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Crosslinked Electrospun Poly (Vinyl Alcohol) Nanofibers Coated by Antibacterial Copper Nanoparticles

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Abstract

Poly (vinyl alcohol) (PVA) nanofibers were prepared via electrospinning of concentrated PVA solutions. The nanofibers were crosslinked to enhance their resistance against the moisture. The chemical crosslinking of the nanofibers was carried out using glutaraldehyde as crosslinking agent in the presence of hydrochloride acid. The chemical structure, water solubility, and morphology of the electrospun PVA nanofibers were characterized by Fourier transform infrared (FTIR) spectrometer,water durability test, and scanning electron microscope (SEM), respectively. In addition, the crosslinked nanofibers were coated by copper nanoparticles (CNPs) using electrospraying technique. For this purpose, colloidal CNPs were synthesized through the chemical reduction of copper ions in the presence of different stabilizers, i.e. poly (vinyl alcohol) and ethylene glycol (EG), in an aqueous media. The effect of the stabilizer concentration (0.001 and 0.005 M) and reduction temperature (25 and 70°C) were investigated on the CNP dispersion in the media using UV-visible spectroscopy. Furthermore, the dispersion of the CNPs on the PVA nanofibers was studied by means of SEM. The SEM micrographs showed that the nanofiber scould properly imprison the CNPs. Successful the proposed approach would be exploited to prepare polymer nanofibers incorporating metal nanoparticles which might have interesting properties such as antibacterial activity.

Keywords: *Copper Nanoparticle, Electrospinning, Coating, Crosslinking, PVA Nanofibers*

1. Introduction

Polymer nanofibers are one of the most important nanostructured materials with various interesting applications, such as healthcare, catalysts, electronics, protective clothing, biotechnology, and waste water treatment. A number of processing techniques, such as drawing, template synthesis, phase separation, and electrospinning have been used to produce polymer nanofibers in recent years [1-3]. Electrospinning is a simple method for fabricating submicron fibers. In this process, a polymer solution or melt is placed into a syringe with a millimeter-size nozzle and is subjected to a high electric field. Under the high applied electrostatic force, the polymer is ejected from the nozzle as a filament whose diameter is significantly reduced as transporting to and depositing on a collector [5,6].

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In thepast few decades, PVA has been intensively studied because of its good film forming, biodegradability, hydrophilicity, biocompatibility, processability, and chemical resistance [7,8]. However, when the electrospun PVA nanofibersare immersed in water, they would be dissolved because of the high PVA water-solubility. Although the applications of PVA are limited by its hydrophilicity, chemical crosslinking can improve PVA stability in the aqueous media. The chemical crosslinking of PVA has been well studied using glutaraldehyde (GA) in which the PVA hydroxyl groups and GA aldehyde groups react with each other in the presence of a strong acid [9]. Generally, Crosslinking of PVA is a useful method because it renders the polymer insoluble in all solvents and increases its mechanical properties for applications such as membrane and hydrogel preparation [10].

Recently, the incorporation of metal nanoparticles on polymer nanofibers has attracted the interest of scientists and industries because the metal nanoparticles can endow the polymer nanofibers with distinctive properties, such as optical, electronic, catalytic, and antimicrobial properties [11–13]. Electrospinning,electro-spraying, and metal vaporization are the most important approaches to incorporate the nanoparticles on the nanofiber mat [14–16]. Metallic nanoparticles have attracted significant attention due to their unique properties, which lead to some potential applications in preparing catalysts, sensors, and anti-bacterial agents [17–19]. Among various metal particles, CNPs have attracted more attention because of their proper optical and electrical conducting properties and especially their low cost. CNPs are also particularly attractive for applications in flexible electronics, catalysts, biocompatibility, and biocides [20, 21]. These nanoparticles have been synthesized by different methods, i.e. thermal reduction, thermal decomposition, direct electrochemical reduction, mechano-chemical process, chemical reduction, electro-exploding wire (EEW), and ion beam radiation [22–24]. Chemical reduction is the most convenient, fast, clean, and economical method to synthesize the metallic nanoparticles because the synthesis process is simple and the size and shape of nanoparticles can easily be controlled. Nevertheless, the control of nanoparticles dispersion in the colloidal media is one of the most important challenges because of their high agglomeration tendency. Various types of stabilizer were used to control the dispersion state of nanoparticles in the aqueous media [25–27].

