

# Polyvinyl alcohol/CuO nanocomposite hydrogels: facile synthesis and long-term stability

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## Abstract

*Within this study, Polyvinyl alcohol/CuO nanocomposite hydrogels were synthesized through dispersing CuO nanoparticles in a PVA solution, using the freeze-thawing procedure in order for physically crosslinking. The average particle size of CuO nanoparticles which was added to the hydrogel was determined as 3.51 nm according to the XRD analysis after the ball milling process. The presence of CuO nanoparticles in nanocomposite hydrogels was determined by UV-vis spectroscopy, FESEM, EDS, and FTIR analysis. Also, the rheological properties of neat hydrogel and PVA/CuO nanocomposite hydrogels were examined. The addition of CuO nanoparticles to the polymer structure develops rheological features of PVA hydrogels. The Effect of CuO content of nanocomposite hydrogels on the swelling behavior and long term stability was investigated. These nanocomposite hydrogels demonstrated unique properties for biomedical applications due to their high swellability at pH 2.1 as the pH values of the stomach and long term stability. According to these results, the addition of CuO to the hydrogel structure improved the swelling characteristics of neat PVA hydrogel.*

**Keywords:** Long-term stability, swelling behavior, PVA, CuO nanoparticles, ball milled.

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## Polivinil alkol/CuO nanokompozit hidrojel: kolay sentezi ve uzun-süreliliği

### Özet

*Bu çalışmada, polivinil alkol/CuO nanokompozit hidrojel, fiziksel olarak çapraz bağlanma için donma-çözme prosedürü kullanılarak PVA çözeltisi içinde CuO nanopartiküllerin dağıtılması yoluyla sentezlenmiştir. Hidrojele eklenen CuO nanopartiküllerinin ortalama partikül boyutu bilyalı öğütme işleminden sonra yapılan XRD analiz sonuçlarına göre 3,51 nm olarak belirlenmiştir. Nanokompozit hidrojelde CuO nanopartiküllerin varlığı UV-vis spektroskopisi, FESEM, EDS ve FTIR analizi ile belirlenmiştir. Ayrıca saf hidrojel ve PVA/CuO nanokompozit hidrojelinin reolojik özellikleri incelenmiştir. Polimer yapısına CuO nanopartiküllerinin ilave edilmesi, PVA hidrojelinin reolojik özelliklerini geliştirmiştir. Nanokompozit hidrojelinin CuO içeriğinin, nanokompozitlerin şişme davranışı ve uzun süre kararlılığı üzerine etkisi araştırıldı. Bu nanokompozit hidrojel, pH 2.1' deki yüksek şişebilirliklerinden dolayı, mide pH'ları ve uzun süreli kararlılıkları nedeniyle biyomedikal uygulamalar için benzersiz özellikler göstermiştir. Bu sonuçlara göre, CuO'nun hidrojel yapısına eklenmesi, saf PVA hidrojelinin şişme özelliklerini geliştirmiştir.*

**Anahtar kelimeler:** Uzun süreli kararlılık, şişme davranışı, PVA, CuO nanopartiküller, bilyalı öğütme.

### 1. Introduction

Hydrogels are physically or chemically cross-linked three-dimensional hydrophilic, linear, or branched polymers that are insoluble in aqueous solutions, which can absorb and retain liquid in large quantities. Hydrogels have excellent hydrophilic properties with a high swelling rate and biocompatibility, the ability to respond to external stimuli such as temperature, pH, salt, light, electric field, and absorb different contaminants such as dyes, metal ions, and proteins. Thanks to these excellent properties, they are widely used in biomedical fields such as hydrogels, drug, and cell distribution system, enzyme immobilization, antibacterial, tissue engineering, and biosensors. Hydrogels have also found widespread use as sorbents for the removal of various contaminants from agriculture and from aqueous solutions [1-3]. Among the polymers, Poly (vinyl alcohol) (PVA) is an easily processable inert polymer, which is a kind of hydrophilic semi-crystalline widely used because of the toxicity, biocompatibility, excellent chemical resistance and mechanical strength in biomedical applications [4, 5].

Recently, various fillers have been incorporated into the hydrogels to improve the properties of hydrogels for use in various applications [3]. In the last few years, inorganic nanoparticles (NPs) among these reinforcing materials have received intense interest in polymeric nanocomposites due to their high homogeneity, flexible machinability, adjustable physical properties, and unique properties. Among these materials, metal

nanoparticles and oxides with naturally antimicrobial and anticancer activity have tremendous application in biomedical and surgical applications such as wound healing ointments, dental work, food processing and packaging, water treatment, synthetic textiles. In addition, composites prepared using metal nanoparticles and polymers are also requested, due to improved antimicrobial activity [6, 7]. As a p-type semiconductor with a narrow band gap (1.2 eV), among the metal nanoparticles, copper oxide (CuO) has unique properties such as significant antibacterial properties, easy synthesis, photoconductivity, high thermal and electrical conductivity, high mechanical strength and high-temperature resistance features as well as being easily removed from the human body. Due to these unique properties, copper oxide nanostructures are of considerable interest in many important scientific fields such as gas sensors, magnetic phase transitions, catalysts, superconductors, pollution control, and nano-toxicology, cellular imaging, photothermal therapy and biocides [2, 6, 8]. For these reasons, copper oxide is widely used in the preparation of a wide variety of organic-inorganic nanostructured composites [6].

Recently, copper oxide nanocomposite hydrogels with various polymers such as carboxymethylcellulose [2] chitosan [9] poly (N-iso propyl acrylamide-allyl acetic acid) copolymer microgel [6] have been studied. However, nanocomposites of CuO with polyvinyl alcohol have rarely been studied. In their study, nanocomposites of CuO with chitosan and poly (vinyl alcohol) were prepared and investigated to remove Pb (II) [4]. Nevertheless, there were no studies investigating the long-term stability of CuO and polyvinyl alcohol hydrogel nanocomposites. It has also been reported in the literature, that further work is needed in many issues such as long term stability and so on [10]. For these reasons, in this work, Polyvinyl alcohol/CuO Nanocomposite Hydrogels were synthesized using mechanically treated CuO nanomaterials and polyvinyl alcohol. Also, the swelling properties and long term stability of these samples at different pHs were examined.

