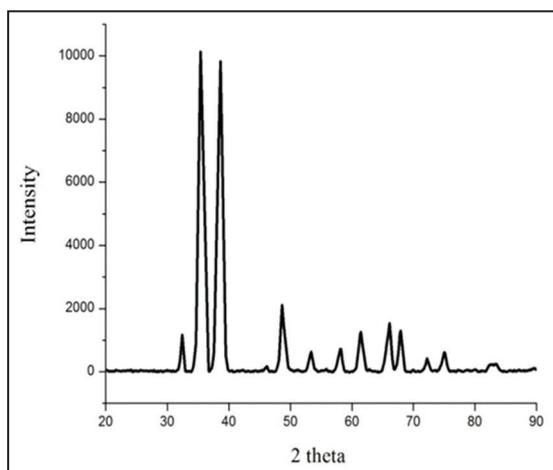


Figure 1: Powder X-ray diffraction spectrum for pure CuO nano particles.

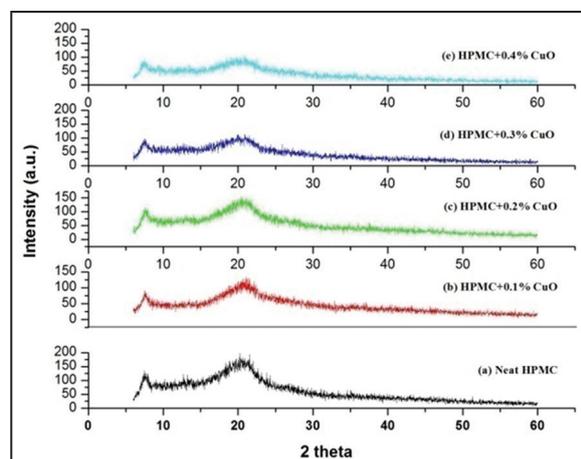


Figure 2: X-ray diffraction scans of hydroxypropyl methylcellulose/CuO nano composite films.

and the values were found to be in good agreement with literature values (JCPDS file no. 45-0937) [5].

XRD patterns of pure HPMC and HPMC-CuO nanocomposites having 0.1, 0.2, 0.3 and 0.4 wt.% of CuO. The crystalline nature of HPMC results from the strong intermolecular interaction between HPMC polymer networks. XRD profiles of the composites showed slight shifting or broadening of peak at $2\theta = 20.88^\circ$. The intensity of HPMC-CuO nanocomposite peaks decreases with increase in nanofiller concentration. This is because the interactions between HPMC and nano-CuO lead to the decrease in the intermolecular interaction between HPMC chains, thereby leading to the grain size of the nanocomposite decreases with higher the percentage of NPs inclusion [6]. However, in this case, there was unusual increase in crystalline size to some extent and decrease at 0.4 wt.%. The crystallite size (dXRD) of HPMC/CuO nanocomposite measurement could be carried out using the Scherer equation as enlisted in Table 1 [7].

3.2. Fourier Transform Infrared (FTIR) Analysis

The prepared CuO nanomaterials were examined by FTIR analysis and are shown in Figure 3. There are two absorbance bands which appear at around 650 and $3600-3100\text{ cm}^{-1}$. Sharp absorption band at 650 cm^{-1} is associated with Cu-O stretching mode. A broad band in the range of $3600-3100\text{ cm}^{-1}$ is

Table 1: Crystallite size of HPMC/CuO nano composites.

Sample	2θ	FWHM	Crystallite size-D (Å)
Pure	20.882	4.522	18.66
HC-1	20.841	4.875	17.3
HC-2	21.034	4.508	18.72
HC-3	20.884	4.438	19.01
HC-4	20.505	5.296	15.92

HPMC=Hydroxypropyl methylcellulose

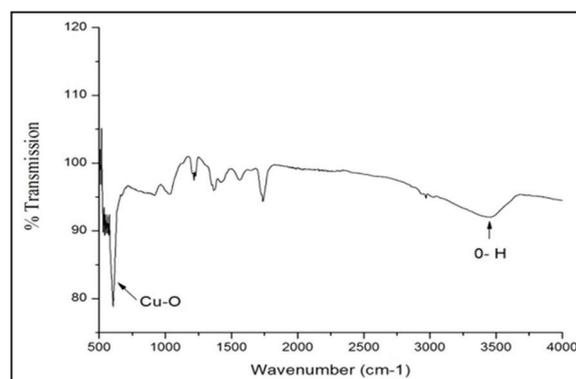


Figure 3: Fourier transform infrared spectra of the prepared CuO nano materials.

due to the stretching in water molecules associated with CuO. The result suggests the presence of Cu-O bonds and some constitutional water is incorporated in the copper oxide structure. Thus, the formation of copper oxide is confirmed from the FTIR study. In Figure 4, the sample shows that peaks at 3441-3439 cm^{-1} are due to OH stretching vibration and intermolecular H-bonding [8]. The peak at 2918 cm^{-1} is attributed to stretching vibration of $-\text{CH}_2$, and band at 1645 cm^{-1} indicates the presence of stretching vibration of six-membered cyclic rings. The band at 1055 cm^{-1} is for stretching vibration of $-\text{C}-\text{O}$ groups. The peak at 945 cm^{-1} is due to the pyranose ring [9].

