Original Article

Preparation and characterizations of multifunctional PVA/ZnO nanofibers composite membranes for surgical gown application

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\begin{abstract}
Herein, we developed the multifunctional; antibacterial, ultraviolet rays (UV) protected and self-cleaning surgical gown by blending of zinc oxide (ZnO) nanoparticles with poly vinyl alcohol (PVA). For this objective, ZnO NPs were blended in three different concentrations: 5 wt\%, 7 wt\% and 9 wt\% in 10 wt\% of PVA solution. The morphology of resultant nanofibers was observed under scanning electron microscope and transmission electron microscope and these studies showed the bead-free nanofibers and good dispersion of nanoparticles on nanofibers. Fourier Transform Infrared spectroscopy was used for chemical interactions, wide-angle X-ray diffraction (WAXD) was used for analyzing the crystalline structure, agar diffusion plate method was used for antibacterial activity and it showed the effective response of bacteria killing. UV transmission analysis was done by Ultraviolet transmission analyzer, photo-catalytic activity was done by the solar simulator, stress–strain behavior was studied by tensile strength, and water contact angles measurements were done by contact angle meter. On the behalf of characterization results, PVA/ZnO nanofibers were exhibited the desired objectives for the surgical gown. This multifunctional surgical gown is beneficial for medical surgeon against the bacteria, stains and UV blocking to save his/her life.
\end{abstract}

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1. Introduction

Healthcare associated infection is one of the world’s largest devastating problems, causing millions of deaths and billions of dollars in healthcare each year. Medical textile materials are very susceptible to microbial growth. Therefore, the antimicrobial treatment of medical textiles such as surgical gowns, bed-sheets, uniforms, aprons and masks, is essential to reduce the spreading of pathogenic microorganism [1].

Nanofibers are ideally suited to form the multifunctional medical products [2]. The protected products are needed to reduce occupational exposure for individual involved with the hospital, chemical industry, emergency response and also military. A number of methods for development of nonwoven and non-washable medical products like surgical gowns but the use of electrospin nanofibers for the non-washable protective garments has grown over the past few decades since they are relatively inexpensive, lightweight and effective protection [3,4]. Electrospinning is a potential technology for use as a platform for multifunctional and hierarchically organized composites because it allows extensive tenability in the materials properties and functions through the selection of the polymeric nanofibers and composite nanofibers [5–7,2].

Recently, some researchers worked on the antibacterial surgical gown by different methods such as Virk et al. in 2004 used antibacterial finishing on nonwoven fabric [8], Huang et al. in 2000 used antibacterial and fluorochemical repellent finishing on nonwoven fabric [9], Sarkar et al. in 2011 used different antibacterial agents on different types of fiber for medical textiles [10], Radetić et al. in 2008 used Ag nanoparticles on the surface of fabric to form the antibacterial medical textiles [11] and El-Shishtawy et al. in 2011 used Ag nanoparticles on the cotton fabric for medical textiles [12]. But none of them used antibacterial properties on nanofibers based surgical gown. Therefore we attempted to form the multifunctional surgical gown based on nanofibers by making the composite nanofibers by blending of ZnO nanoparticles in poly vinyl alcohol (PVA/ZnO). ZnO nanoparticles can be used for antibacterial, UV protections and self-cleaning properties [13]. We are first to develop the nanofibers based multifunctional; antibacterial, UV protection and self-cleaning surgical gown.

In this report, we developed the multifunctional nanocomposite by blending of ZnO nanoparticles with PVA for the surgical gown. The morphology of nanofibers was investigated by SEM and TEM. The chemical interaction was studied by FT-IR, investigation of crystalline structure was done by XRD, photo-catalytic activity was done by solar simulator, stress–strain behavior was studied by tensile strength tester, water contact angles measurements were done by contact angle meter, and UV protection data was obtained by Ultraviolet transmission analyzer and for antibacterial agar diffusion test was done.

2. Experimental

2.1. Materials

Poly vinyl alcohol (PVA) (MW: 85,000–124,000, 87–89% hydrolyzed) was purchased from Sigma-Aldrich Corporation USA. Glutaraldehyde (GA, 50% in aqueous solution) was purchased from MP Biomedical. ZnO nanoparticles were purchased from Sigma-Aldrich Corporation USA with a dispersion of concentration of 50.1 wt%. Methylene blue (powder form soluble 4 mg/4 ml) was purchased from Sigma-Aldrich Corporation USA and Water.