## **2. Materials and method**

### **2.1. Materials**

Polyvinyl alcohol (PVA, Mw:85,000–124,000) with a hydrolysis degree higher than 99% and copper chloride (CuCl<sub>2</sub>) were purchased from Sigma Aldrich and used without purification.

### **2.2. Preparation of m-CuO nanoparticles**

CuO nanoparticles were prepared from CuCl<sub>2</sub>, using the identical procedure defined in our previous publication. The size and morphology of CuO nanoparticles were determined as 5.18 nm flower-like nanostructure in our previous study [11]. Finally, the CuO sample was subjected to freeze-drying processes for 14 h at -45°C. Afterward the prepared CuO nanoparticles were ball milled in a Mixer Mill MM 400 (Retsch, Germany) at 30 Hz-speed for 60 min (Fig. 1). The sample was labeled m-CuO.

### **2.3. Preparation of Polyvinyl alcohol/CuO nanocomposite hydrogels**

For preparing PVA (5 wt%) solution, 1g of PVA was dissolved in 20 mL ultra-distilled water and stirred for 4h at 90°C. After the obtained solution was cooled to room temperature, certain amounts of m-CuO were dispersed in the obtained solution with a

magnetic stirrer for 16h. At the end of this period, the PVA/CuO solutions were sonicated for 1h at 0°C (sweep function, 100 W, 37 kHz), and the PVA/CuO solutions were poured into a petri dish and kept at -24°C for 16h. In order to carry out the freezing-thawing (F/T) process the samples were kept at room temperature for 8h, this cycle was repeated five times. After F/T process, all products were freeze-dried during 14 h at 4°C and stored for characterization (Fig. 1). The polyvinyl alcohol/CuO nanocomposites (PVA/CuO) were denoted being PVA (0 g of m-CuO), PVA/CuO-0.05 (0.05 g of m-CuO) and PVA/CuO-0.15 (0.15 g of m-CuO).

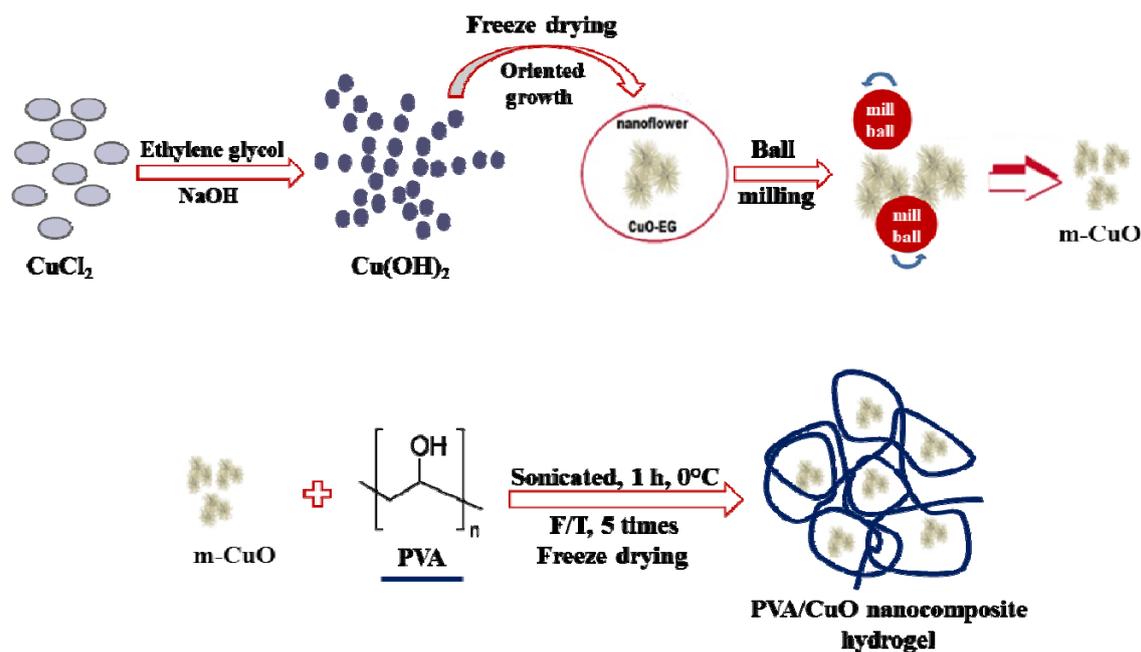


Figure 1. Schematic illustration of the synthesis of m-CuO nanoparticles and PVA/CuO nanocomposite hydrogel.

#### 2.4. Characterization

The internal morphology and energy dispersive X-ray spectrum analysis (EDS) of m-CuO and PVA/CuO nanocomposite hydrogels was observed by field-emission-scanning electron microscopy (FESEM: FEI Quanta 450 FEG, 20-30 kV). The samples were gold-plated with a thin layer using five mA sputter current for the 60's before FESEM measurements. The Fourier transform infrared (FTIR) spectra of samples was recorded on a Thermo Scientific Nicolet IS10 model FTIR spectrometer using an ATR equipment (Attenuated Total Reflectance) over a range from 450 to 4000  $\text{cm}^{-1}$ . These analyzes were conducted at Hitit University Scientific Technical Application and Research Center (HÜBTÜAM).

The rheological characterization, to observe the variation of storage modulus ( $G'$ ), loss modulus ( $G''$ ) and viscosity ( $\eta$ ) of PVA based nanocomposite hydrogels were performed by a Malvern Gemini II rheometer. Rheometry experiments were carried out on the nanocomposite hydrogels after addition of the m-CuO nanoparticles to aqueous PVA solutions before F/T process. The viscosity tests were carried out at a constant shear rate of

100 s<sup>-1</sup>, at 20 °C by using cone-plate (CP 4°/40 mm measuring system). The sweep oscillatory shear measurements were performed using a parallel plate (PP 20 measuring system) at 25°C in a frequency ranging from 10 Hz to 0.1 Hz with a shear stress of 2 Pa and a gap of 1 mm to measure storage (G') and loss modulus (G''). These analyzes were conducted at Hitit University Scientific Technical Application and Research Center (HÜBTÜAM).

The optical absorbance of PVA based nanocomposite hydrogels was recorded on Genesys 10S-Thermo USA using UV-visible spectrophotometer in the range 200-800 nm. Samples for the optical absorption study were prepared in the same way as in the rheometry experiment.

