



Fabrication and characterization of electrospun PVA/Cs/CNT fibers

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ABSTRACT

Polyvinyl alcohol (PVA)/chitosan (CS) and PVA/CS/carbon nanotube (CNT) nanofibers were fabricated by electrospinning method. Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) analysis and water contact angle (WCA) tests were used to evaluate the morphology, types of bounds and wettability of electrospun fibers. The results showed that the most appropriate mass ratio of PVA/Cs resulting in uniform and smooth nanofibers was 2.8:1, and this morphology was not affected by the addition of CNT. However, the presence of CNT (0.5, 1 and 2 wt%) caused a significant decrease in fibers' diameter from 519 nm to 85 nm. The compatibility of CNT with PVA/Cs and crosslinking between the components was confirmed by the XRD and FTIR analysis. Improving the hydrophilic properties of the fibrous mat was admitted by the WCA test.

Keywords: Polyvinyl alcohol (PVA);chitosan (CS); Carbon nanotube (CNT), Electrospinning.

1. Introduction

Since the discovery of Chitosan (Cs), it has found a great deal of attention in different fields of science. Chitosan is derived from Chitin, a natural polymer mainly obtained from shells of crustaceans. This natural renewable resource is famous for its biodegradability, biocompatibility, non-toxicity and safe degradation products [1]. The presence of the amino groups in chitosan structure, differs it from chitin and leads it to behave like a biodegradable material. Chitosan is

indeed the only natural cationic polysaccharide and can form ionic complexes with natural or synthetic anionic parts of other molecules. Many research are conducted on Cs applications in diverse scientific areas i.e. biomedical, biodegradable packaging and membranes [2]. The results showed that it cannot be processed alone, due to some weaknesses in mechanical properties, electrical conductivity, and as well as its structural integrity especially under wet conditions. These disadvantages caused to limit chitosan's application in numerous fields such as

tissue engineering. Combination of Chitosan with some nano-fillers, i.e. graphene oxide or Carbon nanotubes can improve physical and mechanical properties of this organic material remarkably [3].

CNT has a high aspect ratio, low density and excellent mechanical, chemical, thermal and electrical properties and can be a good candid for improvement of chitosan properties [4]. It is clear that the unique properties of the resultant composite are highly dependent on the dispersion and the microscopic orientation of carbon nanotubes in the polymer matrix, and their interfacial interactions with the polymer. Introducing functional groups on the surface of CNTs can significantly improve their combination with a wide variety of polymers, resulting in better dispersion and improved mechanical properties [2, 5-10]. In the study of Dozois et al. the electromechanical properties of cardiac cells improved by adding carbon nanomaterials which also reproduced the behavior of the native heart cardiomyocytes [5]. Mallakpour et al. successfully fabricated well dispersed AA-MWCNTs in GPS matrix in a nano-sized range and significant improvement of electrical properties of GPS/AA-MWCNTs composite was

achieved [6]. Giersig and coworkers [7] reported that interconnected multiwall carbon nanotubes (MWCNTs) can support a very good growth of mouse fibroblast cells, confirming the idea that 3D MWCNT-based network is an appropriate alternative scaffold in tissue engineering. Similarly, Ji et al. [8] and Hou et al. [9] reported considerable improvement in mechanical properties of polymer nanofibers with highly aligned MWCNTs.

Various methods can be used for the fabrication of chitosan/CNT fibers such as phase separation, self-assembly and electrospinning. Electrospinning is a promising method because it results in fibers much smaller than those obtained by the conventional techniques [11]. In addition, nanofibers produced by electrospinning can be very smooth and oriented resulting in better mechanical and thermal properties [12].

Many attempts have been made to fabricate fibers from pure chitosan by electrospinning method, but a lot of them rejected the possibility of producing electrospun fibers from its aqueous solution without a second polymer [13]. This is due to the Chitosan's long chains entangled in each other and high viscosity that prevents the movement of polymeric

