Original Article

Processing and characterizations of rotary linear needleless electrospun polyvinyl alcohol(PVA)/Chitosan(CS)/Graphene(Gr) nanofibrous membranes

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ABSTRACT

The traditional electrospinning needles are easily blocked and the processing is not suitable for mass production. In order to address the problems, this study uses a rotary linear electrode for electrospinning for the production of polyvinyl alcohol (PVA)/chitosan(CS)/graphene(Gr) nanofibrous membranes. The membranes are observed for micro-structure and tested for thermal stability, surface resistivity, and hydrophilicity, thereby examining the influence of the content of chitosan. The test results show that the presence of chitosan improves the hydrophilicity as well as affects the morphology of PVA/CS/Gr nanofibrous membranes where the nanofiber diameter is smaller. Moreover, FTIR results suggest that chitosan and PVA interact to generate hydrogen bonds that stabilize the thermal properties of nanofibrous membranes. In particular, the maximum thermal decomposition temperature of PVA/CS/Gr nanofibrous membranes composed of PVA/CS ratio being 9:1 is 297.7 °C. Finally, using chitosan also increases the electrical conductivity and decreases...
1. Introduction

Electrospinning process is considered an easy method to produce continuous nonwoven nanofibrous membranes [1,2], which feature a large surface area, high aspect ratio, random orientation, high air permeability, and water permeability. Therefore, nanofibrous membranes have been commonly used in biomedical (e.g., tissue engineering, drug delivery), environmental applications (e.g., filtration), and optoelectronic applications (e.g., sensors) [3–7]. Furthermore, electrospinning technique advances from needle electrospinning to needleless electrospinning, eliminating the disadvantage of clogged needles and significantly raising the efficiency and the yield of electrospinning process [8,9]. Needleless electrospinning is a process of self-organization, during which the surface of the liquid is triggered into jets that form nanofibers. It is difficult to control the process [10] and hence there are many types of nozzles to manipulate the needleless electrospinning process, including static bubble, magnetic fluid assisted, pyramid and coil needleless electrospinning, dynamic roller, disc, spiral coil and linear needleless electrospinning [11–18].

Chitosan (1-4-linked-2-amino-2-deoxy-D-glucopyranose) has extraordinary biology features, such as good biocompatibility, biodegradation, low immunogenicity, antimicrobial activity, and nontoxicity [19]. Moreover, skeleton is composed of amino groups. Namely, -NH₂ with positive charges can interact with microorganism cell membranes with negative charges, which accelerates the healing of wounds and demonstrates higher antibacterial activity [20,21]. Daels et al. [22] combined electrospinning nanofibers and different antimicrobial agent, such as nano-silver, bronopol, and dimethylamino 2-hydroxy-1,3-propanedil in order to remove Gram-negative and Gram-positive bacteria. The test results showed that the poliamide-based WSCP functional membranes had higher removal efficacy of microorganism. However, a large number of amino groups present on the chitosan molecule, and the repulsive force of the ionic group in the polymer skeleton increases under the action of high electric field in the electrospinning process. This reason results in the fact that chitosan was not suitable for electrospinning [23]. Chitosan could be blended with highly electrospinning polymers, such as PVA and PEO, for efficient electrospinning, which could also mitigate the interaction inside chitosan [23–25].

Graphene has a very high specific surface area, surface conductivity, and transmission of medicine to targeted cells. When used as a nanfiller, graphene can remarkably improve the mechanical properties of PVA nanofibrous membranes as well as retain the original biocompatibility, which considerably strengthens the properties of polymer-based composites at low load [26–30]. Moreover, both acetyl hydrophobic groups and the amino groups existed in chitosan molecule. The former could bind onto the surface of graphene and the latter improve the dispersion of graphene in water, which result in good distribution of the graphene in nanofibers [31]. The combination of chitosan, PVA and graphene is feasible for electrospinning. The functional groups of PVA and chitosan interact and generate strengthened hydrogen bonds, which benefits the formation of nanofibers via the electrospinning process [32]. As for biomedical materials, PVA/CS membranes are more advantageous for cell culture than pure PVA membranes because chitosan nanofibers have been proven to be fine biomaterials, especially for the use as tissue scaffolds or wound healing materials.