XRD analysis of the synthesized m-CuO nanoparticles was performed at a scanning speed of 2°/min using a Rigaku DMAX IIC model X-ray diffractometer (35 kW, 15 mA, CuK $\alpha$ , 1.541871 Å). XRD analysis was used to calculate the mean crystallite grain size of m-CuO nanoparticles which were used as ready in the study and determined as 5.18 nm particle size by SEM analysis in our previous study [11]. The mean m-CuO crystallite size was calculated from the Scherrer equation (Eq. (1)) using full widths ( $\beta$ ) of the peak ( $2\theta$ ) half height of the reflection planes (-111), (-202), (020), (202), (-311), (220) and (004) and the 0.9 K factor:

$$d_{XRD} = \frac{0,9\lambda}{\beta \cos \theta} \quad (1)$$

where  $\lambda$ : X-ray Wavelength (1.541871 Å),  $\beta$ : peak half height full widths,  $\theta$ : Bragg angle [12].

### **2.5. Swelling ability and long-term stability**

The swelling ability (water uptake) of the dried neat hydrogel and nanocomposite hydrogel were determined by immersing samples (~0.1 g) in 25 mL different buffer solutions (pH = 2.1, 3, 5.5, 7.4 and 10) at room temperature until equilibrium swelling was reached (~7 days). The excess water on the surface of swollen samples was blotted and then re-weighed. The percentage of swelling degree (SD %) was calculated using the equation below:

$$\%SD = \frac{M_t - M_0}{M_0} * 100 \quad (2)$$

where  $M_0$  is the initial weight of samples in the dry state (g) before swelling and  $M_t$  is the swollen weight at various time points of samples (g) [13].

The long-term stability of samples was also studied in the same buffer solution by allowing 70 days of swelling at room temperature [5]. After the swelling ability study, a measurement was performed by weighing the samples for every week throughout the study. At the end of immersion for 70 days, the swollen samples were dried by lyophilization, and the final weight was denoted as  $M_f$  (g). After reaching the equilibrium, any weight loss

indicates that the polymer chain and nanoparticles have moved away from the network structure [5, 13, 14]. Hereby, the percentage of nanocomposites hydrogel mass losses can be defined as shown in Eq. (3):

$$\% \text{ mass loss} = \frac{M_0 - M_f}{M_0} * 100 \quad (3)$$

where  $M_0$  is the initial weight of samples in the dry state (g).

### 3. Results and discussion

In our work, PVA/CuO nanocomposite hydrogels were prepared by F/T process to obtain high long term stability. PVA and CuO were used due to their distinctive features such as biodegradability, hydrophilicity and large specific surface area, high reactivity, respectively.

#### 3.1. Characterization

##### 3.1.1. XRD analysis of m-CuO nanoparticles

The x-ray diffraction pattern of m-CuO is presented in Fig. 2. The diffraction peaks at around  $32.5^\circ$ ,  $35.5^\circ$ ,  $38.7^\circ$ ,  $48.7^\circ$ ,  $53.4^\circ$ ,  $58.3^\circ$ ,  $61.5^\circ$ ,  $66.2^\circ$ ,  $72.4^\circ$  and  $75.2^\circ$  are associated with (110), (-111), (-202), (020), (202), (-113), (-311), (220), (311) and (004) reflection planes of CuO according to JCPDS 97-009-2367, respectively. The XRD spectrum of m-CuO shows that the synthesized m-CuO is in a monoclinic phase without observable impurity peaks [11,15]. In addition, the mean particle size of CuO nanoparticles was determined as 3.51 nm according to XRD analysis results (Table 1).

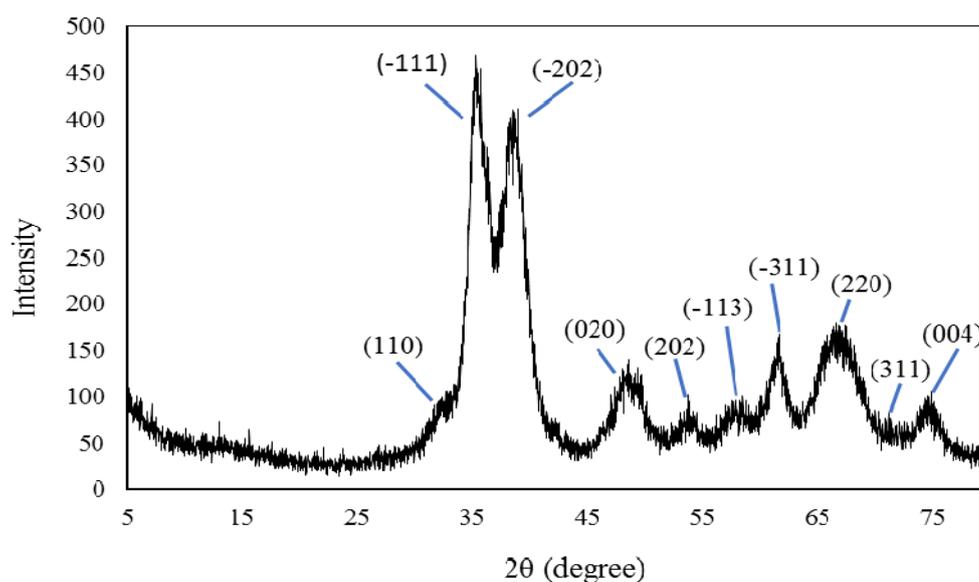


Figure 2. XRD pattern of m-CuO nanoparticles

Table 1. Parameters obtained from XRD analysis results of m-CuO nanoparticles

(hkl) reflection planes	2 $\theta$ (°)	FWHM (°)	Particle size (nm)
(-111)	35.5	2.52	3.31
(-202)	38.7	1.88	4.48
(020)	48.7	3.86	2.26
(202)	53.4	1.84	4.84
(-311)	61.5	2.14	4.32
(220)	66.2	4.78	1.99
(004)	75.2	2.98	3.37
Average particle size (nm):			3.51

### 3.1.2. Rheological characterization of the hydrogel solutions

Rheometry was used to observe the storage modulus ( $G'$ , elastic property), loss modulus ( $G''$ , viscous) and complex viscosity ( $\eta^*$ , the overall change in the viscoelastic property) of nanocomposite hydrogel [16, 17].