Although some scientists have investigated the effect of various process parameters on the morphology of PVA electrospun-nanofibers, less attention has been paid to the use of these materials as a support for noble metal nanoparticles [28]. In this research work, PVA nanofibers were prepared via electrospinning process. Thereafter, the prepared nanofibers were crosslinked using a crosslinking agent, i.e. glutaraldehyde (GA), in the presence of a strong acid as the catalyst of the chemical reduction to increase the water solubility of the nanofibers. Additionally, the preformed colloidal CNPs were deposited on the nanofibers via electrospraying technique to create anew multifunctional nanofiber material.

2. Experimental

2-1. Materials

All reagents were purchased from Merck Co. (Darmstadt, Germany), unless otherwise stated. Copper (II) sulfate trihydrate salt, $CuNO_3 \cdot 3H_2O$, was prepared. Sodium borohydride ($NaBH_4$,Reagent Plus 99%, Sigma-Aldrich) was used as the reducing agent. Poly(vinyl alcohol) (88% hydrolyzed PVA, Aldrich) with molecular weight of 67,000 and 147,000 g.mol^{-1} and ethylene glycol (EG, Aldrich) were purchased and used without any further purification. Glutaraldehyde (25% aqueous solution) and hydrochloric acid (37% purity) were purchased and used as received. Distilled deionized water (DDI) was prepared in the author's laboratory. *Escherichiacoli* bacteria were prepared from Iranian Research Organization for Science and Technology (IROST) and its Persian type culture collection code was 13. Lysogenic broth was prepared by mixing 3 g of yeast and 5 g peptone in one liter of DDI.

2-2. Synthesis of colloidal CNPs

The four-step preparation scheme for copper nanoparticles (with two different concentrations, stabilizing agents and temperature) starts with dissolving the copper (II) nitrate trihydrate salt (0.001 M and 0.005 M), in 10 ml DDI [29–31]. Next, the stabilizing agent (0.5% wt PVA and ethylene glycol) was dissolved in 10 ml DDI and then added to the aqueous solution containing the copper salt stirred vigorously [31–33]. In the third step, sodium borohydride (0.1 M) was dissolved in 10 ml water and then added to the salt solution, while the solution was kept at two different temperatures 25 and 70°C. An instant color change occurred in the aqueous solution. The appearance of color change indicated that the reduction reaction had started. The source of electrons for the reaction was BH_4^-. The mixture was further stirred rapidly about 10 min in ambient atmosphere to complete the reaction [33–36]. Table 1 indicates the sterilizer type, reduction temperature, and the salt concentration which were used to prepare colloidal CNPs dispersions.

Table 1. Ingredients used for preparing colloidal CNP dispersions.

Code	Stabilizer	$CuNO_3$(M)	Temperature(°C)
CNP1	EG	0.001	25
CNP2	PVA (M_W=67000)	0.001	25
CNP3	PVA (M_W=67000)	0.005	25
CNP4	EG	0.005	25
CNP5	EG	0.001	70
CNP6	PVA (M_W=67000)	0.001	70

2-3. Preparation of PVAnanofibers

PVA solution, 12 wt%, was prepared by dissolving 2.4 g PVA powder in 20 ml distilled water and stirred at 80°C for 4 h [37,38]. The solution was placed into a 5 ml syringe pump with a blunt-ended metallic needle whose inner diameter was 0.5 mm. The rate of spinning was 1 mlh^{-1}. Electrospinning was performed at room temperature and 20% humidity. The process was carried out under applied voltage of 18 kV using a power supply device (HV35P OC, FNM Corp., Iran). The electrospun-nanofibers were collected on a cylindrical stainless still drum at a distance of 17 cm from the syringe needle [38,39].

