



Impact of Nanosized CuO Insertion on Structural and Mechanical Properties of PVA: HPMC Based Polymer Blend Nanocomposites

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Insertion of metal-oxide nanoparticles to polymers stipulate the modification of physical properties of polymers over and above the accomplishment of new features in the polymer matrix. In the current study, an attempt was made to disperse the CuO nanoparticles in the polyvinyl alcohol and hydroxypropyl methylcellulose (HPMC) blend to investigate the structural, mechanical and optical properties of the nanocomposite. Blend was prepared in different ratios using PVA and HPMC, viz. 25:50, 50:50 and 75:25 wt%. The CuO nanoparticles were added to the 75:25 PVA:HPMC blend in different percentage like 0.5, 1 and 1.5%. The polymer with and without CuO incorporation were subjected to X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, UV-visible spectral analyses and mechanical strength, etc. The results revealed that the incorporation of the CuO nanoparticles enhanced the structural and mechanical properties of the polymer by forming successful nanocomposite.

Keywords: CuO nanoparticles, Nanocomposite, Structural property, Mechanical property.

INTRODUCTION

Traditional composite materials are made up of a three-dimensional mixture of at least two chemically different materials, separated by a discrete interface. This was created to obtain qualities that could not be reached by using a single component [1]. Polymer nanocomposites (PNCs) are the materials, which contain a continuous phase of polymer and a discontinuous phase of nanofillers. These are a type of substance, which can have a variety of physico-chemical properties that are impossible to achieve with individual components functioning alone [2]. The foremost interesting characteristic of nanocomposite polymer is the intricate interfaces involving in nanofillers and polymer matrices. The huge definite surface area is produced due to these small scales, which accentuates the importance of polymer-nanofiller interactions. Therefore, studying the intercalation process between nanoparticles and polymers is essential for achieving optimal mechanical, thermal, optical and electrical properties [3].

Pure polymers with poly-conjugated structures have a low electrical conductivity, whereas oxidized nanofillers in polymers

shows significant conductivity to some extent. There are few studies were reported on and metal oxide nanoparticles encapsulation into the polymer. Since many decades, a strong importance is given to the development of polymer nanocomposites, which exhibit the better electrolytic and gas sensing properties [4]. Poly(vinyl alcohol) (PVA) and hydroxypropyl methylcellulose (HPMC) polymers nanocomposites can be easily fabricated with better chemical stability and generally considered for electronic and optical applications [5].

Copper oxides are intrinsic p-type semiconductors with tiny band gaps and a variety of desirable features which can be applied to a variety of applications [6]. Copper oxide (CuO) nanoparticles are of particular interest because of their heat transfer efficiency as nanofluids [7]. It is the foundation for a large number of high-Tc superconductors, which makes it ideal for photoconductive and photo thermal applications. Unlike n-type semiconducting metal oxides, CuO is a p-type semiconductor with even a narrow band gap of 1.2-1.9 eV [8].

In this study, the fabrication of PVA and HPMC polymer blend with nano-CuO as nanocomposite is reported. The synthesized nanocomposite were subjected to the different

characterization like X-ray diffraction studies, FTIR, SEM, *etc.* The prepared nanocomposite were analyzed for its mechanical properties and compared with the pure polymers.

EXPERIMENTAL

Preparation of HPMC and PVA polymer by solution casting method: To prepare water soluble polymer, poly(vinyl alcohol) (PVA) and hydroxy propyl methyl cellulose (HPMC) was taken in definite weight ratio. Pure 3% of PVA and HPMC polymer were prepared by solution casting method. Polymer blend was fabricated using PVA and HPMC using different ratio like 25:75, 50:50 and 75:25, respectively. Later, among of three prepared polymers, the best neat blend was found by 75:25 (PVA:HPMC) ratio. Pure polymers and fabricated blends both were subjected for the characterization. The PVA:HPMC blend (75:25) was carried forward for further studies.