For the rheological characterization, the viscosity measurements of the solutions were primarily performed, and the results are given in Table 2. The neat PVA hydrogel solution has demonstrated lower viscosity as compared to PVA/CuO nanocomposite hydrogel solutions, that was possible because of the interactions between the CuO nanoparticles and polymer chains [18].

Table 2. The solution compositions and viscosity of neat PVA hydrogel solution and PVA/CuO nanocomposite hydrogel solutions

Solutions	% PVA (w/v)	CuO nanoparticles (g)	Viscosity (Pa.s)
Neat PVA	5	0	0.0535
PVA/CuO-0.05	5	0.05	0.0610
PVA/CuO-0.15	5	0.15	0.0666

For representing the elastic and viscous behavior of nanocomposite hydrogels prepared using different CuO contents ( 0.05 and 0.15 g),  $G'$  and  $G''$  plots are shown in Fig. 3. The  $G'$  of all samples were much larger than their  $G''$  at all frequencies, which is a typical property of a “strong” hydrogel. This means that PVA/CuO nanocomposite hydrogels have more strength [19]. As a result,  $G'$  considerably increased with the increase of CuO nanoparticles content. Also,  $G'$  of PVA/CuO-0.15 nanocomposite hydrogel solution indicated just about no dependence on frequency and showed the highest  $G'$ . This indicates that this nanocomposite hydrogel has good stability [20].

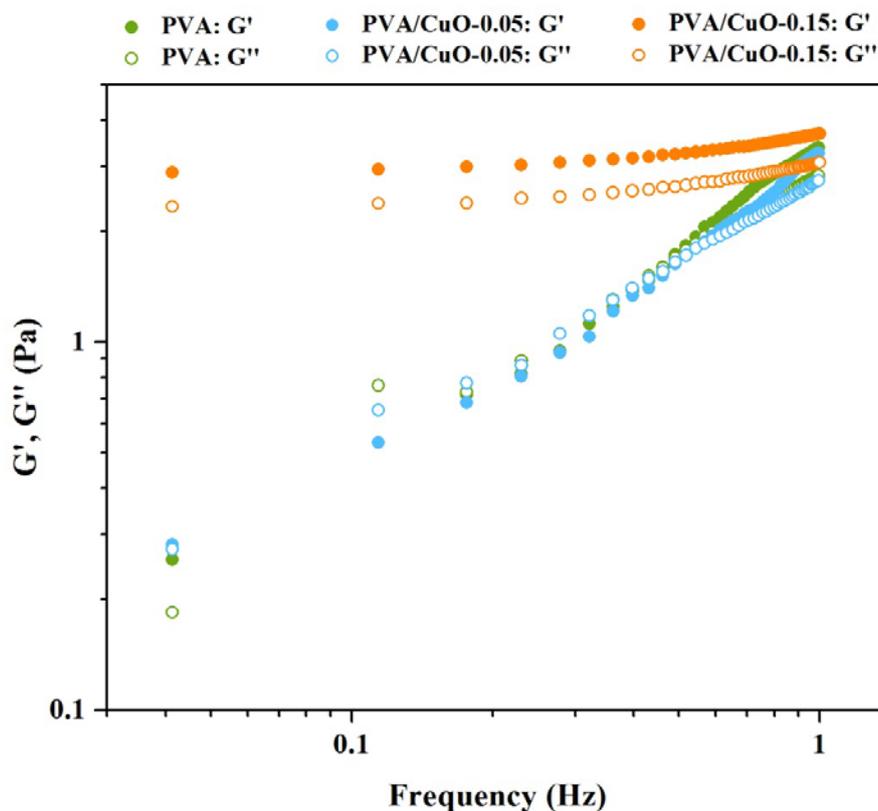


Figure 3. Frequency-dependent of rheometry studies for neat PVA hydrogel solution and PVA/CuO nanocomposite hydrogel solutions

### 3.1.3. UV-Visible Spectroscopy

The UV-visible absorption spectrum of neat PVA and PVA/CuO nanocomposite hydrogel solutions shows successful interaction of PVA and CuO nanoparticles as can be seen from Fig. 4. A broad absorption peak at 275 nm is for the PVA solution whereas PVA/CuO-0.05 and PVA/CuO-0.15 nanocomposite hydrogel solutions exhibit broad absorption peaks at 282 nm and 300 nm because of the intrinsic transition of CuO, respectively [21, 22]. The spectrum of nanocomposite hydrogel solution also demonstrates that the absorption peak shifted toward a longer wavelength (300 nm), and the intensity of this peak increased with the increasing loading content of CuO nanoparticles in a polymer solution that may be based on the homogeneous dispersion of the nanoparticles in PVA matrix [23]. According to the UV-visible absorption results, CuO nanoparticles gets embedded in the PVA matrix and interacts mightily with hydroxyl groups of PVA by way of hydrogen bonding [24].

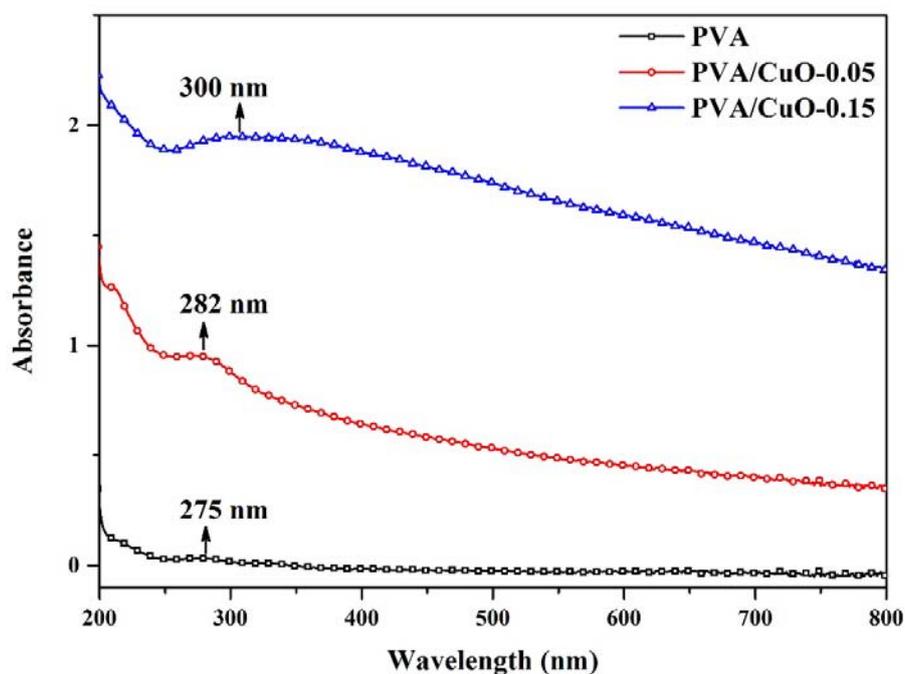


Figure 4. UV-visible Spectra of neat PVA hydrogel solution and PVA/CuO nanocomposite hydrogel solutions