In this study, a custom made linear-electrode electrospinning device is used. The influences of the content of chitosan are investigated in terms of the viscosity and electrical conductivity of PVA/CS/Gr mixtures as well as the morphology, hydrophilicity, surface resistivity, micro structure, and thermal stability of the PVA/CS/Gr nanofibrous membranes. The preparation and property evaluations of PVA/CS/Gr nanofibrous membranes can be a valuable reference for mass production of nanofibrous membranes in the future.

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA, Mw =84000–89000) is purchased from Changchun Chemical, China. Chitosan (CS, Changchun Chemical, China) has degree of deacetylation ≥95%. Polyvinylpyrrolidone (PVP, K13-18, Mr =10000) is purchased from Shanghai Macklin Biochemical, China. Multi-layered graphene (Gr, P-ML20, Enerage, Taiwan) has an average thickness of 50–100 nm, specific surface area <50 m²/g, and the conductivity >700 S/m. Deionized water is also used in this study.

2.2. Preparation of PVA/CS/Gr nanofibrous membranes

Acetic acid (5 g) and chitosan powder (5 g) are added to 90 mL of deionized water, and then mixed with a magnetic mixer at room temperature for 12 h in order to obtain a 100 mL chitosan solution with a concentration of 5 wt%. Next, 7.5 wt% PVA/Gr mixture is made as follows. Graphene is added to a 1% PVP solution and processed with ultrasound machine for 3 h, after which PVA powder is added and mixed for another 2 h using a magnetic stirrer. Five different PVA/Gr mixtures are composed of 0.1 g of graphene and 7.5 wt% of PVA/Gr solution in 100, 90, 80, 70, and 50 mL. Based on the PVA/CS volume ratios (10:0, 9:1, 8:2, 7:3, and 5:5), 5 wt% chitosan solution and 7.5 wt% PVA
solution are mixed at room temperature for 6 h using magnetic stirrer, forming PVA/CS/Gr mixtures.

PVA/CS/Gr mixtures are electrospun at 25°C and a relative humidity of 23%. The linear electrospinning device is composed of a rotary linear spinning head, a high voltage power source, a mesh collector that connects to the ground, and a nozzle with a length of 15 cm and a diameter of 0.8 mm. PVA/CS/Gr mixture is poured into the Spinning slot. The rotary speed of the rotary linear spinning head is 72 r/h and both the voltage and collection distance are specified as Fig. 1.

2.3. Characterizations nanofibrous membranes

The viscosity of the mixtures was measured using a viscometer (NDJ-8S, Bangxi Instrument Technology, China). The completely dissolved mixtures were measured for the viscosity using No. 2 rotor. To ensure the accuracy of the viscosity measurement, the data was collected between 10% and 90% of the effective range of the rotor and the corresponding rotary speed.

Electric conductivity of the mixtures was measured using a tester (CT-3030, ST3100MZH/F, OHAUS, US). The probe of the tester was immersed in the mixtures and the electric conductivity is detected.

Morphology and diameter of the nanofibers were measured as follows. A scanning electron microscopy (SEM, TM3030, HITACHI, Japan) was used to observe the morphology of the nanofibers. A bundle of 100 nanofibers was used to compute the average diameter.

The wettability of the membranes were measured according to water contact angle. A surface contact angle instrument (JC2000DM, Shanghai Zhongchen Digital Technic Apparatus, Shanghai, China) and deionized water were used to measure the water contact angle at 25°C, thereby examining the wettability of the PVA/CS/Gr nanofiber membranes.

The thermogravimetric (TG) measurement was conducted using a thermogravimetric analyzer (TG 209F3, NETZSCH, Bavaria, Germany) with nitrogen gas at a flow rate of 60 mL/min. The relative mass loss of the samples was recorded from 25°C to 700°C with a heating rate of 10°C/min, thereby characterizing the thermal stability of the nanofiber membranes.

The crystallization, melting behaviors, and thermal properties of nanofibrous membranes were measured using differential scanning calorimetry (DSC, 200F3, NETZSCH, Germany). Samples were heated from room temperature to 260°C at increments of 30°C/min in order to eliminate the thermal history. Next, samples were heated to 260°C at increments of 10°C/min in order to observe the crystallization and melting behavior.

Fourier Transform infrared spectroscopy (FTIR) measurement was conducted to analyze the chemical bonds of the nanofibrous membranes in a range of 400-4000 cm⁻¹ using FTIR (Bruker Tensor, Germany).

X-ray diffraction (XRD) measurement was conducted using an X-ray diffraction in a range of 5-50° (XRD, BRUKER-D8, Advance Spectrometer, Germany).