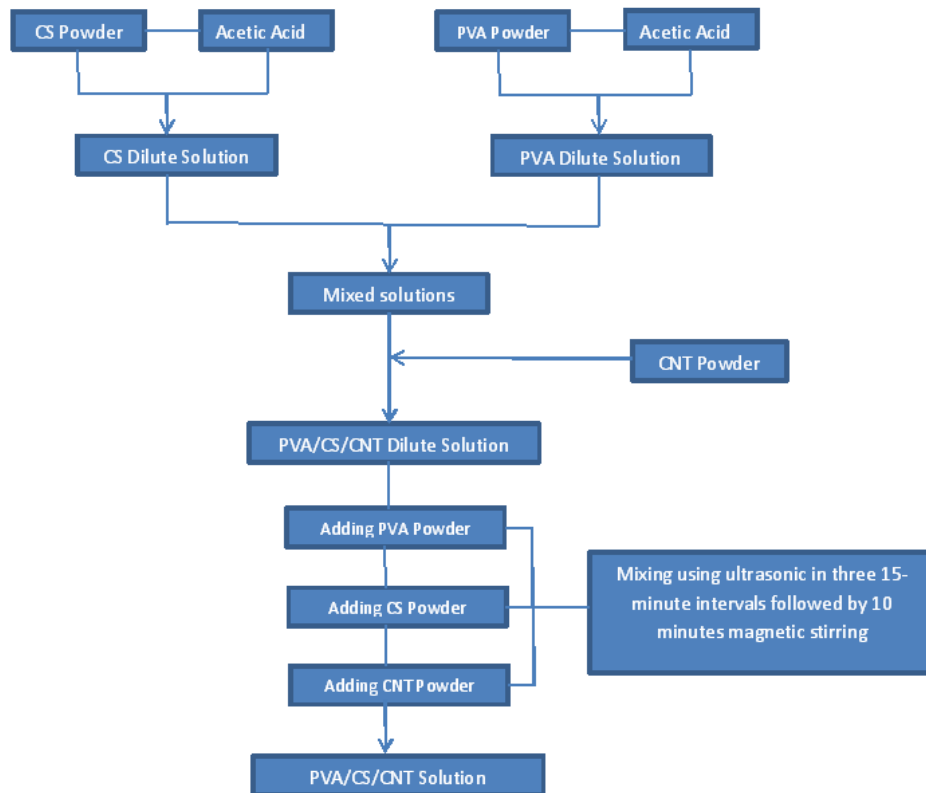


Fig. 1- Flow chart of different steps of solution preparation.

chains. Furthermore, some research was done on the electrospinning of Cs with other solvents such as 1,1,1,3,3,3-hexafluoro-2-propanol or tri-fluoro acetic acid to make pure Cs fibers. But, the toxic properties of these solvents limits the application of these fibers in biomedical projects [14]. One successful approach is the combination of polyvinyl alcohol (PVA) as a water-soluble synthetic polymer with excellent biocompatibility and good physical and fiber forming properties [15]. There are some reports studying the electrospinning of Cs/PVA blends that prove the uniform distribution of Cs and PVA in electrospun fibers [16] which is due to the strong hydrogen bonding that PVA can have with chitosan on a molecular level [17].

To the best of our knowledge a systematic study on fabrication of chitosan/CNT/PVA fibers by electrospinning has been of little attention. In this study, chitosan/CNT/PVA fibers are prepared by electrospinning and the electrospinning parameters are optimized to obtain fibers with uniform and smooth morphology. Also, the effect of different CNT contents on the morphology of fibers are studied.

2. Experimental Methods

2.1. Materials

PVA (molecular weight = 72,000, >98% hydrolyzed) was purchased from Merck company (Germany). Chitosan (medium molecular weight, degree of deacetylation > 90%), glutaraldehyde (4% in aqueous solution), and acetic acid glacial were prepared from Carl Roth Co., Ltd. (Germany). MWCNTs (diameter = 20–30 nm, length = 300 μm) with carboxyl residues were supplied by Neutrino Co, (Iran).

2.2. Preparation of the solutions

For preparation PVA solution 10 gr PVA powder was dissolved into 100 ml acetic acid (70 wt%) using vigorous magnetic stirring at 80°C for 4 h and for making CS solution, 7 gr CS powder was dissolved in 100 ml aqueous acetic acid (70 wt%) to obtain Cs solution (7 wt%). These solutions were mixed at different PVA/CS mass ratio of 0.75:1, 1:1, 1.5:1, 2.5:1, 2.8:1 to obtain the electrospinning solutions. Afterward, MWCNTs were added to the solutions at different weight percent (0.5, 1 and 2 wt %). Dispersion of the mixture was carried out in an ultrasonic bath in three 15-minute intervals followed by 10 minutes magnetic stirring. Figure 1 shows the details of preparation of the solution.