3.3. Structural Studies

Figure 5 shows the scanning electron microscope (SEM) image of the prepared CuO NPs. The size and morphology of CuO NPs have been examined by SEM. It shows that the CuO NPs are in feather shape. SEM micrographs clearly show the surface features, by which it highlights that CuO NP was successfully prepared and it can be seen that the particles congregate together and the size of which is within 50 nm.

3.4. Mechanical Properties

The effects of NPs on mechanical properties of the HPMC/CuO nanocomposite films were evaluated up to their failure. We have calculated TS, Young's modulus and elongation at break (%) of HPMC/CuO NP nanocomposites by stress-strain curves and enlisted in Table 2.

There were unusual changes in the TS and modulus of the nanocomposites has been experienced as higher the dosage of CuO. Furthermore from Table 2, we observed that percentage elongation at break (E) increases with the increase in the percentage of NPs at certain extent and gradual decrease often at 0.3 wt% of nano material inclusion.

A possible explanation for this result will be, TS of the all composite film was increased compared with the neat matrix due to the reinforcing effect of NPs. As the percentage raise of nanofiller inclusion, the stiffness in polymer chain decreases and the NPs itself acts as a plasticizer.

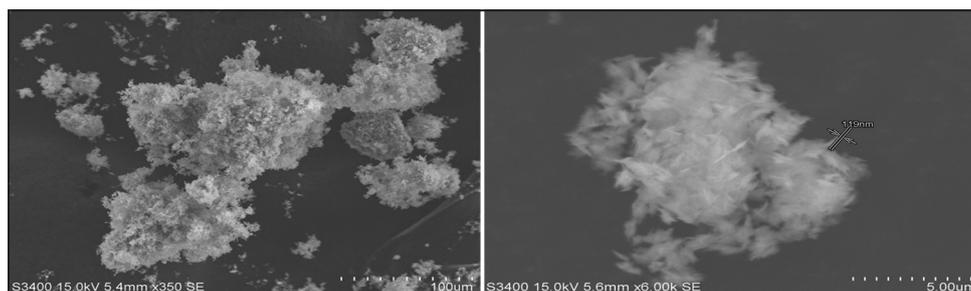


Figure 5: Scanning electron microscope images for pure CuO nanoparticles.

3.5. Optical Properties

The structural modifications produced in HPMC/CuO NP nanocomposites due to dopant would cause a change in the molecular structure of the polymer. As a result, a modification within the optical band gap is expected. The information about the optical band gap is accessible from the absorption edge of the ultraviolet-visible spectra of the HPMC/CuO nanocomposite films, which is given in Figure 6. The optical band gap was calculated by extrapolating straight regions to $(h\nu)$ axis in the plots of $(\alpha h\nu)^{1/2}$ versus $(h\nu)$, where, α is the absorption coefficient and $h\nu$ is the energy of incident light photon. It has been found that the optical band gap of the films improves, as the progressive addition of nanomaterial as shown in Figure 7.

Table 2: Mechanical properties of nano composite films.

Sample	TS (MPa)	Young's modulus (MPa)	% Elongation
Pure	10.6	1744.98	5.84
HC-1	16.4	1596.74	9.95
HC-2	14.6	1626.45	9.96
HC-3	15.7	1720.54	5.96
HC-4	13.1	1484.09	4.96

TS=Tensile strength

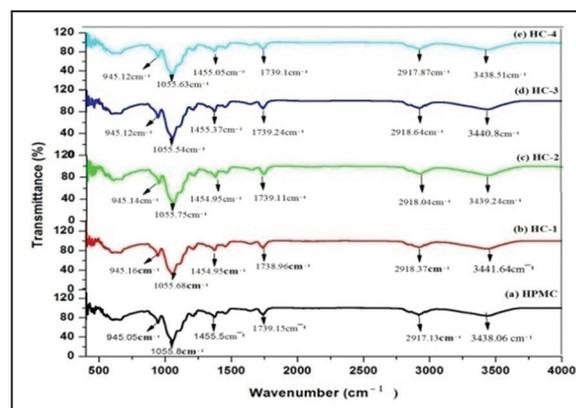


Figure 4: Fourier transform infrared spectra of nanocomposite films.

3.6. Thermal Properties

Differential scanning calorimeter (DSC) is an analytical technique used to determine a material's thermal stability and glass transition temperature (T_g) by monitoring the heat flow that occurs as a sample is heated. Figure 8 shows DSC thermograms of HPMC/CuO nano composite films.