Synthesis of CuO nanoparticles: Incorporating the nano-CuO nanoparticle in to the polymer modifies the physico-mechanical properties of polymer and employed the innovative aspects in the polymer matrix. Copper sulphate (0.1 M) was dissolved in double distilled water. To the usual reaction, 0.5 M NaOH was added to 0.1 M copper sulphate solution. The ratio of the mixture was 1:3 and continuously stirred for 15 min. The solution was then micro waved for 10 min (at 2.45 GHz and 800 W power) before being allowed to cool at ambient temperature [9]. A black coloured, precipitated colloidal solution was obtained from the above reaction. The reaction mixer was subjected in to the ultra-centrifugation and supernatant was discarded. The pellet was washed with distilled water followed by ethanol three times. At last, pellet was washed with acetone to remove the organic impurities and then, collected and dried at 40 °C for 24 h using hot air oven. The obtained CuO nanoparticles were stored in air tight container for further use [10].

Fabrication of nanocomposite film: To evaluate the influence of produced CuO nanoparticles on the characteristics of PVA, three samples of different weight percentages of PVA were used. Three samples of different weight percentages of PVA:HPMC (75:25) blend/CuO was made by adding a known weight of CuO to a blend produced in an aqueous medium, stirred and sonicating it for 45 to 50 min to improve dispersion. (The average molecular weight of PVA approximately was 1.25 k Dalton and HPMC E-15 LV). A small laboratory set up was made for evaporation by using sodium vapour lamp under constant temperature. In order to obtain bubble free uniform thickness of film. The prepared nanocomposite films were air bubble free and thickness of the film was considered kept for standard size of 0.09-0.21 mm [11,12]. Table-1 shows the composition of 0.5%, 1% and 1.5% weight of PVA:HPMC (75:25) blend-CuO composite.

UV-visible spectroscopy: Synthesized CuO nanoparticles and nanocomposite polymers were subjected to the UV-visible spectral analysis (Beckman-Coulter UV-vis spectrophotometer – DU-730, USA) with wave length (λ) scanned as of 200 to 800 nm in different time intervals [13].

SEM and EDAX analysis: The samples of synthesized nanoparticles were placed in different port on carbon coated plate. Extra powder was removed and gold coated with spatter-

TABLE-1
WEIGHT OF PVA:HPMC-CuO
NANOPARTICLE INCORPORATION

Sample code	Nanocomposite	Weight of CuO nanoparticle (%)
A	Pure PVA	–
B	Pure HPMC	–
C	PVA:HPMC (75:25)	–
D	PVA:HPMC-CuO	0.5
E	PVA:HPMC-CuO	1.0
F	PVA:HPMC-CuO	1.5

coater gold coating instrument to increase the conductivity also give fine picture. Imaging was done to analyze morphological structure and size of synthesized CuO nanoparticles using scanning electron microscope (Hitachi-S-3400N and Japan). This analysis was performed to identify the crystalline nature of nanoparticles and also detect the optical absorption peak from the surface plasma response; the EDAX (Thermo Fisher Scientific, Noran System 7, USA) was done for identifying elemental signals, which were present in the synthesized CuO nanoparticles.

XRD analysis: The crystal structure identification for prepared nanocomposite, CuO nanoparticles and pure PVA and HPMC was done in powder XRD (RIGAKU X-Ray diffractometer of 3 kW with $\text{CuK}\alpha$ source at 2θ angle of 10° - 80°). The CuO fine powder and nanocomposite film were placed in a plate at different time scanning to detect FWHM of XRD peaks at a rate of $3^\circ/\text{min}$. An average size of CuO and nanocomposite were estimated using Debye Scherrer's formula ($n\lambda = 2d \sin \theta$).

Fourier transform-infra red spectroscopy (FTIR): The analysis of functional groups for prepared nanocomposite, CuO nanoparticle, PVA:HPMC blend and pure PVA and HPMC were confirmed by FTIR (PIKE Technologies, Spectrum Two, USA) at 4000-600 cm^{-1} range of wavelength.

Mechanical property: The effect of CuO incorporation on mechanical property of polymer blend was studied using tensile strength of the film, Young's modulus and percentage elongation at break of PVA:HPMC/CuO nanocomposite, PVA:HPMC, pure PVA and pure HPMC, respectively.