2.3 Electrospinning

The electrospinning process was done using a laboratory electrospinning device manufactured by Nano Azma Company (Iran). A fixed electrical potential of 18 kV was applied to the steel capillary needle with an inner diameter of 0.4 mm. The distance between the needle tip and the cylindrical collector was kept constant 15 cm. Feeding rate of the solution was 0.6 ml/h controlled by a syringe pump. The electrospun nanofibers, with and without MWCNTs, were air dried for 48 h before characterization and crosslinking treatment.

2.4. Crosslinking of nanofibers

The electrospun PVA/CS and PVA/CS/MWCNTs nanofibrous mats were crosslinked via a GA vapor crosslinking method. Briefly, a Petri dish containing GA solution (4% aqueous solution, 5 ml) plus a drop of hydrochloric acid as a catalyzer was placed at the bottom of a desiccator. Then the electrospun nanofibrous mats deposited onto the supporting aluminum foil was placed on the top of the petri dish. The mats were exposed to GA vapor for 3 hours. Then, the nanofibrous mats were rinsed 3 times with alcohol to remove the excess GA. All the treated mats were soaked in water to examine their water stability.

2.5. Characterization techniques

SEM pictures were used to study morphology and diameter of fibers of electrospun PVA/Cs fibers. For this purpose the morphology and diameter of electrospun samples with different PVA/Cs ratio was evaluated. Microscopic evaluation was performed using a Cambridge Stereoscan 320 scanning electron microscope with an accelerating voltage of 30 kV. To avoid charge built up the fibers were coated with gold using a Palaron SC 7640 equipment. The fiber diameter distribution histogram was analyzed using ImageJ 1.51d software. At least 50 randomly selected nanofibers in different SEM images were analyzed for each sample.

Fourier Transform Infrared Spectroscopy (FTIR) was used to elucidate the compatibility of composite components and the performance of cross-linker. For this purpose, Infrared spectra for the electrospun samples before and after cross-linking were detected by an attenuated reflectance Fourier transform (Thermo Scientific) spectrometer. Transmission mode with KBr pellets

was utilized for all samples and spectra were taken in the spectral range of 400-4000 cm^{-1} .

XRD analysis was conducted to observe whether there was any change in the crystalline structure of CNTs by a Bruker D8 Advanced X-ray diffractometer with using CuK_α radiation. The anode voltage and current were set at 40 kV and 40 mA, respectively. The diffraction angle 2θ was scanned from 5 to 70° at a scan rate of $0.5^\circ/\text{s}$.

The wettability of the mats was evaluated via water contact angle (WCA) test. The test was performed at room temperature equipped with a Jikan CAG-10 optical contact angle measuring system using the sessile drop method. $8\mu\text{l}$ of deionized water was dropped on the samples and images at 0 and 5 s were taken and the contact angle was measured. The WCA of each sample was the average value of three different spots.

3. Results and Discussion

Electrospinning process is mainly affected by solution properties and strong macromolecular interaction in Chitosan makes it impossible to form electrospun fibers from pure Chitosan. Therefore, PVA was added to interfere with the chitosan molecular interaction and improve the electrospinnability properties of the blend. It is assumed that PVA interacts with Chitosan through the hydrogen bonds between hydroxyl groups of PVA hydroxyl groups of Chitosan [18-20]. CNT was also reported to do so by forming hydrogen bonds between its carboxyl groups and PVA hydroxyl groups [17]. In this work, the electrospinnability of PVA/Cs was studied for some PVA to Chitosan mass ratios. Then, the influence of carbon nanotubes on morphology and fiber diameter of the electrospun mats was investigated.

3.1 Microscopic Evaluations

3.1.1 PVA/Cs Fibers

SEM pictures were used to study morphology and diameter of fibers of electrospun PVA/Cs fibers. For this purpose the morphology and diameter of electrospun samples with different PVA/Cs ratio was evaluated. Figures 2-a to 2-f elucidate the dependency of morphology of fibers on the PVA/Cs ratio. As seen in figures 2-a to 2-f, there is an obvious enhancement in the fibers uniformity as ratio of PVA to Cs increases. Comparison of SEM micrographs show that the number of discrete fibers decreases as PVA/Cs increases. As a result, the PVA/Cs = 2.8:1 seems to be the best ratio of PVA to Cs

