Manufacturing Process and Property Evaluations of Polyethylene Oxide/Water-Soluble Chitosan Electrospun Nanofiber Membranes

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ABSTRACT

This study proposes making polyethylene oxide (PEO) and water-soluble chitosan (WSC) nanofiber membranes via electrospinning. PEO/WSC mixtures are evaluated in terms of viscosity and conductivity, and are then electrospun into PEO/WSC nanofiber membranes using different voltages. Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR) are performed to examine the structure of the nanofiber membranes. The test results indicate that a combination of a voltage of 20kV and a PEO/WSC ratio of 70:30 can form complete electrospun nanofibers. In addition, increasing the viscosity of the PEO/WSC mixtures can decrease the amounts of beads in the nanofibers.

INTRODUCTION

A great deal of spinning techniques have been developed for the production of nanofibers, such as dry spinning, wet spinning, melt spinning, polymer self-assembly, drawing, and electrospinning. Electrospinning is a relatively simple and efficient method, and it has advantages of ease of use, high surface area, the
ultrafine diameter, and high degree of porosity [1, 2]. These advantages enable the nanofiber membranes to facilitate the reorganization of skin tissues, and help the removal of secretion as well as the preservation of moisture. As a result, nanofiber membranes have been commonly used as biomedical textiles [3].

Natural polymers include sodium alginate, chitosan, and gelatin. Chitin is an organic matte that has ease of access, and it is a polymer composed of N-acetyl-D-glucosamine and glycosidic linkage. Chitosan is the product of acetylated chitin [4]. As it has high biocompatibility, avirulence, antibacterial properties, anti-inflammatory features, and promotes coagulation, chitosan is widely used as a hemostasia dressing, drug carrier, and dialyzer in the medical field. Chitosan is only dissolved in acid, which raises concerns about possible damage to cells in biomedicine. Thus, using water-soluble chitosan may exclude the toxicity caused by acid solution and damage to biological cells clinically [5, 6].

Polyethylene oxide (PEO), also known as PEG, is a polymer that exhibits crystallinity, ease of workability, and water solubility [7]. PEO has a molecular weight more than 20,000 Da, while PEG has a molecular weight lower than 20,000 Da. PEO can modify drug protein and protect drug molecules to prolong their efficacy. In addition, PEO is also used as additive in food [8-10].

This study combines PEO that has a high hydrophilicity and water-soluble chitosan, and the morphology of their nanofiber membranes is then observed. PEO and WSC are blended with ratios of 100:0, 70:30, and 50:50 to form the electrospinning solutions. The high viscosity of PEO is conducive to electrospinning, and can help WSC solution that is not easily electrospun to form PEO/WCS electrospun nanofiber membranes. During the electrospinning, the jet speed of the spinning solution is set to 0.5 mL/hr, while the voltages are set to 15 and 20 kV. The electrical conductivity, viscosity, scanning electron microscopy (SEM), diameter of nanofiber, and Fourier transform infrared spectroscopy (FT-IR) measurements are performed in order to evaluate how voltages and blending ratios affect the PEO/WCS nanofiber membranes.

**EXPERIMENTAL**

**Materials.**

Polyethylene oxide (PEO, Sigma, US) has a molecular weight of 200000 Da. Chitosan powder (Charming & Beauty, Taiwan, R.O.C.) has a molecular weight of 50000 Da.

**Preparation of PEO/WSC Mixtures.**

PEO powders are dissolved in deionized water at 50°C in order to form 1, 2, and 3wt% PEO solution. WSC is dissolved in deionized water at room temperature in order to form a 3wt% WSC solution. Then, PEO and WSC are blended with ratios of 100:0, 70:30, and 50:50 in order to form PEO/WSC mixtures. For 70:30 and 50:50, the solid content of the mixtures is specified as 3wt%.
Preparation of PEO/WSC Electrospun Nanofiber Membranes.

The PEO/WSC mixtures are loaded into a syringe that has a needle point of 18G, and are then electrospun with voltages of 15 and 20kV. The efflux velocity is 0.5 mL/hr, while the distance between the syringe and the collecting aluminum foil is 15cm. The ambient temperature is the room temperature in a closed environment, and the humidity is 40%.

TESTS.

Viscosity Test.