RESULTS AND DISCUSSION

UV-visible studies: UV-visible spectroscopic analysis of the CuO was performed in aqueous solvent, dispersed through ultrasonication. The absorption peaks of CuO nanoparticles at 970 nm are visible in the spectra (Fig. 1). The production of CuO nanoparticles is shown by the enhanced absorbance at higher wavelengths. As the weight percent increases, the size of CuO nanoparticles decreases. CuO nanoparticles with a larger band gap have a smaller size. The band gap and type of electronic transition must be investigated in order to understand the optical properties of the synthesized CuO nanoparticles. An electron transfer from the valence band to the conduction band occurs when photon absorption energy of the semiconductor is greater than the semiconductor band gap. The absorberency of the nanomaterials will grow unexpectedly to the wavelength corresponding to the band gap energy.

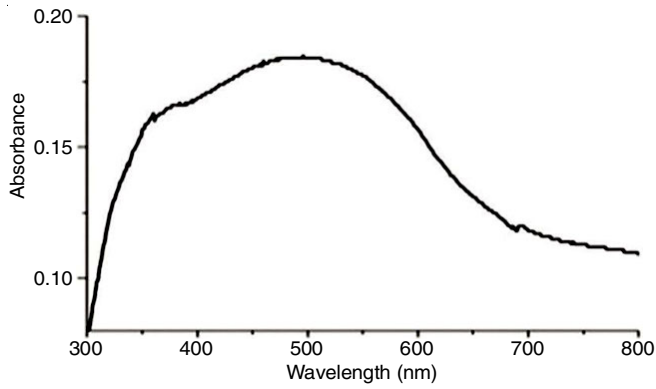


Fig. 1a. Ultraviolet-visible spectrum of CuO nanoparticle

The optical absorption spectra of CuO nanoparticles along with its nanocomposite are shown in Fig. 1b, where the nanocomposite material exhibited two absorption peaks at 250 and 342 nm, which correspond to the he^* transition. The absorbance increases as the wavelength increases, showing the interaction of CuO nanoparticles [13,14].

Energy dispersive X-ray spectroscopy (EDAX) of CuO:

The elemental study of CuO using EDAX investigations demonstrates that the Cu and O phases were present in the sample, thus indicated that the synthesized CuO nanoparticles was pure. Cu and O have theoretical mass percentages of 54.78 and 35.16, respectively (Fig. 2).

SEM studies: As seen in Fig. 3a-b, the synthesized CuO had a feathery appearance. The surface features of CuO nanoparticles were revealed by SEM morphology indicated that the particles assembled together with a size of less than 50 nm. Large elongated feathery with a granular structure showed the evidence of mixed phases which is in unit with the XRD results of the nanoparticles powder (Fig. 3a). These results are in accordance with the values reported in previous literature [15].

XRD analysis: The XRD pattern of CuO nanoparticles and nanocomposite films are shown in Fig. 4. The CuO nanoparticles form a monoclinic single-phase structure with a volume cell of 82.14 Å, the obtained values are $a = 4.683$ Å, $b = 3.473$ Å and $c = 5.122$ Å. At 2θ values of 32.56°, 35.59°, 38.82°, 48.24° and 53.50°, several unique diffraction peaks have been detected. These figures correspond to the JCPDS No. 45-0937