2-4. Crosslinking of the PVA nanofibers

In order to improve the mechanical strength and moisture resistance of the PVA nanofibers, the nanofibers were crosslinked using GA in the presence of hydrochloric acid [40]. For this purpose, the GA solution was prepared by diluting the 50% aqueous GA solution to 0.2 M concentration. The nanofibers attached on a stainless steel frame were subjected to saturated vapor which was equal to GA/HCE (10/1mol/mol) aqueous mixture in a sealed glass chamber at 80˚C. The nanofibers were exposed to the vapor for 1 h, and then placed into a vacuum oven at 50˚C for 24h to complete the cross-linking reactions. Thereafter, the crosslinked nanofibers were washed with DDI three times and dried in an oven overnight at 50˚C to remove any traces of the unreacted agent [41–44].

2-5. Coating the crosslinked PVA nanofiber with CNPs

The colloidal CNP dispersions were loaded on the syringe pump. The electrospray process was carried out with 1 ml h^{-1} flow rate under 5 kV. The distance between the needle and the rotating cylinder was 17 cm and the rotating speed was held at 150 rpm [45–47].

2-6. Characterization

Ultraviolet-visible spectroscopy was carried out on a Lambda 25 double-beam spectrometer (PerkinElmer, USA) to investigate the effect of reduction process parameters on the CNP agglomeration state. If there is a peak in a range of 500 to 600 nm, it shows that the particles are in the scale of nanometer. Dynamic laser light scattering (DLLS) was used to determine the particle size distribution of the CNPs [48–52].

Fourier transform infrared (FTIR) spectroscopy (SHIMADZU, IR solution 8400S) was applied to characterize the presence of specific chemical bonds in the nanofibers before and after crosslinking. The spectra were obtained in the wavenumber range from 650 to 4000 cm^{-1} [40]. The surface morphology of the PVA nanofibers and dispersion state of the CNPs on the nanofibers surface was studied using scanning electron microscopy (Philips XL30 SEM, Eindhoren, Netherlands).

3. Results and discussion

3-1. CNPs preparation

A number of methods have been used to generate CNPs from copper ions, such as chemical reduction, UV photocatalytic reduction, photoreduction, and simple heat treatment [48–51]. Among these approaches, the chemical reduction is the most widely used method to prepare CNPs colloidal dispersion using a suitable stabilizing agent. Copper (II) nitrate is often used as the primary source of copper ions to generate CNPs. For this purpose, stabilizing agents are used to control the growth rate and dispersion state of the CNPs in the aqueous media [51–53]. Table 1 indicates the different process parameters which were investigated for CNPs preparation. The reduction process for CNP1–4 dispersions was carried out at ambient temperature, whereas the other stabilized dispersions, CNP5–6 were prepared at a higher reduction temperature of 70°C. Adding the reducing agent to the copper nitrate solution and consequently reducing the copper ions changed the color of initial dispersion. After a while, the color changed to reddish brown. Fig. 1 shows the UV-visible spectra of the colloidal CNP dispersions prepared using various different solution concentrations, reducing agents, and reduction temperatures. The values of the absorption band atmaximum peak (λ_p) andthe width of half peak height (PWHM) are listed in Table 2. The surface plasmon absorption bands centering around 560–600 nm were first observed for the colloidal dispersions containing CNPs [53–55]. In this case, the higher λ_p exhibits larger CNP agglomerates, while the largerWHPH indicates the broader CNPs size distribution (Table 2). In addition, the increase in the peak intensity shows more particle concentration.For the stabilized CNP2 and CNP3 dispersions, increasing the copper salt concentration from 0.001 to 0.005 considerably shifted the absorption band toahigher wavelength. In fact, the higher copper ion concentration increased the nucleation growth rate and the possibility of gathering the nuclei as bigger CNPs agglomerates. A sharp absorption pattern with a narrower particle size distribution was observed for the CNP dispersion sprepared athigher temperature, CNP5–6 (Fig. 1). In contrast, reducing at ambient temperature resulted in broadening of the plasmon peak and broadened particle size distribution. The higher stability and narrower size distribution for CNPs prepared at the higher temperature may be due to the strong binding that exists between the CNP and PVA hydroxyl groups. In addition,the size distribution of the CNPs became narrower usingthe PVA rather than the EG. This behavior showed that the reduction process at the ambient temperature even in the presence of the proper stabilizing agent, i.e. PVA, cannot provide stable CNPs dispersion [56]. The peak width at half of maxima (PWHM), an approximate broadness characteristic of particle size distribution for the CNP4 dispersion was much higher than that of the other CNP dispersions. In fact, both the lower reduction temperature and using the EG stabilizer further broadened the size dispersion (Table 3). This behavior revealed that the higher temperature reduction and using PVA as the reducing agent resulted in narrower particle size distribution. Therefore, the CNP6 dispersion prepared at higher reduction temperature with lower amount of PWHM parameter (Table 2) was used to coat the prepared PVA nanofibers. DLLS results indicated mean particle size of 70 nm for the CNP6 dispersion [55–57]. In fact, the size and properties of the dispersed CNPs on the nanofibers would be correlated with their initial mean size and morphology.