#### 3.1.4. FTIR

The FTIR spectra of m-CuO, neat PVA and nanocomposite hydrogels with different content of CuO is shown in Fig. 5. In all of the FTIR spectrums of nanocomposite hydrogels, the O-H stretching band in the polymer which is the characteristic peak of alcohols is observed near  $3274\text{ cm}^{-1}$ . The characteristic bands at  $2940\text{ cm}^{-1}$  and  $2904\text{ cm}^{-1}$  is due to the C-H stretching vibration of  $-\text{CH}$  and  $-\text{CH}_2$  and C-O stretching of PVA, respectively. The peaks at  $1422\text{ cm}^{-1}$ ,  $1329\text{ cm}^{-1}$ ,  $1093\text{ cm}^{-1}$ ,  $916\text{ cm}^{-1}$ , and  $850\text{ cm}^{-1}$  are attributed to a  $\text{CH}_2$  scissoring mode, the  $\text{CH}_2$  deformation, the C-O stretching vibrations, C-C stretching vibrations and the  $\text{CH}_2$  rocking mode, respectively. The peak at  $1658\text{ cm}^{-1}$  corresponds to the O-H bending of the  $-\text{OH}$  groups in PVA, while the peaks at  $1235\text{ cm}^{-1}$  and  $1143\text{ cm}^{-1}$  are attributed to the C-O-C vibration in the vinyl acetate group and the C-O stretching vibration in crystalline phase of PVA, respectively [25, 26]. In the FTIR spectra of m-CuO, the peaks observed near  $538$  and  $587\text{ cm}^{-1}$  are observed for CuO nanocrystals which are assigned to the  $n(\text{Cu-O})$  stretching vibration of CuO [4]. The presence of the peaks corresponding to CuO nanoparticles and PVA in the spectrums of nanocomposite hydrogels can confirm the existence of an interaction between CuO nanoparticles and polymers. Also, their stabilization is the realization of interplay such as chelation between some hydroxyl ions of hydrogel networks and CuO nanoparticles [27].

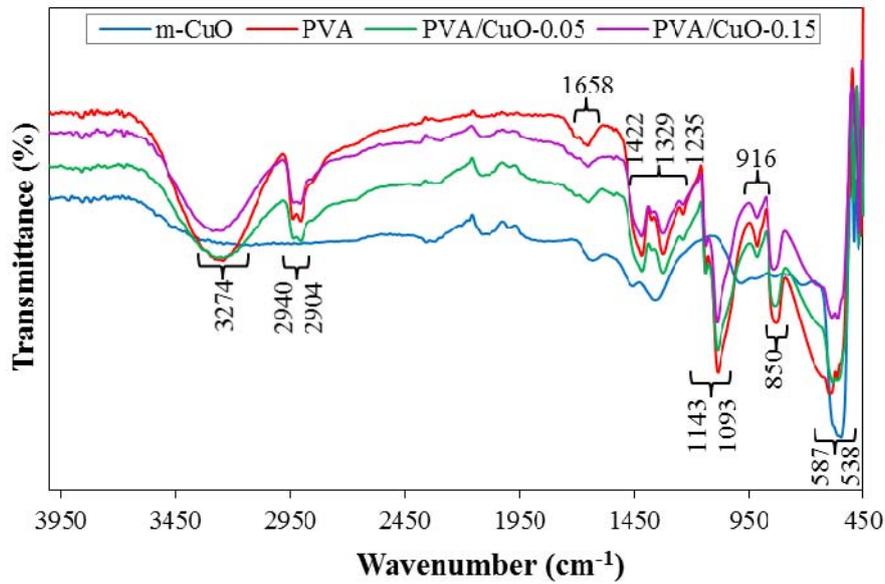


Figure 5. FTIR spectra of m-CuO, neat PVA and PVA/CuO nanocomposite hydrogels

### 3.1.5. Morphology studies

The surface morphologies of the nanocomposite hydrogels were prepared using different CuO contents ( 0.05 and 0.15 g) are shown in Fig. 6. Based on the inset FESEM image of CuO placed inside Fig. 6a, non-uniform CuO nanoparticles shows flower-like nanostructure. As can be seen from the FESEM images, the surface microstructure of the hydrogels was influenced by the addition of semiconductor material. Fig. 6c and 6d show that the hydrogel nets are not as pronounced when the CuO is added to the structure, while a porous honeycomb-like structure for neat PVA is shown in Fig. 6b. This may be due to the ability of CuO nanoparticles to function as cross-linkers [1, 9].