The surface resistivity of the nanofibrous membranes was measured using a surface resistance instrument (RT-1000, OHM-STAT, Static Solutions, Hudson, NY, USA) as specified in JIS L1094. The instrument equipped with a 5-pound weight ensured that the two parallel electrodes were in good contact with the surface of the sample. Twenty samples for each specification were taken for the mean.

3. Results and discussion

3.1. Effect of content of CS on diameter and morphology of nanofibers

Fig. 2 shows the SEM images and fiber diameter distribution of PVA/CS/Gr nanofibrous membranes composed of specified 0.1 wt% graphene as related to different PVA/CS ratios. Fig. 2 (a–e) shows that the PVA/CS/Gr nanofibrous membranes made of PVA/CS ratio of 10:0, 9:1, 8:2, 7:3, and 5:5, respectively. The morphology and diameter of nanofibers are highly dependent on the properties of electrospinning mixtures. When the ratio is 9:1 and 8:2, some of the nanofibers are spindle-shaped. Furthermore, a ratio of 7:3 generates a great amount of spindle-shaped and some bead-shaped nanofiber. More contained chitosan results in greater amount of spindle-shaped fibers, which indicates the bad formation of nanofibers. When the PVA/CS ratio is 5:5, the mixtures fail to form nanofibers but create large size beads. When chitosan is more than 50 wt%, the mixture cannot be electrospinning into nanofibers. With an increase in the content of chitosan, the diameter of nanofibers first increases and then decreases. The nanofibers have a diameter with corresponding PVA/CS ratio as 120 nm for 10:1, 124 nm for 9:1, 132 nm for 8:2, and 122 nm for 7:3. The diameter distribution becomes narrow, and therefore, the properties of PVA/CS/Gr mixtures remarkably affect the diameter and morphology of the nanofibers.

Fig. 3 shows the relationship between the conductivity and the concentration of PVA/CS/Gr mixtures. When PVA/CS ratio changes from 9:1 to 5:5, the conductivity and viscosity
of the mixtures increase significantly. Increasing the content of CS improves the conductivity of the mixtures from 1.11 to 3.56 mS/cm and the viscosity from 242 mPa·s to 609 mPa·s. In addition, chitosan is a polyelectrolyte while PVA is a nonionic polymer. Hence, the addition of PVA to the chitosan solution can reduce the intermolecular force of the spinning solution, resulting in a decrease in the viscosity of the solution, which is advantageous for the formation of electrospinning nanofibers. During the electrospinning process of sleek nanofibers, a relatively higher conductivity and viscosity are beneficial factors. Highly viscous polymer solutions exhibit longer stress relaxation, which prevents the rupture of the electrospinning jets. Meanwhile, highly conductive polymer solutions help to strengthen the electric field, which in turn improves winding instability as well as the formation of fibers. Nonetheless, the conductivity of the traditional chitosan solution does not allow a large-scale electrospinning as the solution undergoes the atomization and then splits into polydisperse electrosprays. Therefore, when the PVA/CS ratio is 9:1 or 8:2, the increase in the diameter of nanofibers is attributed to the rise in the viscosity of PVA/CS/Gr mixtures. Moreover, a PVA/CS ratio of 7:3 provides the nanofibers with a finer diameter, which is attributed to the higher conductivity of the mixture. Thus, the conductivity demonstrates a greater influence than the viscosity. When the PVA/CS ratio is 5:5, the conductivity of PVA/CS/Gr mixture is too high due to the excessive chitosan. As a result, the solution is highly atomized and thus splits into polydisperse electrosprays, so fibers are poorly formed [30].

In sum, the conductivity of mixtures is proportional to the content of chitosan, which adversely affects the formation of PVA/CS/Gr nanofibrous membranes and produces bead- and spindle-shaped nanofibers. Noticeably, a PVA/CS ratio of 5:5 renders the nanofibers with a great amount of beads [33].