3-2. Antimicrobial test ofCNPs

In this study, the antimicrobial activity of the CNP6 dispersion with an average size of 70 nm was tested against *Escherichia.coli*, gram-negative bacteria. This bacteria is responsible for 80% of infections. The antibacterial test was carried out on solution containing CNP6 and in a control solution. The Erlenmeyers were put into the shaker at 37°C for 24 h. Then, the samples were observed for the bacterial growth for one week. For the only sample containing the nanoparticles, inhibitory zones were evident. The results indicated that the CNP6 held broad-spectrum antibacterial property against the *E.coli* (Fig. 2).

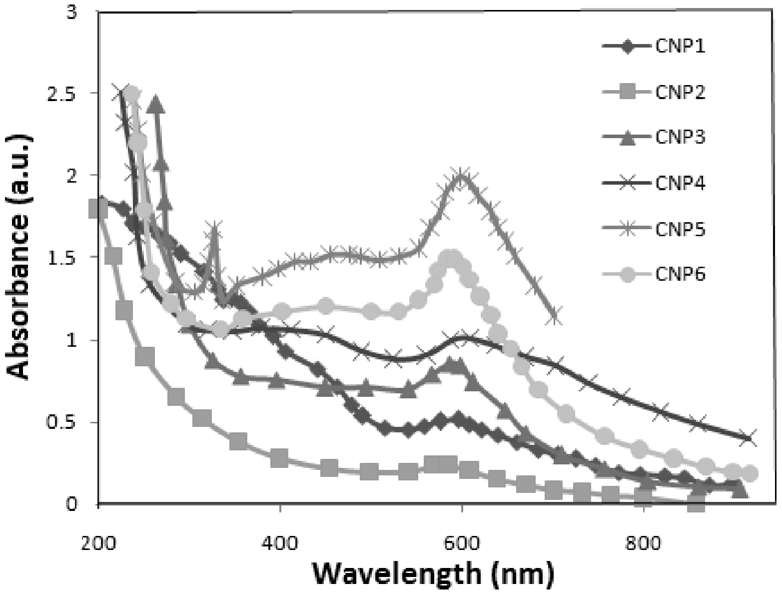

Figure 1. UV-visible absorption spectra of the colloid CNP dispersions.

Table 2. Characteristics of the CNP colloid dispersions determined by the UV-vis spectrum.

Code	Stabilizer	CuNO$_3$ Con. (M)	Temperature (^{o}C)	λ_p (nm)	WHPH (nm)
CNP1	EG	0.001	25	588	48
CNP2	PVA	0.001	25	596	42
CNP3	PVA	0.005	25	592	40
CNP4	EG	0.005	25	596	76
CNP5	EG	0.001	70	600	60
CNP6	PVA	0.001	70	576	36

$\lambda_{p:}$ Absorption band of peak;HMPW: the width of half peak height

Table 3. Vibration modes and band frequencies of the uncrosslinked and GA-crosslinked PVA nanofibers

Material	Chemical group	Wavenumber (cm^{-1})
PVA	O-H	ʋ 3550–3200
PVA+GA	O-H	ʋ 3550–3200
PVA	C-H alkyl group	ʋ 2840–3000
PVA+GA	C-H aldehyde	ʋ 3550–3200 peaks in □ 2830–2695
PVA	C=O	ʋ 1750–1735
PVA+GA	C=O	ʋ 1750–1735
PVA	C-O crystalline structure	ʋ 1141
PVA	C-O-C	ʋ 1150–1085
PVA+GA	C-O-C	ʋ 1150–1085
PVA	CH$_2$	δ 1461–1417