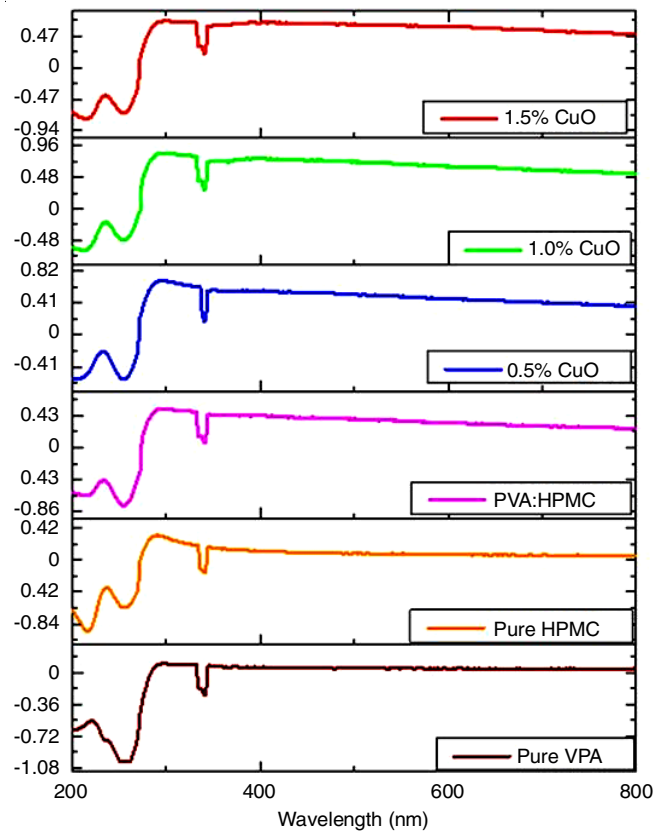


Fig. 1b. UV-vis spectral analysis of polymer nanocomposites

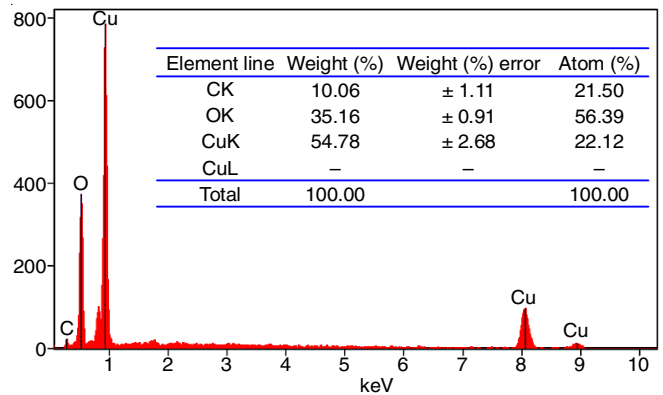


Fig. 2. EDAX spectrum of CuO nanoparticles

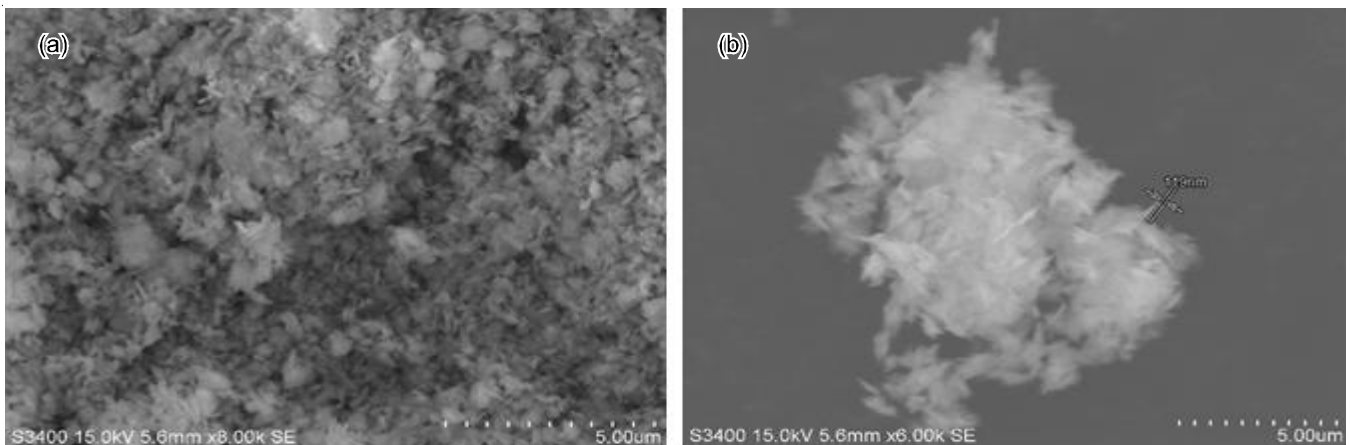


Fig. 3. Scanning electron microscopy image of CuO nanoparticles

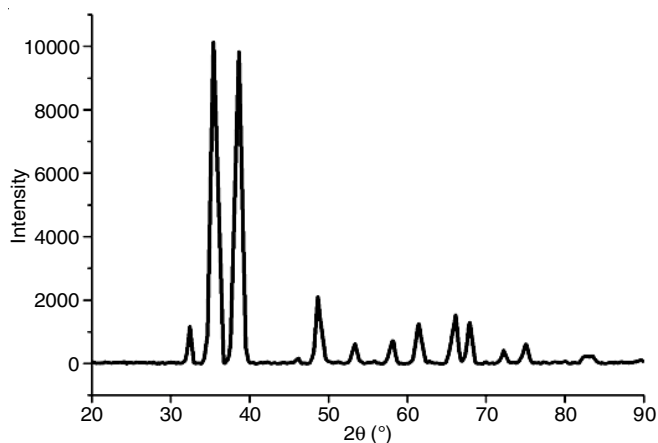


Fig. 4a. X-ray diffraction pattern of pure CuO nanoparticles

[16]. In the XRD pattern, no impurity peaks were found. Using the Scherrer formula, the average size of CuO nanoparticles was found to be 12-14 nm. The well-matched crystalline structure for manufactured nanocomposite is revealed by JCPDS files No. 039-1840, 027-1977, 028-1946 and 032-1501. The average particle size for different nanocomposite was obtained from the main peaks using Debye-Scherrer's formula for peak width broadening as a function of the particle size [16].

$$D = \frac{0.89\lambda}{\beta \cos \theta}$$

The average size of the composite particle measured was range of 7.0 and 9.0 nm, while pure CuO particles had an average size of 13.9 nm. This shows that the CuO nanoparticles in the PVA + HPMC blend were well distributed [17].