3.2. Effect of content of CS on hydrophilicity of PVA/CS/Gr nanofibrous membranes

Fig. 4 shows the water contact angle of PVA/CS/Gr nanofibrous membranes as related to the content of chitosan. Namely, the water contact angle indicates the hydrophilicity of the membranes. Chitosan and PVA are both hydrophilic and can be dissolved in water. Because PVA has considerable hydrophilic –OH groups and CS has –NH₂ and –COOH groups, which results in a high affinity with water molecules and provides nanofibers with greater moisture absorption capacity. The membranes have a water contact angle of 26.6° for a PVA/CS ratio being 10:1 and 56° for a PVA/CS ratio being 9:1. The presence of chitosan increases the water contact angle of the PVA/CS/Gr nanofiber membrane. This is because the addition of chitosan makes the conductive filler more uniformly dispersed in the spinning solution. After electrospinning, more uniform dispersion of the hydrophobic graphene in the composite fiber membrane reduces the hydrophilicity of the nanofiber membrane. Afterward, the water contact angle of membranes decreases as a result of more chitosan. The molec-
3.3. Effect of content of CS on thermal properties of PVA/CS/Gr nanofibrous membranes

Fig. 5 shows the DSC curves of PVA/CS/Gr nanofibrous membranes. As the content of chitosan increases, the endothermic peak decreases from 219.5° to 212.7° (Table 1), and meanwhile becomes broader and shorter. This indicates that the increase of CS content hindered the formation of crystallization in the nanofibers during electrospinning as confirmed by XRD analysis hereafter.

Figs. 6 and 7, respectively, show the TG analysis and the DTG analysis of PVA/CS/Gr nanofibrous membranes as related to the content of chitosan. The curves can be divided into three stages. The first stage is the initial heating stage where the weight loss is ascribed to the evaporation of water before the temperature reaches 200°. The second stage shows a drastic weight loss. At temperature between 200° and 400°, the weight loss is attributed to the thermal decomposition of polar groups, dehydration of polymer, and formation of polyacetylene structure. In the final stage occurring between 400° and 550°, the weight loss is due to the thermal decomposition of PVA and chitosan main molecular chains, which subsequently releases CO₂ and forms oxides [36,37]. Two weight loss acceleration peaks are found in the Fig. 7. As the chitosan content increases, the maximum decomposition temperature gradually increases from 253.2° to 297.7° (see Table 1). The amino groups from chitosan and hydroxyl groups from PVA produce hydrogen bonds. The greater the content of chitosan,
the more hydrogen bonds, making the degradation of polar groups more difficult. Based on Table 1, when the PVA/CS ratio changes from 10:0 to 5:5, the residual mass increases from 15.2% to 34.3% as a result of increasing content of chitosan. As for the thermal stability of PVA/CS/Gr nanofibrous membranes, the presence of chitosan undermines the crystallinity of PVA. Similarly, the presence of water also has a negative influence on the thermal stability of nanofibrous membranes. More chitosan is detrimental to the crystallinity of PVA and the initial decomposition temperature of membranes. Therefore, increasing the content of chitosan causes a low mass loss, which equivalently means a high residual mass.

3.4. Effect of content of CS on FTIR of PVA/CS/Gr nanofibrous membranes

Fig. 8 shows the FTIR spectrum of PVA/CS/Gr nanofibrous membranes as related to the PVA/CS ratio. The nanofibrous membranes are made of a specified 0.1 wt% of graphene. The group stretching vibration corresponding to each characteristic peak is shown in Table 2 [38–41]. Most of the absorption peaks did not change significantly after adding Gr. Meanwhile, the characteristic band of the glycation structure is at 847 cm\(^{-1}\), 1095 cm\(^{-1}\), and 1152 cm\(^{-1}\). The FTIR spectrum shows that increasing the content of CS strengthens the absorption peak of PVA/CS nanofibers while the absorption peak of the Amide I group is decreased and the absorption peak of the Amide II group is increased. Furthermore, the absorption peak caused by stretching vibration at 1293 cm\(^{-1}\) for C–O is also improved, which indicates that the O–H group of PVA forms a hydrogen bond with the N–H and O–H groups [42,43].