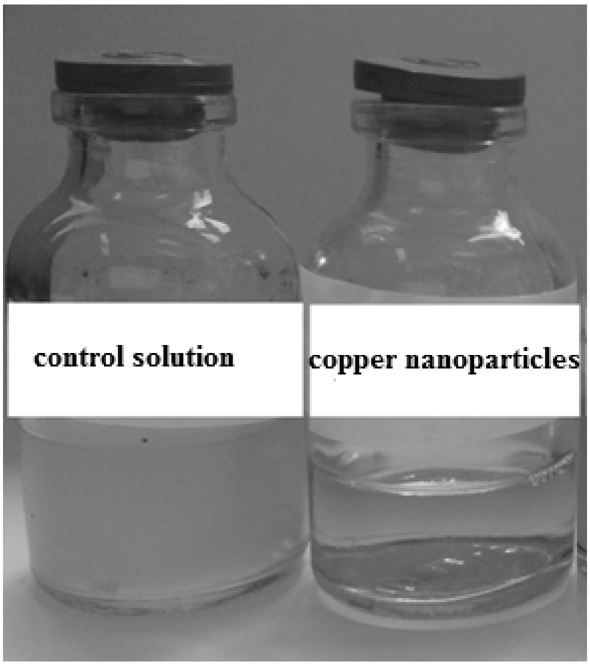

Figure 2. Antimicrobial test of the CNP6 dispersion.

3-3. Morphology of thenanofibers

The morphology of nanofibers is an important factor that affects their performance as the supporting substrate for the coated nanoparticles. Some factors including the physicochemical properties of polymer solution and other electrospinning process parameters sufficiently influence the nanofibersmorphology [58–59]. In this research work, the effect of PVA molecular weight (67000 and 146000 g.mol^{-1}) and flow rate of the electrospinning process (0.8 and 1.5 mL.h^{-1}) on the nanofiber morphology were investigated. SEM micrographs (Fig. 3) indicate the morphology of the electrospun nanofibers prepared using PVA with different molecular weights of 67000 and 146000 g mol^{-1}. In this case, the electrospinning of 10 wt% PVA solution was carried out at solution flow rate of 0.8 mL.h^{-1} and applied voltage of 18 kV. As shown, increasing the molecular weight enhanced the mean nanofiber diameter from 112 nm to 230 nm. This behavior can be attributed to longer length of the higher molecular weight (HMW) PVA chains, which enhances both the viscosity and elasticity of the spinning solution due to increasing chains entanglement density [38,39]. A shift in the size distribution curve to higher nanofibers diameters was observed when the molecular weight increased (Fig. 4). In addition, the morphological structure of the nanofibers can be altered by changing the solution flow rate. As shown in Figure 5a, only a few small beads were observed on the lower molecular weight (LMW) PVA nanofibersprepared at the lower flow rate of 0.8 mL.h^{-1}. On the contrary, the increase of the flow rate to 1.5mL.h^{-1} resulted in the nanofibers with more numbers of beads (Fig. 5b). When the flow rate was increased above a critical value, the delivery rate of the solution jet, the rate at which the solution was removed from the tip by the electric force, was exceeded to the capillary tip. This shift in the mass-balance caused an unstable jet and formednanofibers with bigger and higher numbers of beads [28,39]. Besides, the increase of the flow rate shifted the size distribution curve, to some extent (Fig. 6).

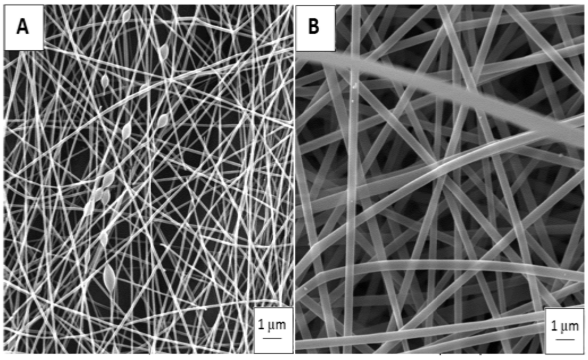

Figure 3. SEM micrographs of the nanofibers prepared with different PVA molecular weight (a) 67000 and (b) 146000 g.mol^{-1}.