for electrospinning uniform fibers. The reason of decreasing the number of ultrafine secondary fibers with increasing PVA can be attributed to the fact that the probability of the formation of hydrogen bonds between PVA and chitosan molecules improves [18]. The verification of this claim was further conducted by analyses of FTIR and XRD. It is clear that when the PVA/Cs ratio is low, the formation of hydrogen bond is limited and in such case a proportion of chitosan may remain without interaction with PVA that results in the non-uniform and discrete fibers as shown in figures (2-a to 2-d). These secondary fibers are believed to form as a result of the ionic (amino) groups of Chitosan that can increase the repulsive force in the surface of the electrospinning solution jet and decrease fibers diameter significantly. However, they are unable to form continuous fibers because of high viscosity and poor electrospinning properties of the dominant component, Chitosan. Also, a TEM-EDS analysis measuring the percentage of nitrogen, as the characteristic element of Chitosan, confirmed the imbalance of Chitosan distribution along the fibers and beads [20].

It is very interesting to know that the non-uniformities mentioned here are themselves fibers and they are not droplets nor beads. Therefore, the specific surface area they possess is larger than that of beads and the original fibers and regardless of the mechanical weaknesses they may cause in the whole structure, we can assign some benefits to them such as resembling the morphology of collagen and elastin in the extra cellular matrix in tissue scaffolding [21].

3.1.2. PVA/Cs/CNT Fibers

SEM images were also used to study the effect of addition of carbon nanotubes on the morphology and PVA/Cs (2.8:1) fibers diameter (figure 3). As can be seen in the figures, all samples included with some smooth and uniform fibers, and there is no any evidence of beads. Looking at in more details on the micrographs one may conclude that addition CNT causes to decrease the fiber diameter. The electrospun fibers formed without CNT showed an average fiber diameter of 519 nm. However, the diameter decreased significantly by adding CNT to the solution. PVA/CS/CNT solutions with 0.5%, 1% and 2% wt. CNT formed fibers with average diameters of 144 nm, 91 nm and 85 nm respectively. This reduction in nanofibers' diameter originates from the addition

of MWCNT which enhanced conductivity of the polymer solution. Therefore, there is an increase in electric current during electrospinning which induces large charge density in the solution jet. This allows strong electrostatic repulsion among jet sprays that can easily overcome the surface tension of the jet. Consequently, sufficient elongation of the jet occurs and fibers with reduced diameters are formed [22-24]. Another key factor that can affect the electrospinning process is viscosity. Reduction in viscosity could happen by the incorporation of CNTs to the solution, resulting in break-up and destroying the rigid interaction between polymer chains resulting in better electrospinnability [23].

3.2. FTIR Analysis

FTIR analyses were conducted in order to investigate the intermolecular interactions in PVA/Cs/1wt%CNT nanocomposites and their spectra are represented in figures 4 and 5. There is a broad and sharp peak centered at 3430 cm^{-1} in all curves which is contributed to the stretching vibrations of O–H moieties in all components and N–H bonds in Cs. The characteristic peaks around 2850 cm^{-1} and 2920 cm^{-1} refer to the aliphatic $\text{sp}^3\text{ C-H}$ stretching in the compounds. The existence of this peak in CNT spectrum is not fully understood but it could be due to the defects occurred during