3.5. Effect of content of CS on XRD of PVA/CS/Gr nanofibrous membranes

Fig. 9 shows the XRD chart of PVA/CS/Gr nanofibrous membranes. Comparing with pure PVA, PVA/CS/Gr nanofibrous membranes have three typical peaks around \(2\theta = 10.7^\circ, 19.3^\circ\) and \(22.5^\circ\). The diffraction model of CS powder showed three typical peaks at \(2\theta = 10.5^\circ, 15.4^\circ\) and \(19.9^\circ\). When CS and PVA molecules have no or a low interaction, either CS or PVA has its own crystal area, and the XRD curve will be represented as a simple mixing curve for CS and PVA. These evidences further conclude that CS and PVA molecules trigger strong interaction. In addition, graphene shows a distinct diffraction peak at \(2\theta = 26.8^\circ\) for PVA/Gr and CS/PVA/Gr also have strong peaks around \(2\theta = 26.8^\circ\) [44,45]. Besides, CS/PVA/Gr nanofibrous membranes exhibit two major diffraction peaks at \(2\theta = 10.1^\circ\) for chitosan and \(2\theta = 19.8^\circ\) for PVA. Compared with the PVA/Gr composite membrane, the CS/PVA/Gr composite membrane gradually increased at a peak of \(2\theta = 10.1^\circ\) as the chitosan content increased. Moreover, the characteristic peak of the CS/PVA/Gr composite nanofibers at around 19.8° shifted to the left and showed a relatively blunt broad peak. This observation proves that the employment of electrospinning delays the crystallization rate of PVA/CS/Gr nanofibrous mem-

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**Table 2 – FTIR characteristic peaks.**

<table>
<thead>
<tr>
<th>(\sigma) (cm(^{-1}))</th>
<th>3271</th>
<th>1653</th>
<th>1556</th>
<th>1448</th>
<th>1324</th>
<th>1095</th>
<th>847</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>O–H</td>
<td>Amide I</td>
<td>Amide II</td>
<td>–CH₂–</td>
<td>–OH</td>
<td>C–O</td>
<td>C–C</td>
</tr>
</tbody>
</table>

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Fig. 8 – FTIR spectrum of PVA/CS/Gr nanofibrous membranes as related to PVA/CS ratios of a) 10:0, b) 9:1, c) 8:2, d) 7:3, e) 5:5, and f) pure PVA.

Fig. 9 – XRD chart of PVA/CS/Gr nanofibrous membranes.
the presence of chitosan helps the distribution of graphene in the PVA/CS/Gr mixtures, allowing graphene to be evenly dispersed in the nanofibrous membranes. Hence, there are more conductive paths that decreases the surface resistivity. Moreover, the presence of chitosan also increases the dissociative charged particles in the membranes, thereby strengthening their conductivity.

4. Conclusion

In order to realize the controllable large-scale production and obtain better properties of nanofibrous membranes, this study uses a rotary linear-electrode electrospinning technique to produce PVA/CS/Gr nanofibrous membranes. The influences of the content of chitosan on the viscosity and conductivity of the electrospinning solutions as well as the morphology, diameter, and properties of nanofibrous membranes are investigated. The test results show that more chitosan causes more spindelike nanofibers and a poor formation of nanofibers. The diameter of nanofibers first increases and then decreases with the increasing content of chitosan. When PVA/CS ratio changes from 9:1 to 5:5, the conductivity of the PVA/CS/Gr mixtures increases from 1.11 to 3.56 mS/cm while the viscosity increases from 242 mPa·s to 609 mPa·s. Similarly, increasing the content of chitosan first increases and then decreases the water contact angle of the nanofibrous membranes because chitosan triggers an even dispersion of conductive fillers and chitosan molecular chains are composed of hydrophilic amino and hydroxyl groups. A decrease in the absorption peak of the Amide I group at 1653 cm⁻¹ and an increase in the absorption peak of the Amide II group at 1556 cm⁻¹, which indicates that hydrogen bond binding between the O–H group of PVA and the N–H and O–H groups. Due to the increase in chitosan and the hydrogen bonds between chitosan and PVA, the nanofibrous membranes exhibit constantly increasing temperature for maximum thermal decomposition rate from 253.2 °C to 297.7 °C as well as more residual mass. As for DSC results, increasing the content of chitosan decreases the temperature of absorption peak from 219.5 °C to 212.7 °C, which proves that the content of chitosan affects the crystallization of nanofibers. Moreover, the peak at 29° = 10.1° is gradually strengthened whereas the peak at 19.8° shifts leftward and is thus exhibited in a flat peak. The observation indicates a drastic interaction among CS, PVA, and graphene, suggesting the formation of hydrogen bonds. Finally, the surface resistivity of nanofibrous membranes also decreases as a result of the increasing content of chitosan. This study provides the possibility of mass-production of electrospinning PVA/CS/Gr nanofibrous membranes in the future. In the future, we will discuss the applications of these fabricated PVA/CS/Gr nanofibrous membranes in medical field.
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