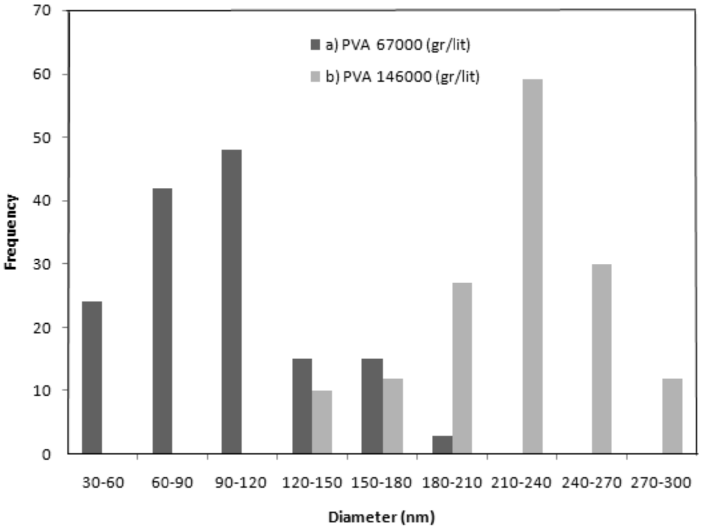

Figure 4. Effect of PVA molecular weight on the diameter distribution of the nanofibers: (A) 67000 and (B) 146000 g mol^{-1}.

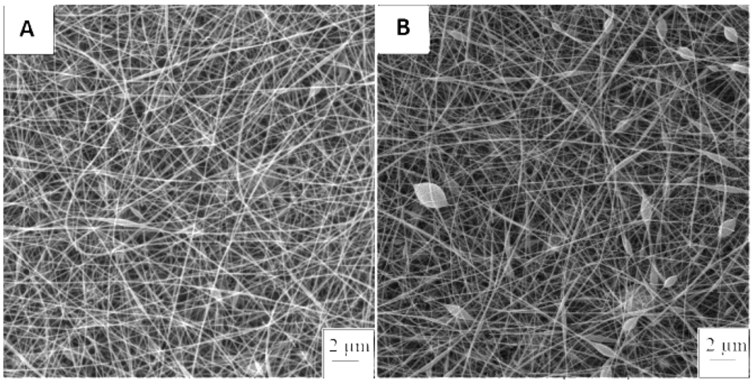

Figure 5. Morphologies of the electrospun PVA nanofibers with different solution flow rate: (a) 0.8 and (b) 1.5ml h^{-1}.

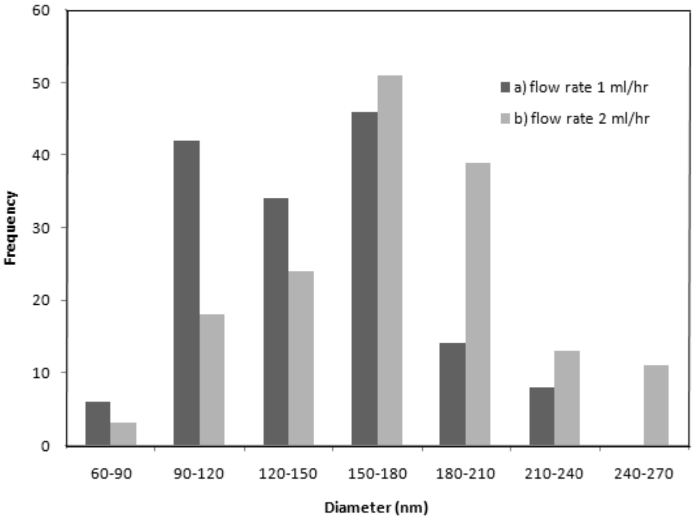

Figure 6. Effect of the spinning solution flow rate on the diameter distribution of the nanofibers: (a) 0.8 and (b) 1.5 mL.h^{-1}.