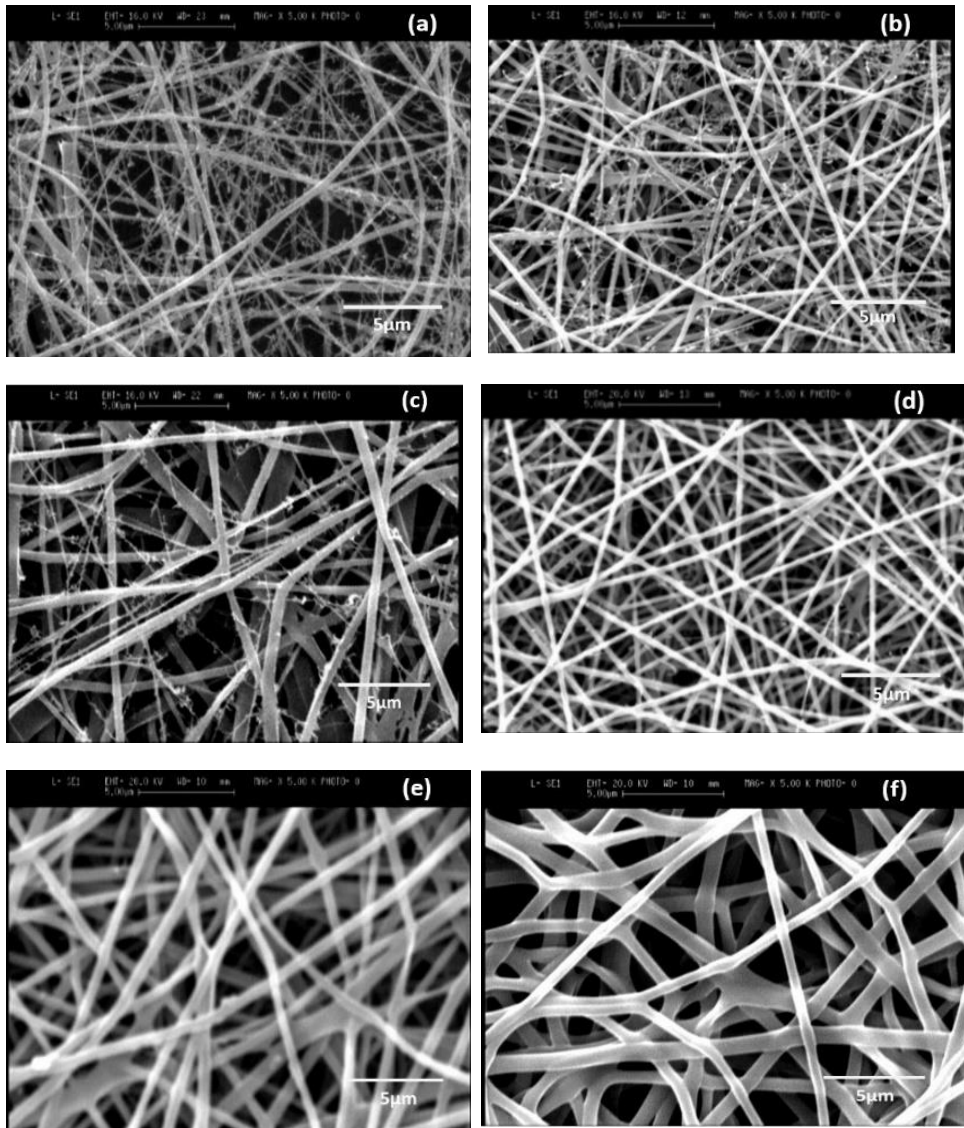


Fig. 2- SEM images of PVA/Cs fiber mats for different ratios of PVA to Cs a) 0.75:1, b) 1:1, c) 1.5:1, d) 2.5:1, e) 2.8:1 and f) pure PVA.

the processing steps of producing CNTs and the absorption band at 2350 cm^{-1} is arising from the presence of CO_2 molecules existed in the path of the IR beam between the source and the detector [25]. The band observed at 1735 cm^{-1} in the spectra of PVA (figure 4) is related to the of carbonyl moieties of unhydrolyzed acetate groups remained from the imperfect hydrolysis of polyvinyl acetate to polyvinyl alcohol [26]. Amide $\text{C}=\text{O}$ stretching vibration indicated at 1625 cm^{-1} is a result of binding between the COOH groups of CNT and NH_2 groups of Chitosan [26, 27] (figures 5-b, 5-d). The comparison between these two carbonyl vibration peaks before and after adding CNT, confirms a relative increase in the intensity of amide carbonyls of CNT rather than PVA carbonyl groups [28]. Peaks in 1648 cm^{-1} and 1596 cm^{-1} are related to the binding energies of $\text{C}=\text{N}$ and NH_2 bending respectively. $\text{C}=\text{N}$ bonds are formed through the crosslinking reaction of aldehyde groups with NH_2 groups of Chitosan [29] after which, the intensity of this peak increased in comparison to the NH_2 peak (relative intensities) (figure 4-c, 4-d). CO has a clear peak at 1090 cm^{-1} in all components spectra. The sharp peak in the range of $1243\text{-}1278\text{ cm}^{-1}$ in PVA curve (figure 4-a) that became broader ($1201\text{-}1317\text{ cm}^{-1}$) in crosslinked PVA (figure 4-b). This

increase in the width of the peak could be due to the appearance of a new peak in this area which suggest that the acetal bonds formed between PVA chains after the crosslinking. Furthermore, the characteristic peak of $\text{O}-\text{H}$ and $\text{N}-\text{H}$ vibrations became narrower and shifted to the higher wave numbers after both adding CNT and crosslinking reaction occurred. This is due to the formation of new bonds between $\text{CNT}-\text{COOH}$ and NH_2 as well as the nucleophilic reaction which consumes a number of $\text{N}-\text{H}$ and $\text{O}-\text{H}$ bonds resulting in the vibration peak of this area became narrower.