The XRD patterns of the fabricated polymer nanocomposite are illustrated in Fig. 4b. The diffraction peaks located at 2θ of 9.8301° (blend A), 20.669° (blend B), 28.086° (blend C) 31.795° (blend D), 28.37° (blend E), 31.651° (blend F), 19.51° (blend G) and 19.51° (blend H). These planes confirmed the orthorhombic structure for the fabricated nanocomposite.

A modest displacement or broadening of the peak at $2\theta = 19.51^\circ$ was noticed in the XRD profiles of the manufactured composites. The intensity of blend-CuO nanocomposite peaks at different weight percentage decreased as the nanofiller content increased. Because of the interactions between the polymer mixture and the CuO nanoparticles. The decreased intramolecular interaction between CuO and the PVA:HPMC blend resulted in the larger nanocomposite, which reduced as the proportion of nanoparticle inclusion increased [18]. In comparison with the result of XRD and FTIR the crystalline nature of the polymer decreased at 1% and 1.5% CuO incorporation to the blend.

FTIR analysis: The IR spectra of pure CuO and PVA + HPMC nanocomposites are shown in Fig. 5a and 5b, respectively. FTIR spectra shows two absorbance bands at 3500 and 670 cm^{-1} (Fig. 5a), which attributed to the stretching of water molecules associated with CuO and the presence of Cu-O bonds, as well as some constitutional water in the CuO structure, respectively. As a result, the FTIR analysis confirmed the formation of CuO.