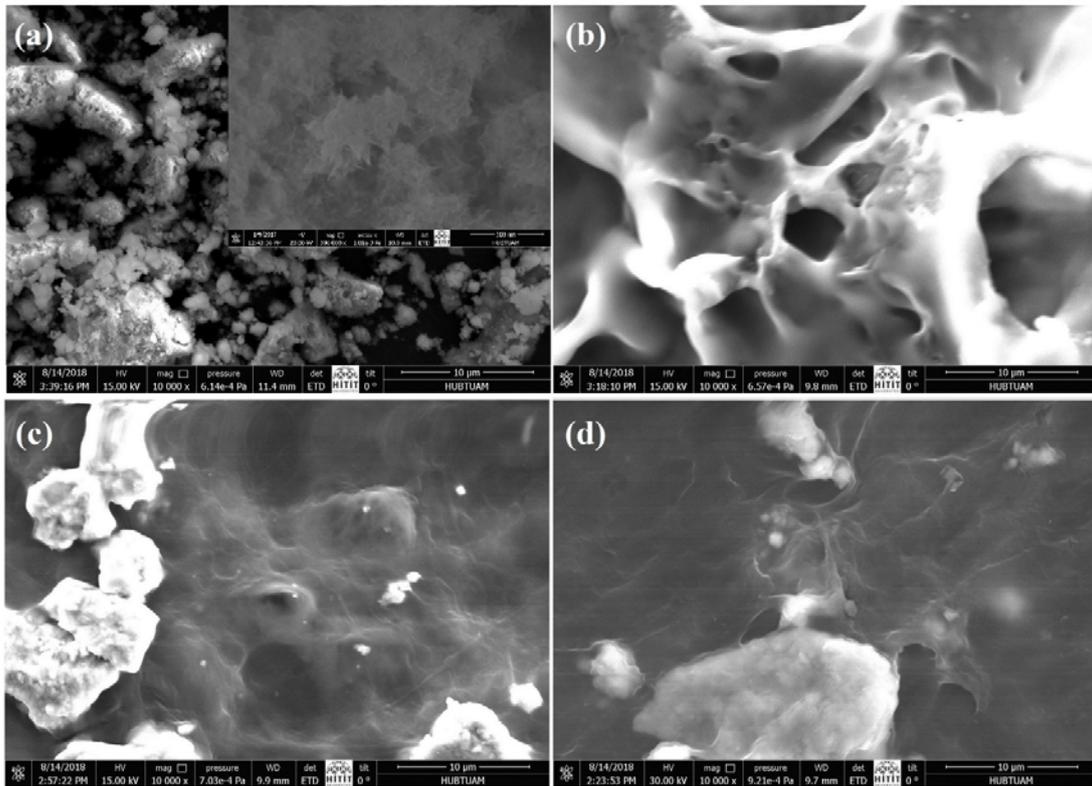


Figure 6. FESEM images of (a) m-CuO (a magnification of 10000 $\times$  and inset: a magnification of 300000 $\times$ ) (b) neat PVA hydrogels (a magnification of 10000 $\times$ ) (c) PVA/CuO-0.05 nanocomposite hydrogel (a magnification of 10000 $\times$ ) and (d) PVA/CuO-0.15 nanocomposite hydrogels (a magnification of 10000 $\times$ )

Fig. 7 shows the EDS analysis of all prepared samples. The EDS spectrums demonstrate that elemental Cu is found in the nanocomposite hydrogels, which represents that the CuO nanoparticles were accomplishedly loaded into the hydrogel nets.

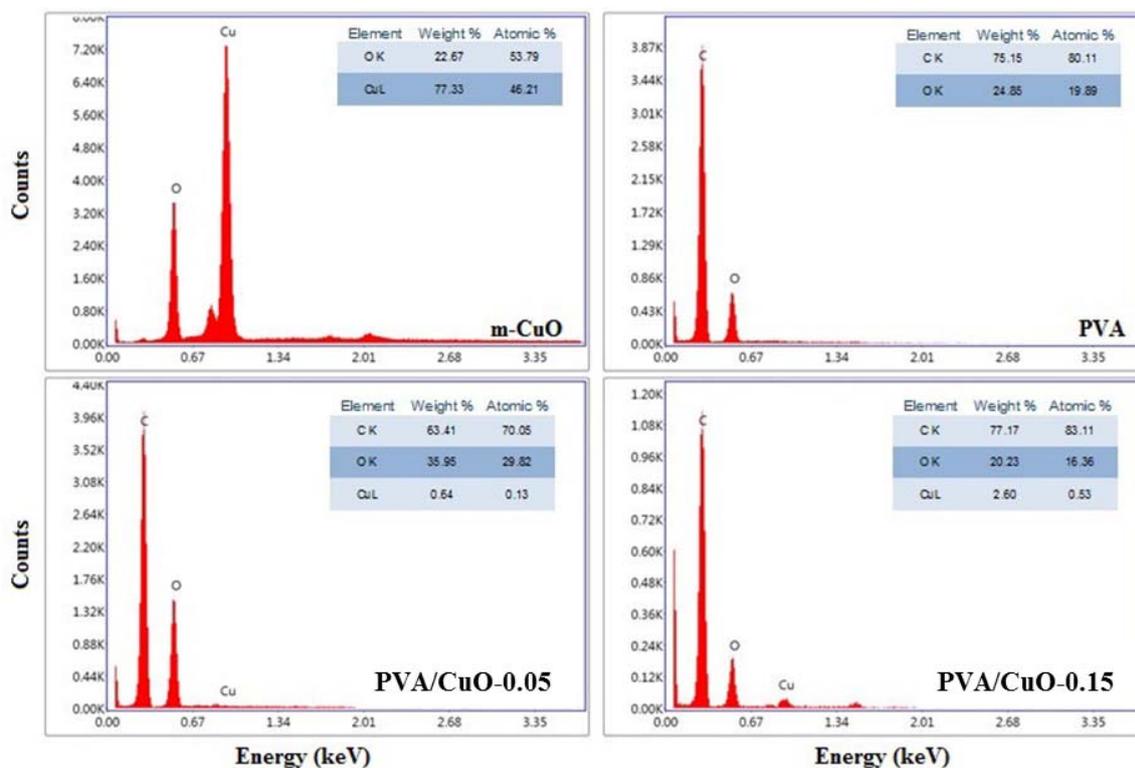


Figure 7. EDS spectrums of m-CuO, neat PVA and PVA/CuO nanocomposite hydrogels with elemental composition

### 3.2. The swelling ability of the hydrogels

The Swelling ability is prominent to designate the end-use applications. Because it is associated with increased swelling properties of improved drug delivery [5] and the pH of each region in the body is different. For instance, the pH values of stomach, blood, and dermis are 2.1, 5.5 and 7.4 pHs, respectively. For this purpose, the swelling behavior of the nanocomposite hydrogels prepared with two different mass ratios of m-CuO nanoparticles were examined at different pH values of 2.1, 3, 5.5, 7.4 and 10 so as to examine the pH sensitivity in Fig. 8, 9, 10, 11 and 12, respectively. The swelling degree of all hydrogels is rapidly increased within four hours and reached equilibrium in about seven days except for the PVA/CuO-0.15 nanocomposite hydrogel at pH 5.5. As shown in Fig. 10, the PVA/CuO-0.15 nanocomposite hydrogel did not reach equilibrium at pH 5.5 within seven days. Based on this, we can say that the PVA/CuO-0.15 nanocomposite hydrogel will give a higher swelling degree at pH 5.5 than the other samples, given that more time is given for the swelling grade. As illustrated in Fig. 11 and 12, the swelling degrees of nanocomposite hydrogels decreased with increasing CuO addition. This decline may be attributed to chelating of some of the hydroxyl groups of the hydrogel networks with nanoparticles, which lead to the knot tying function of CuO or more cross-linking points [1, 9].