Thermal behavior of parent HPMC and HPMC/CuO nanocomposite films were studied by DSC analysis. The derivative of the DSC thermograms, rate of thermal transitions was also plotted against temperature as shown in Figure 8. From the DSC graph, it was found that two temperature regions can be identified over which the thermal transitions occur. In the present system, DSC thermogram shows the overlap of glass transition temperature. In the present investigation, DSC thermogram of HPMC and HPMC/CuO nanocomposite films show two endothermic peaks which are interpreted as glass transition temperature (T_g) and melting temperature (T_m). The glass transition temperature of HPMC is shifted to higher temperature from 53.33°C for pristine HPMC to 60.26°C by the progressive addition of CuO in the nanocomposite films. This indicates that while increasing the % weight of CuO, the crystallinity increases as confirmed by the XRD crystallite size data. Increase in HC-2 and decrease in HC-3 and HC-4. It is clear that the thermal transitions of pure HPMC are shifted toward higher temperature with addition of CuO. Therefore, the thermal stability of the HPMC is enhanced in the presence of CuO due to slight increase of crystalline regions. The trend of increasing melting temperatures is also observed in the analysis up to HC-3 and thereafter it decreases may be because of nanomaterial domination over the polymer matrix.

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5. CONCLUSIONS

We observe that there are changes observed by incorporation of NPs have significant influence on structural, mechanical, optical and thermal properties in HPMC polymer matrix. From XRD study of CuO incorporated HPMC films, it has been found that there are much changes in the intensity of the X-ray reflections. The significant change in structural parameters in the polymer is due to the random dispersion of NPs in the matrix of HPMC, lowers the short-range interaction between the layers of HPMC, leading to increase in disorder in the lattice. There were unusual differences in TS, Young's modulus

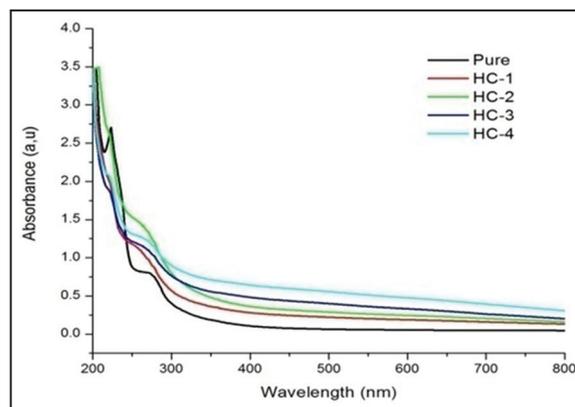


Figure 6: Absorption spectra of nano composite films.

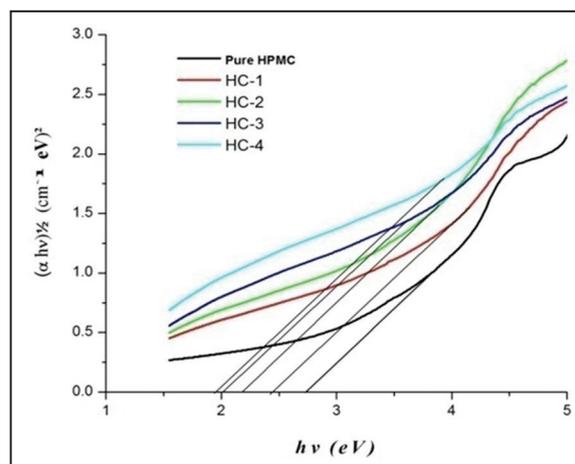


Figure 7: Optical band gap of hydroxypropyl methylcellulose/CuO films.

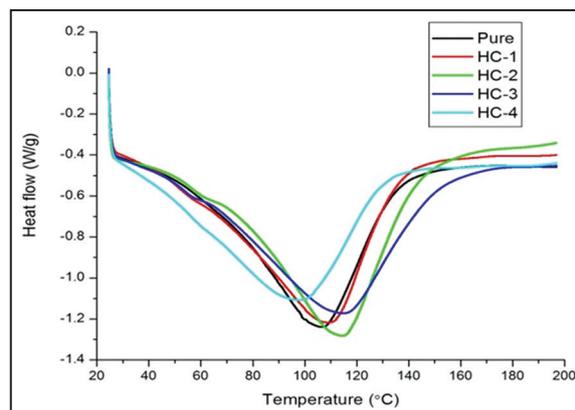


Figure 8: Differential scanning calorimeter thermograms of nanocomposite films.

and percentage elongation at break, and increases as the CuO concentration increases up to certain extent compare to pure matrix. We have also examined the reasons for such changes in terms of weakening of intermolecular interactions (Vander Waal's forces) often 2-3% loading. The doping of NPs also improves the thermal stability of films and optical band gap.

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*Bibliographical Sketch



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