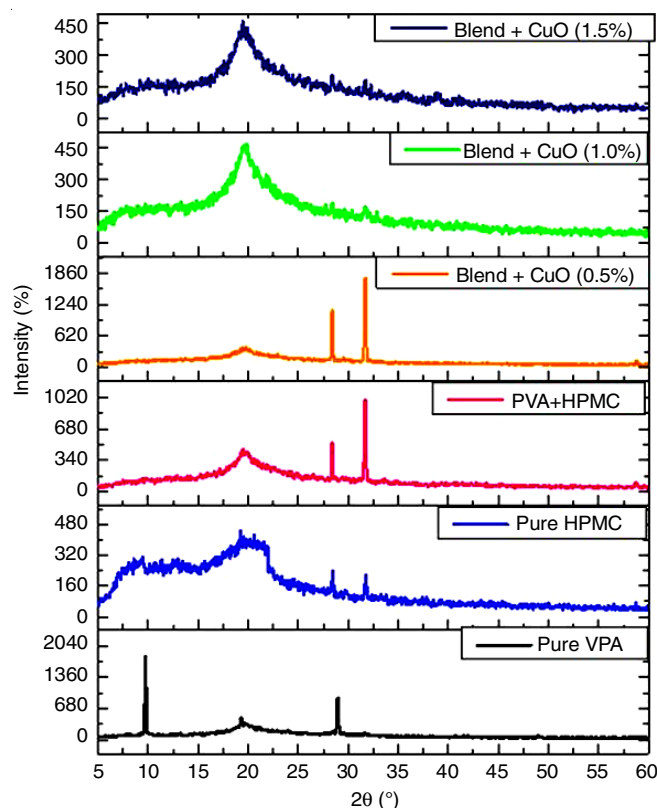


Fig. 4b. X-ray diffraction pattern of prepared nanocomposites with different concentration of CuO nanoparticles

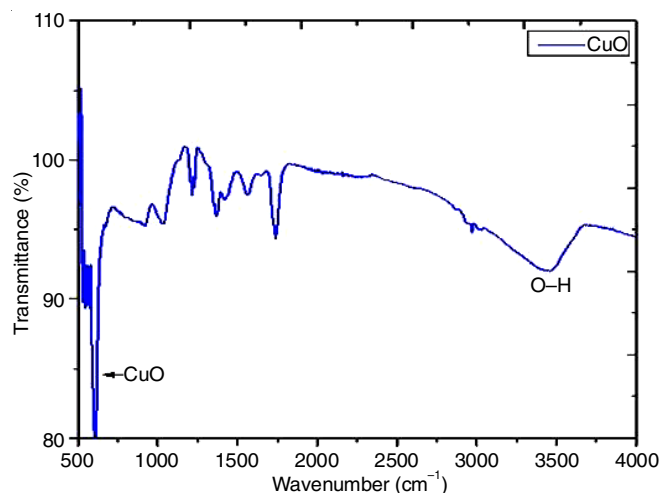


Fig. 5a. FT-IR analysis of CuO nanoparticles

The peaks at $3441\text{--}3439\text{ cm}^{-1}$ are attributable to -OH stretching vibration and intermolecular H-bonding (Fig. 5b) [19]. The peak at 2919 cm^{-1} is attributed to -CH stretching vibration, whereas the band at 1715 cm^{-1} suggests the presence of six-membered cyclic rings stretching vibration. For stretching vibration of -C-O groups, the peaks at 1041 , 1060 and 1022 cm^{-1} were attributed to the blending. For pure PVA, the peaks at 1551 and 1385 cm^{-1} were attributed to the C=N and C=C stretching modes of vibration. The presence of CuO in the nanocomposite causes the peaks in the $510\text{--}480\text{ cm}^{-1}$ range. The IR-spectrum of PVA + HPMC-CuO nanocomposites is nearly equal to that of pure PVA, although all peaks move

TABLE-2
MECHANICAL PROPERTIES OF NANOCOMPOSITE FILM

Sample code	Content	PVA:HPMC-CuO ratio	Tensile strength (MPa)	Elongation (%)	Young's modulus
A	Neat PVA	3%	1.28	99.85	1072.82
B	Neat HPMC	3%	7.04	99.73	1716.05
C	PVA + HPMC	25:75	0.20	22.79	1262.86
D	PVA + HPMC	50:50	0.52	9.84	1746.52
E	PVA + HPMC	75:25	0.71	23.11	2000.90
F	Blend E + CuO	0.5%	0.14	12.89	1423.37
G	Blend E + CuO	1.0%	0.17	19.54	1524.34
H	Blend E + CuO	1.5%	0.24	27.83	1605.25