3-4. Effect of crosslinking on the nanofiber morphology

Fig. 7 shows the morphology of the crosslinked HMW PVA nanofibers using different GA concentration solutions. Crosslinking using GA/PVA ratio of 100/1 mol/mol destroyed the discrete nanofibers morphology (Fig. 7b). Using more dilute aqueous GA solution and, consequently, less GA concentration in the equilibrium vapor phase does not result in more efficient crosslinking. Thus, the partially crosslinked nanofibers would be impaired when immersed into water.On the contrary, crosslinking with GA/PVA mole ratio of 140/1 seems to be more suitable because of the establishment of nanofiber smorphology (Fig. 7c).

3-5. Nanofiber characterization

The electrospun nanofibers were instantaneously soluble in water. Crosslinking with the GA reagent prevented the solving of the nanofibersin water. FTIR was used to prove the chemical crosslinking of the PVA nanofibers. Fig. 8 shows the FTIR spectra of the uncrosslinked and crosslinked PVA nanofibers. The most important characteristic bands of thes pectra are summarized in Table 3. As seen, the strong bands observed between 3200 and 3550cm^{-1} correspond to OH stretching bands of intermolecular and intra-molecular hydrogen bonds. The vibrational band observed between 2840 and 3000 cm^{-1} refers to C-H stretching of alkyl groups. The peaks between 1730 and 1750 cm^{-1} are due to C=O and C-O stretching frequencies of acetate group remaining from the PVA chains. On the other hand, the reaction of the PVA hydroxyl group with GA results in a significant decrease in the intensity of the OH peaks. This indicates a possible formation of acetalbridgesas a result of the reaction. Since GA has two aldehyde groups, one of the groups may react with the PVA hydroxyl groupto forma hemi-acetal structure, while the other group does not react because of conformational and kineticbarriers. This explains the possibility of the presence of the aldehyde peaks in the crosslinked nanofibers due to the incomplete reaction between the GA and OH groups [40–44, 60].

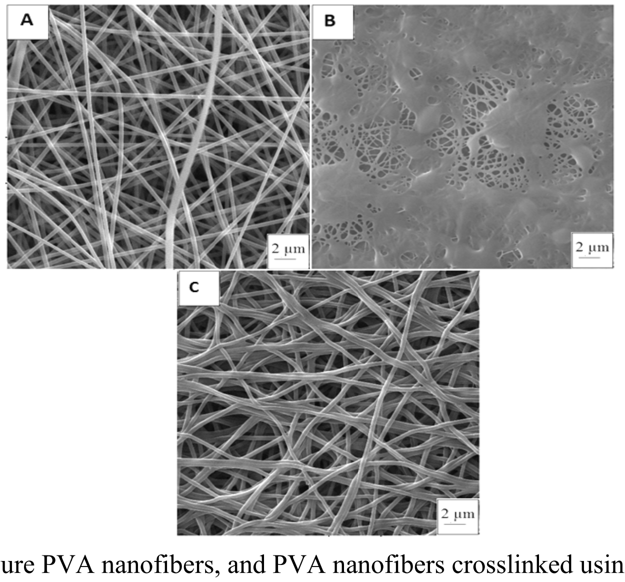

Figure 7. (a) Pure PVA nanofibers, and PVA nanofibers crosslinked using different GA amount: (b) GA/PVA=100/1 and (c) GA/PVA=140/1 mol/mol.