3.3. XRD

Figure 6 shows the results of X-ray diffraction analysis for PVA, Cs, CNT and their composites before and after crosslinking. The pure PVA powder exhibited two broad peaks at $2\theta = 23^\circ$ and $2\theta = 43^\circ$ and characteristic peaks of Chitosan were observed at $2\theta = 14.5^\circ$ and $2\theta = 20.4^\circ$; both demonstrating an amorphous structure. After mixing and electrospinning, however, the little crystallinity of each polymer completely disappeared and the pattern of PVA/Cs fibers includes a weak and broad peak at $2\theta = 21^\circ$. This decrease in the crystalline reflections of PVA/Cs sample confirms the formation of a completely amorphous structure

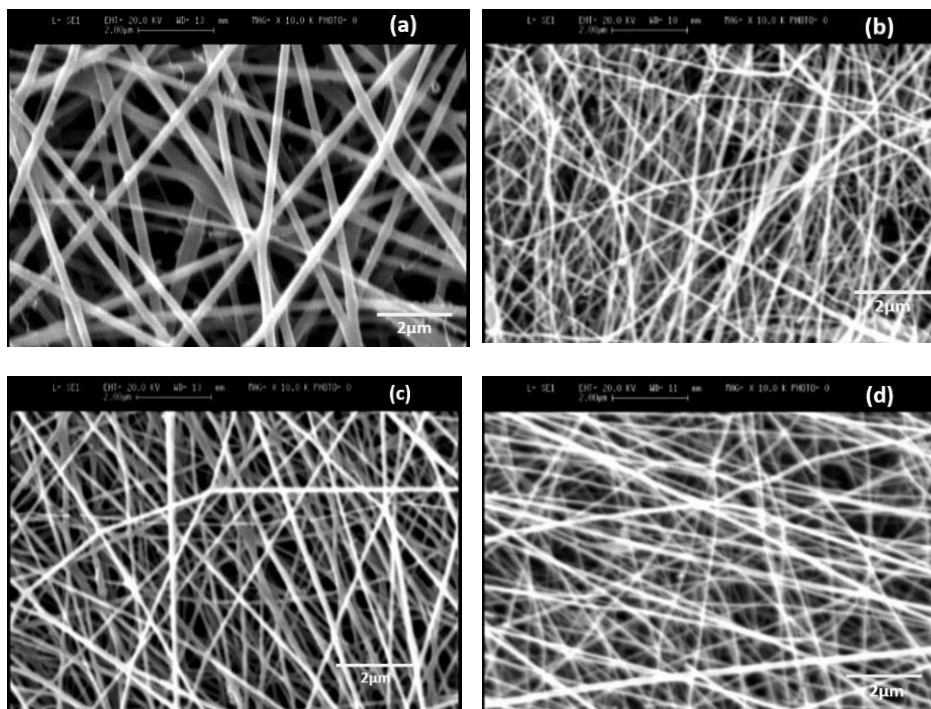


Fig. 3- SEM images of PVA/Cs fibers with a) 0%wt CNT b) 0.5%wt CNT, c) 1%wt CNT and d) 2%wt CNT.

after electrospinning. The flowing current of the polymer and fast polymerization of the solution through the transformation of the polymer solution to the fibers in the electrospinning process could be a certain reason for the reduction in the crystallinity of electrospun fibers in, here and in some other reports [30, 31].

By comparing figures 6-a and 6-b, it is clear that there are two peaks at the same angles of the CNT pattern [32] in the PVA/Cs/1wt%CNT pattern which are contributed to the CNT content of the composite. These peaks are broadened and weakened in the composite state which is due to the entanglement of CNT with the polymers and its small fraction regarding the whole composite. The interesting point here, is the appearance of a new sharp peak in the position that is known as the routine peak of Cs. It is believed that addition of nano-fillers to a polymer matrix could interfere

with the order of polymeric chains which results in reduced crystallization [33]. But, the carboxyl groups of the CNTs can form regular bonds with the NH₂ groups of Cs which create a semi-crystalline arrangement in the composite fibers, even higher than that of the pure Cs powder. It is clear that the intensity of all peaks will be increased as the CNT and Cs content increase.