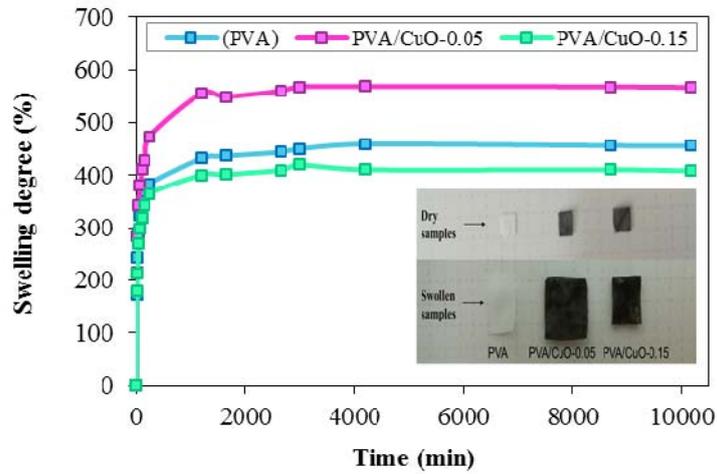


Figure 8. Swelling degree of neat PVA and PVA/CuO nanocomposite hydrogels in pH 2.1 (Inset: photographs of dry and swollen samples in pH 2.1)

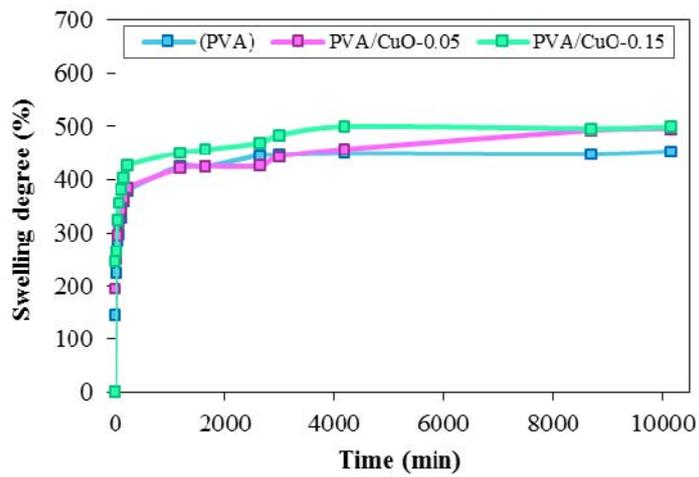


Figure 9. Swelling degree of neat PVA and PVA/CuO nanocomposite hydrogels in pH 3

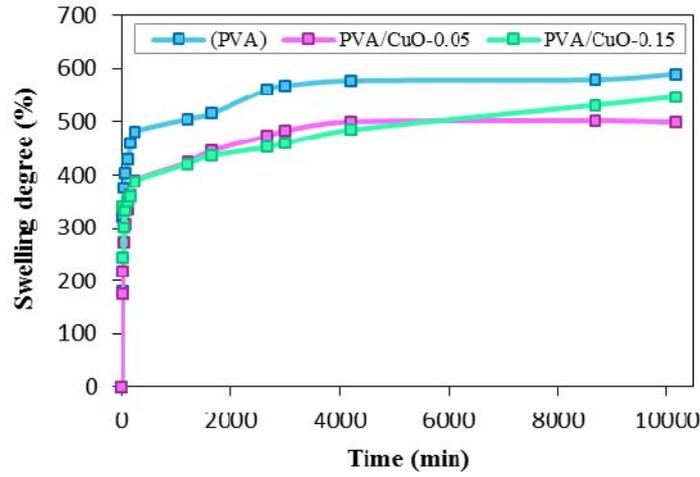


Figure 10. Swelling degree of neat PVA and PVA/CuO nanocomposite hydrogels in pH 5.5

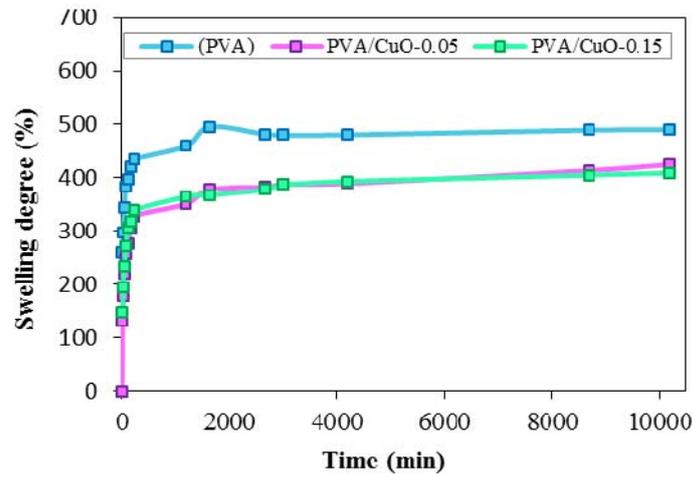


Figure 11. Swelling degree of neat PVA and PVA/CuO nanocomposite hydrogels in pH 7.4