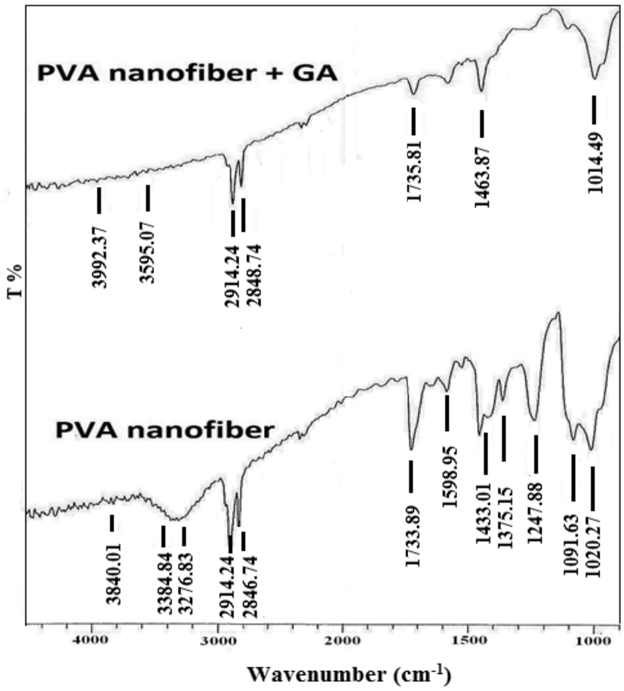

Figure 8. FTIR spectra of the uncrosslinked and crosslinked PVA nanofibers.

3-6. Morphology of the PVA nanofibers coated with CNPs

Electrospraying throws the CNPs on the nanofibers surface under a strong electrostatic force [61,62]. Fig. 9 shows the morphology of the crosslinked PVA nanofibers coated with a colloidaldispersion, i.e. CNP6. As it is shown, there is a rather good dispersion of the CNPs on thenanofibers. Nevertheless, a few particle agglomerates were observed (Fig. 9a). The applied high electric field on the stabilized CNP dispersion may cause partial destabilization, which forms agglomerated particles. Fig. 9b indicates the coated nanofibers at the higher magnification. The nanoparticles with various particle sizes and spherical and nonspherical particulate morphologies are obvious. The interaction between the OH groups of copper oxide on the nanoparticle surface and on the crosslinked nanofiber may provide a strong interaction due to formation of good hydrogen bonds.

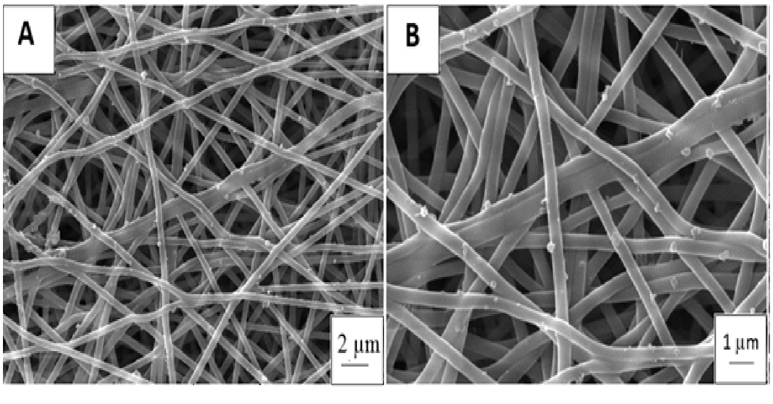

Figure 9. The crosslinked PVA nanofibers (GA/PVA=140/1 mol/mol) which were coated by CNPs.

4. Conclusions

PVA nanofibers were successfully fabricated through controlling the electrospinning conditions such as the polymer molecular weight and spinning solution flow rate. The SEM micrographs showed that the preparation of nanofibers at higher PVA concentration and lower flow rate resulted in more stable nanofibers. In addition, the nanofibers were successfully crosslinked when subjected to the vapor of the aqueous GA/HCl solution with GA/PVA and GA/HCl ratios of 140/1 and 10/1 mol/mol, respectively. This work advanced the body of knowledge by demonstrating successful preparation of the crosslinked PVA nanofibers containing CNPs. For this purpose, CNP dispersions were synthesized through the chemical reduction of the copper ions in the presence of the PVA and EG stabilizers. The reducing agent type, copper salt concentration, and reduction temperature indicateda crucial role on the CNP agglomeration state.

UV spectra exhibited the most stable CNP dispersion prepared using PVA stabilizer at higher reduction temperature (70°C) and the lower salt concentration (0.001 M). This colloidal dispersion with 70 nm mean size was used to cover the crosslinkednanofibers via electrospraying method. A rather good dispersion of the CNPs on the nanofibers surface was observed.

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