2.2. Electrospinning

Poly vinyl alcohol (PVA) 10% by weight was dissolved in water at 70 °C with stirring for 5 h and GA was adding in that solution 2.5% by wt for cross-linking of the solution. ZnO nanoparticles were embedding by stirring for 5 h in three different concentrations 5%, 7% and 9% by weight. The solution was loaded in the plastic syringe having the diameter of 0.60 mm, in which a Cu electrode was adjusted. The distance from the capillary tip to the collector was 12 cm and the supply of voltage was 14 kV. The nanofibers were formed without beads at room temperature and at 45% humidity.

2.3. Characterization

The morphology of nanofibers was investigated by SEM (JSM-5300, JEOL Ltd., Japan) accelerated with the voltage of 12 kV and TEM (JSM-5300, JEOL Ltd., Japan) accelerated with 200 kV. The chemical interactions were study by FT-IR (IR Prestige-21 by shinmadzu Japan), Wide angle X-ray diffractions (WAXD) were performed for evaluation of crystal structure at room temperature with nanofibers samples using a Rotaflex RT300 mA and Nickel-filtered Cu Kα radiation was used for measurements, along with an angular range of 5 ≤ 2θ ≤ 50°, photo-catalytic activity was done by solar simulator (XES-403S, San-ei Electric, Japan) in which light intensity was 1000 W/m2 and wavelength range of 350–1100 nm and the self-cleaning efficiency was calculated as following Eq. (1).

\[
\text{Degradation (\%)} = \frac{R_i - I_d}{R_i} \times 100.
\]

stress–strain behavior was studied by tensile strength tester (Universal Testing Machine, Tenilon RTC 250A, A&D company Ltd., Japan), water contact angles measurements were done by contact angle meter (Digidrop, GBX France), UV protection data was obtained by UV-1000F, Ultraviolet transmission analyzer (Labsphere, USA) using EN 13758-1-2001and for antibacterial AATCC test was done.

3. Results and discussions

3.1. Morphology of nanofibers

The exterior morphology of PVA/ZnO nanofibers was evaluated by SEM in which it was investigated that nanofibers had the good cohesiveness to each other and beat free nanofibers as shown in Fig. 1. With the blending of ZnO nanoparticles in the PVA solution there was no effect of morphology but diameter of nanofibers was increased as the concentration of ZnO was increased and in order to determine the presence of ZnO nanoparticles in the PVA/ZnO nanofibers scanning electron microscope images with corresponding energy dispersive
3.2. FT-IR study of nanofibers

In order to investigate the chemical interaction between PVA and ZnO nanoparticles, Fourier Transform Infrared spectroscopy study was done as shown in Fig. 3. Spectra showed that in the neat PVA nanofibers the bands at about 3320 cm\(^{-1}\), 2940 cm\(^{-1}\), 1437 cm\(^{-1}\), 1093 cm\(^{-1}\) and 850 cm\(^{-1}\) are assigned to the vibrations of \(-\text{OH}, -\text{CH}_2\text{CH}_2, \text{C–C}\) and \text{C–O} group of PVA, respectively. The new intense broadband 1100 cm\(^{-1}\) to 1000 cm\(^{-1}\) and at 750 cm\(^{-1}\) are assigned to Zn-O vibrations of ZnO nanoparticles that indicating the nanofibers composed of PVA and ZnO.
3.3. XRD analysis of nanofibers

In order to investigate the crystalline structure of PVA/ZnO nanofibers wide-angle X-ray diffraction (WAXD) was studied as shown in Fig. 4. The neat PVA exhibits the peak at 20° but there were more peaks in PVA/ZnO nanofibers which were exhibited at 18°, 28°, 32°, and 34°. It means by addition of ZnO nanoparticles the crystallinity was increased and 9% ZnO by weight in PVA/ZnO nanofibers exhibited the peaks same at 18°, 28°, 32° and 34° but with high intensity [14] as shown in Fig. 4.

3.4. Tensile strength analysis of nanofibers

The stress–strain behavior of PVA/ZnO nanofibers was investigated by Universal Testing Machine as shown in Fig. 5. It was observed that neat PVA nanofibers have the largest elongation at 99% but having a low capability of bearing load which is 0.25 MPa. The elongation of blended PVA/ZnO nanofibers was decreased as the concentration of ZnO nanoparticles was increased but capability of bearing load was increased as the concentration of ZnO nanoparticles was increased. The increasing the strength of PVA/ZnO nanofibers by blending of ZnO nanoparticles it is due to the effect of metallic nanoparticles because metallic nanoparticles; always increase the strength of their partner component in the composite [15]. Therefore, 9 wt% PVA/ZnO nanofibers have highest strength than others 7 wt% and 5 wt% PVA/ZnO nanofibers as shown in Fig. 5.