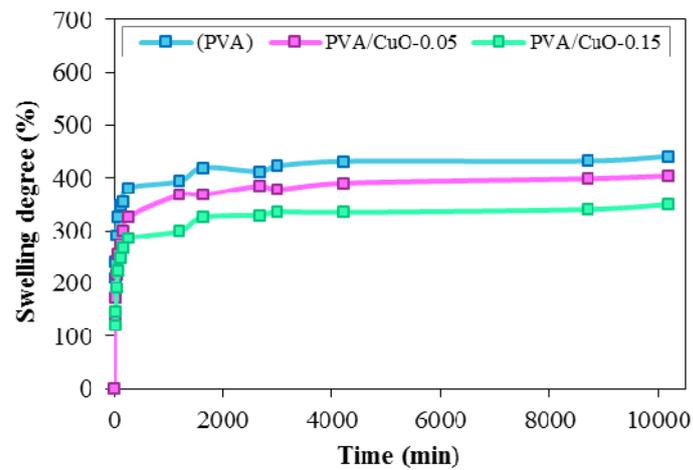


Figure 12. Swelling degree of neat PVA and PVA/CuO nanocomposite hydrogels in pH 10

Fig. 13 clearly shows that the swelling degree of nanocomposite hydrogels increased with the presence of CuO nanomaterial content in the hydrogel at low pHs up to 3. As seen in the photos of swollen and dry samples shown in Fig. 8, PVA/CuO-0.05 revealed a higher swelling degree, compared to the neat PVA and PVA/CuO-0.15 at pH value of 2.1 that is an appropriate value for stomach pH. This indicates that the beneficial effect of the addition of CuO on swellability is only at a low pH, and there is no general tendency. We can explain that the swelling mechanism at low pH includes the protonation of PVA hydroxyl groups leading to chain repulsion which result in diffusion of protons and counter ions together with water in the hydrogel [9, 28]. However, the addition of CuO nanomaterial reduced the swelling degree at higher pH values ( $\text{pH} > 3$ ) as seen in Fig. 10, 11 and 12. With higher CuO content, it can be assumed that the interaction between nanoparticles and polymeric chains leads to more cross-linking points and low free space to enlarge inside the nanocomposites, so swelling capacity is reduced [1]. The highest swelling degree was obtained with PVA/CuO-0.05 nanocomposite hydrogel containing 0.05 g CuO and neat PVA after seven days. The swelling degree of PVA/CuO-0.05 nanocomposite hydrogel and neat PVA reached a maximum value of around 570% at pH 2.1 and 590% at pH 5.5, respectively.

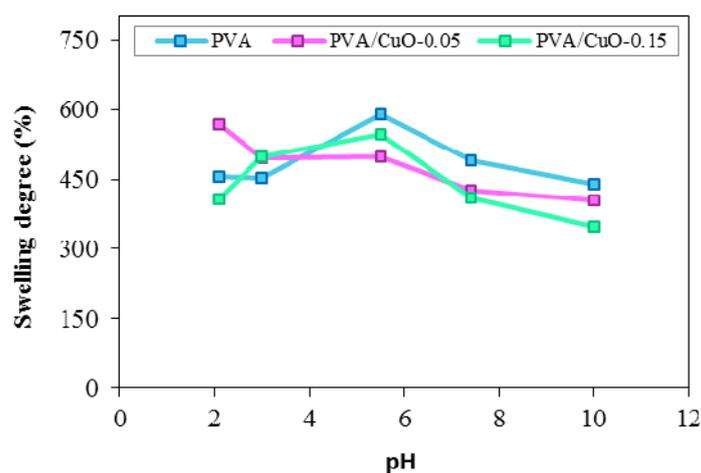


Figure 13. The effect of pH on the swelling degree of neat PVA and PVA/CuO nanocomposite hydrogels

### 3.3. Long-term stability of the hydrogels

Table 3 shows the percentage of the polymer mass losses for neat PVA and PVA/CuO nanocomposite hydrogels. Long-term stability of neat PVA was also studied to compare with the stability of the nanocomposite hydrogels. In this case, the hydrogel samples were immersed in buffer solutions at different pHs and room temperature for 70 days. It was clearly seen that the less CuO nanoparticles addition (0.05 g) determined the most stable nanocomposites hydrogels for all pHs. As a result, the polymer mass loss is reduced to less than about 5% by decreasing the CuO nanoparticle content in hydrogel from 0.15 to 0.05.

Table 3. Long-term stability of PVA and PVA/CuO nanocomposite hydrogels at different pHs

pHs	Initial dry weight (g)	Highest swollen weight (g)	Weight afterwards 70 days (g)	Final dry weight after 70 days (g)	The mass Loss (%)
neat PVA					
2.1	0.109	0.604	0.544	0.099	9.12
3	0.123	0.681	0.639	0.116	6.05
5.5	0.116	0.823	0.741	0.105	9.48
7.4	0.115	0.678	0.613	0.104	9.21
10	0.118	0.647	0.596	0.110	6.98
PVA/CuO-0.05					
2.1	0.103	0.688	0.660	0.099	3.78
3	0.118	0.705	0.675	0.113	4.01
5.5	0.111	0.667	0.633	0.106	4.92
7.4	0.109	0.584	0.549	0.103	5.25
10	0.111	0.589	0.568	0.108	2.87
PVA/CuO-0.15					
2.1	0.109	0.561	0.520	0.101	7.13
3	0.101	0.616	0.602	0.096	5.25
5.5	0.109	0.718	0.650	0.100	8.69
7.4	0.111	0.594	0.557	0.104	6.02
10	0.106	0.541	0.521	0.102	3.57

#### 4. Conclusions

The PVA/CuO nanocomposite hydrogels were successfully synthesized by the freeze/thawing procedure to obtain high long term stability using different content of CuO nanoparticles. The results of XRD analyses of m-CuO nanoparticles showed that the mean particle size was 3.51 nm. According to the results of the rheological analysis of PVA and PVA/CuO nanocomposite hydrogel solutions, the viscosity and strength of the PVA polymer solution were increased with the addition of CuO nanoparticles. The results of UV-vis spectroscopy, FTIR, FESEM, and EDS analyses showed that there was the existence of an interaction between CuO nanoparticles and PVA and the CuO nanoparticles were successfully loaded into the hydrogel networks. The highest swelling degree was achieved with PVA/CuO-0.05 nanocomposite hydrogel containing 0.05 g CuO and PVA/CuO-0.05 nanocomposite hydrogel reached a maximum value of around 570% at pH 2.1. The hydrogels with higher stability were obtained with the addition of 0.05 g CuO to the hydrogel network. Therefore, we can say that the addition of CuO nanoparticles to the hydrogel network improved the swellability and long term stability of neat PVA hydrogel for biomedical application.

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