After crosslinking the polymer (figure 6-b), a very high degree of crystallinity can be seen in the pattern that was expected from the contracted brittle product. Aldehyde groups of GA introduce a new crystalline ordering to the polymeric chains by linking them together.

3.4. Water Contact Angle test

The surface properties are governed by both chemical composition and geometrical structure, which can also significantly affect the performance

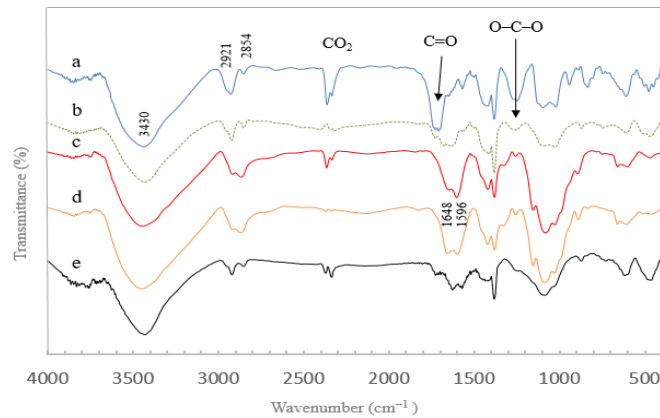


Fig. 4- The FTIR spectra of a) PVA, b) Crosslinked PVA, c) Cs, d) Crosslinked Cs, and e) CNT.

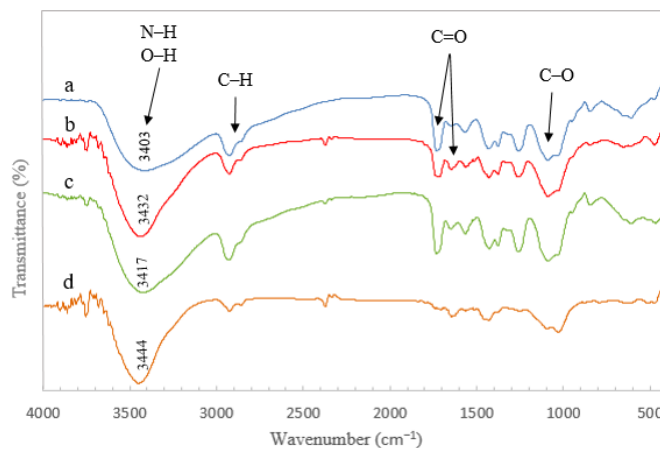


Fig. 5- The FTIR spectra of a) PVA/Cs, b) PVA/Cs/1wt%CNT, c) Crosslinked PVA/Cs, and d) Crosslinked PVA/Cs/1wt%CNT samples.

of nanomaterials. The hydrophilicity of the as-prepared membranes was evaluated by measuring the contact angle. In general, it is believed that the lower the contact angle the higher the hydrophilicity. Figure 7 demonstrates the water contact angle (WCA) of PVA/Cs nanocomposite mats with different percentages of CNT content. The WCA was decreased with the increase in the amount of CNT, indicating that the hydrophilicity

was better with the addition of Carbon Nanotubes. Since the pristine PVA/Cs nanocomposite is less hydrophilic in nature, it exhibited the higher contact angle of 83.1° which matches the literature data reporting a water contact angle of less than 90° for PVA/Cs [34,35]. However, for the PVA/Cs nanocomposites with 0, 0.5, 1 and 2%wt. CNT, the contact angle was observed to be 82.5°, 54.2°, 61.4° and 48.2° respectively. It has to be noted that