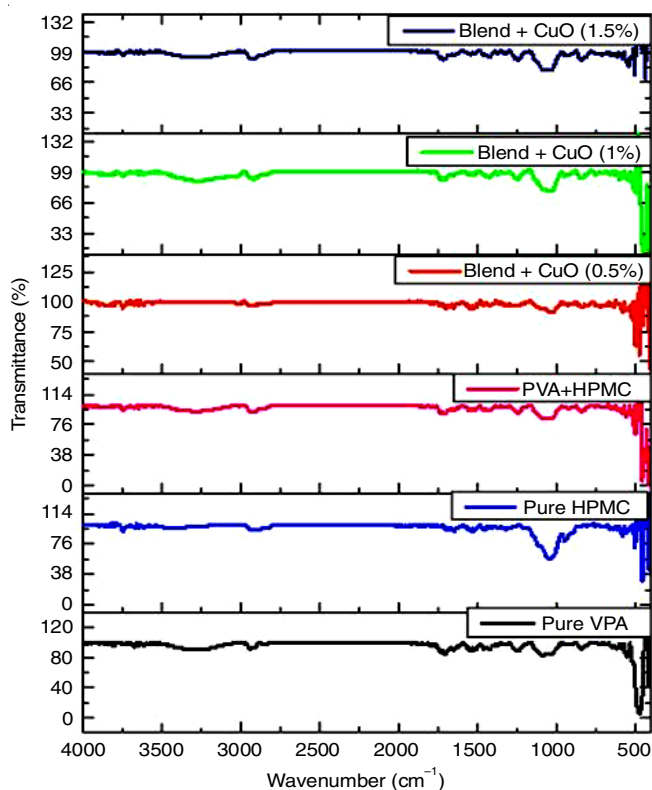


Fig. 5b. FTIR spectra of PVA:HPMC blend with and without CuO nanoparticles

slightly to the red side and the intensity ratio of bands has also altered. These findings suggested that the PVA + HPMC mixture and CuO nanoparticles [20] have intermolecular interactions.

Effect of CuO incorporation on mechanical property of PVA:HPMC blend: All the composite materials were prepared by blending the as prepared PVA and HPMC at different ratio. The tensile strength, % of elongation and Young's modulus of the composite materials with and without CuO nanoparticles were measured (Table-2). The impact of CuO nanoparticles on the mechanical characteristics of PVA+HPMC/CuO nanocomposite films were studied up until the composite was cracked.

The stress-strain curves depicting the tensile strength, Young's modulus and elongation at break (%) of PVA:HPMC/CuO nanocomposites. The tensile strength of the neat PVA and neat HPMC was 1.28 and 7.04 MPa, respectively. The blend of PVA and HPMC showed decreased tensile strength compared to neat PVA and HPMC. Incorporation of CuO nanoparticles to the blend E (75:25 of PVA: HPMC), gradually increased

the tensile strength compared to blend E. Blend E with CuO concentration 0.5, 1 and 1.5% showed the increased tensile strength to 0.14, 0.17 and 0.24, respectively [21]. There will be increased percentage of elongation at break (E) with increased % of the CuO nanoparticles. With the tensile strength, % of elongation and Young's modulus also increased concentration dependently in the CuO incorporated blend [22].

The increase in the tensile strength and % of elongation of the PVA:HPMC blend was due to the incorporation of CuO nanoparticles might be due to the formation of nanocomposites [23]. The increment in mechanical strength is rational since CuO nanoparticles can act as a plasticizer. It is contributing to the load sharing during the test. Moreover, it can also increase the thermal conductivity of the matrix. Although with combining the PVA:HPMC for blend preparation, there was a drastic decrease in the tensile and % of elongation's loss was recovered by the incorporation of the CuO nanoparticles into the blend matrix. This indicates, CuO incorporation increases the mechanical strength of the matrix by forming a composite [24].

Conclusion

In the present study, the nanocomposite of different ratios of PVA:HPMC with and without CuO nanoparticles were prepared and the effect of CuO nanoparticle incorporation on structural and mechanical properties was investigated. The tensile strength and % of elongation were decreased after the preparation of the blend when compared to pure polymers. However, incorporation of CuO into the blend increased the tensile strength as well as percentage of elongation in a concentration-dependent manner. The formation of CuO nanoparticles was confirmed by XRD spectra and CuO included nanocomposite films revealed significant changes in X-ray reflection intensity. Due to the random dispersion of the CuO nanoparticles in the polymer blend, this is responsible for the structural changes of the polymer. The formation of a network between oxygen groups and interaction between the polymer matrix and CuO nanoparticles were confirmed by FTIR. The present work concludes that CuO incorporated nanocomposites showed increased mechanical properties of the polymer. The water phase facilitated its homogeneous distribution in the PVA:HPMC phase and significantly influenced the mechanical properties of the nanocomposite.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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