3.5. Water contact angle measurements of nanofibers

The wetting behavior of PVA/ZnO nanofibers was investigated by the static angle with a contact angle meter by drop method. It was analyzed that neat PVA nanofibers are hydrophilic with contact angle 88° as mentioned in Fig. 6 but the water contact angle of blended nanofibers was reduced as the concentration of ZnO nanoparticles was increased. The 9% ZnO/PVA nanofibers has highest hydrophobicity with contact angle 118°.

3.6. Photo-catalysis activity

The photo-catalysis activity was done by solar simulator in which light intensity was 1000 W/m² and wavelength range of 350–1100 nm. In this phenomenon, a photo-catalyst absorbs UV light and then converts H₂O into hydroxyl radicals (OH⁻), which have the ability to degrade the contaminant to small molecules and finally into CO₂ and H₂O [4,16]. As we done in our previous work [4,14] for the evaluation of self-cleaning properties 2 µl of methylene blue was dropped onto each sample. The photo-catalysis activity was done between neat PVA and 9 wt% ZnO/PVA nanofibers for 3 h as shown in Fig. 7. It was observed that there was no self-cleaning property in PVA but PVA/ZnO has self-cleaning properties, as mentioned in Fig. 7. The self-cleaning properties were done in two ways; first by the naked eye, as shown in Fig. 7a, and second by ATR spectra, in which the intensity of the methylene blue was measured by using Eq. (1).

\[
\text{Degradation} \% = \frac{i_i - i_d}{i_i} \times 100
\]  

(1)

where \(i_i\) is the initial intensity of dyed nanofibers and \(i_d\) is the degraded intensity of dyed nanofibers. Therefore, degradation efficiency/percentage was calculated from ATR spectra, which showed that PVA/ZnO nanofibers have the appreciable self-cleaning efficiency because PVA/ZnO nanofibers showed a 98% self-cleaning efficiency within 3 h in Fig. 7b and c.
3.7. UV transmission

The ZnO nanoparticles strongly absorb in the UV region, so the PVA/ZnO nanofibers were expected to exhibit UV shielding properties. The black spectrum in Fig. 8 shows that neat PVA had a high UV transmission but all other PVA/ZnO nanofibers exhibited nearly 0% UV transmission, while transmission in the visible region showed no significant decline. Absorption by the ZnO nanoparticles was clearly responsible for the different transmissions in the UV and visible regions.

3.8. Antibacterial activity

In order to investigate the antibacterial properties of the PVA/ZnO nanofibers, agar diffusion plate method was used. In this method, the staphylococcus aureus and Escherichia coli were used as model bacteria. The bacteria were used on the neat PVA nanofibers and PVA/ZnO nanofibers. The antibacterial results are shown in Fig. 9. The results indicated that the treated nanofibers with ZnO nanoparticles have an effective antibacterial activity against staphylococcus aureus and Escherichia coli bacteria. When the concentration of ZnO nanoparticles was increased the killing process of bacteria was increased as shown in Fig. 9 and Table 1. It was observed that neat PVA have no antibacterial properties but 9% by weight PVA/ZnO nanofibers membranes has the highest antibacterial properties against staphylococcus aureus as shown in Fig. 9 and Table 1.

4. Conclusions

Herein, we successfully developed the multifunctional nanocomposite for the surgical gown by blending of PVA/ZnO through electrospinning. The blending of ZnO nanoparticles with PVA was in three different concentrations: 5 wt%, 7 wt% and 9 wt% and uniformly dispersion on nanofibers was achieved. The resultant nanofibers have good chemical interactions between PVA and ZnO nanoparticles, crystallinity and strength of the blended nanofibers were increased as concentration of ZnO nanoparticles was increased. The photo-catalysis efficiency of the PVA/ZnO nanofibers was increased as the concentration of the ZnO nanoparticles was increased. The UV transmission of the PVA/ZnO nanofibers...
was decreased as the concentration of ZnO nanoparticles was increased. The antibacterial efficiency of PVA/ZnO nanofibers was increased as the concentration of the ZnO nanoparticles was increased. So this nanocomposite is very beneficial for the medical surgeon to fulfill the stated and implied needs of the customer.

**Conflicts of interest**

The authors declare no conflicts of interest.

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**References**