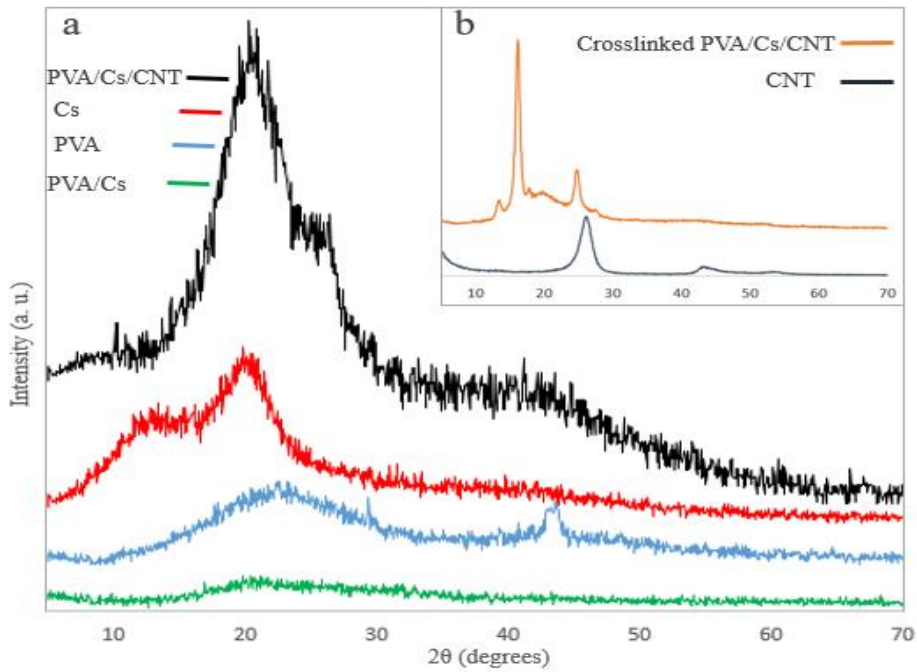


Fig. 6- XRD pattern of different combinations of PVA, Cs and CNT.

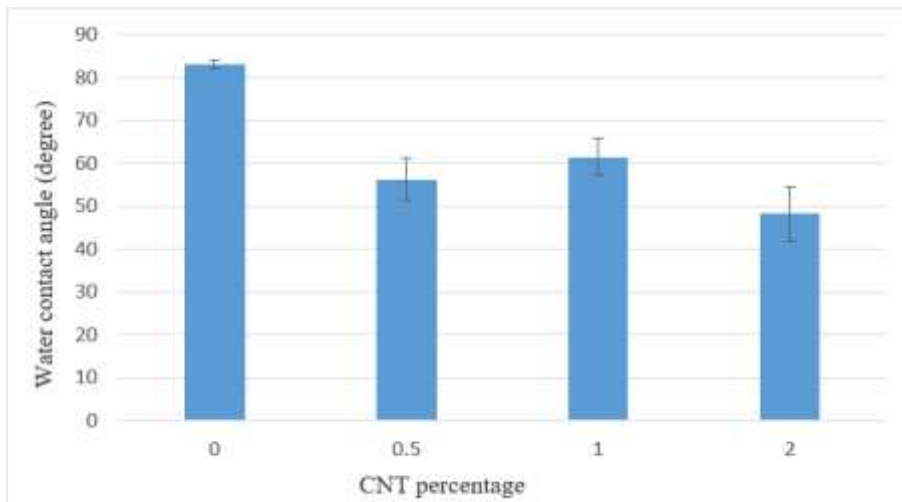


Fig. 7- he effect of various amounts of CNT on the water contact angle of samples.

the contact angle value was found to increase to 61.4° when 1.0 wt.% CNT was added; this might be due to sample defects in the PVA/Cs/1wt%CNT. The decrease in contact angle was attributed to the incorporation of Carbon Nanotubes. Both experimental observations and theoretical studies have revealed that Carbon Nanotube is a strongly hydrophobic material but, the hydrophilic functional Carboxyl groups present in the CNT has changed the interfacial free energy of the fibrous mat.

In addition, roughness is another important factor that can possibly increase the surface hydrophilicity of the samples [34]. It has been reported that super hydrophobicity can be achieved by adding roughness to hydrophobic surfaces (intrinsic CA > 90°), while adding it to the hydrophilic surfaces (CA < 90°) enhances wettability [36]. According to this hypothesis, we can expect an increase in hydrophilicity resulted from increasing roughness due to the existence of

CNT.

4. Conclusion

Smooth and uniform PVA/CS and PVA/CS/MWCNTs nanofibers were successfully fabricated by electrospinning. The most uniform fibers were obtained for the PVA/Cs mass ratio of 2.8:1 to which CNTs were added. SEM images showed that addition of the CNT to the polymer solution decrease the fibers' diameter significantly which was due to its important role in determining solution properties. It is believed that CNT improves electrospinning properties by increasing electrical conductivity and decreasing viscosity of the solution. Compatibility of suspension components to each other and an increase in the crystallinity of composite after the incorporation of CNT was observed resulted from the formation of new bonds. COOH functional groups of CNT play a significant role in rising crosslinking effect of CNT and improving its hydrophilic properties.

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