PEO/WSC mixtures are kept at room temperature, and wait for the temperature of mixtures to decrease. The mold that is attached to the viscosity tester (Viscobasic + L, FUNGILAB S.A., Spain) is then soaked in the mixtures for the viscosity measurement in order to examine the influences of the PEO/WSC ratios.

Electrical Conductivity Test.

PEO/WSC mixtures are kept at room temperature, and wait for the temperature of mixtures decreased. The electrical conductivity tester (EC500, ExStik, US) is used to measure the electrical conductivity of the mixtures in order to examine the influences of the PEO/WSC ratios.

Scanning Electron Microscopy (SEM).

PEO/WSC electrospun nanofiber membranes that are made at volume ratios of 100:0, 70:30, and 50:50 are trimmed into 1 cm x 0.5 cm sections. Samples are affixed to the SEM platform using a carbon adhesive tape, and are then coated with a thin layer of gold by the gilding machine (E-1010, HITACHI, Japan). A scanning electron microscope (S3000N, HITACHI, Japan) is used to observe the morphology of the samples, and the samples are scanned to produce images using an electronic beam.

Fiber Diameter Measurement.

The morphology images of PEO/WSC electrospun nanofiber membranes that are photographed by the SEM are recorded. The fiber diameters are measured using Image-Pro Plus in order to examine the influences of the PEO/WSC ratios.

Fourier Transform Infrared Spectroscopy (FT-IR).

The functional groups of PEO/WSC electrospun nanofiber membranes are evaluated using FT-IR (IR Affinity-1, Canada). Samples made at volume ratios of 100:0, 70:30, and 0:100 are dried for FT-IR. The scanning frequency is 400-4000 cm-1 and the air serves as the background for the scanning. Samples are then scanned in the same frequencies for comparison and analyzed.
RESULTS AND DISCUSSION

Viscosity and Electrical Conductivity

The PEO concentration has a positive influence on the viscosity of the pure PEO solutions, while the viscosity of mixtures decreases when the content of low viscous WSC is increased (Table 1). During electrospinning, the surface tension of the droplets depends on the viscosity of the solutions/mixtures. A viscosity lower than 1000 cP results in a small surface tension, and prevents the formation of a Taylor cone. A viscosity that is over 1000 cP results in a sufficient surface tension that facilitates the formation of Taylor cone and then electrospinning. The nanofibers have a diameter that is proportional to the viscosity [11]. In addition, WSC solution is more electrically conductive than PEO solution, according to the electrical conductivity test results. Therefore, the PEO/WSC mixtures that contain more WSC have a higher electrical conductivity. Moreover, electrical conductivity is associated with the conduction of the mixtures and the drawing force of the droplets to the collecting plate. The higher the electrical conductivity, the greater the drawing force. A PEO/WSC ratio of 70:30 provides the mixtures with the viscosity and electrical conductivity that are required by electrospinning.

| Table 1. Viscosity and electrical conductivity of PEO/WSC electrospun nanofiber membranes. |
|---------------------------------|-----------------|-----------------|
| Ratio                          | Viscosity (cP)  | Electrical Conductivity (µS) |
| PEO1wt%                        | 100 : 0         | 378.4±28.9       | 81.1 |
| PEO2wt%                        | 100 : 0         | 2727.5±65.2      | 85.2 |
| PEO3wt%                        | 100 : 0         | 10880.8±189.4    | 115.4 |
| PEO/WSC3wt%                    | 70 : 30         | 1422.3±33.6      | 2485.6 |
| PEO/WSC3wt%                    | 50 : 50         | 675.4±10.7       | 3756.8 |
| WSC3wt%                        | 0 : 100         | 138.2±3.6        | 6155.2 |

SEM and Fiber Diameter Analyses

Fig. 1 shows that when voltage is 15kV, PEO solution and PEO/WSC mixture (70:30) can be electrospun into nanofibers. The viscosity of these two mixtures is high, which allows the jet to form a Taylor cone and then nanofibers. However, a PEO/WSC ratio of 50:50 does not have enough viscosity, therefore the jet is not able to form a Taylor cone. The nanofibers are thus bead-shaped. Moreover, the average diameter of PEO nanofibers is 324.1nm, while the average diameter of PEO/WSC nanofibers is 317.7nm. The range of diameters falls between 250nm and 400nm, indicating an even distribution of nanofibers.
Figure 1. SEM images of PEO/WSC electrospun nanofiber membranes in relation to blending ratios of 100:0, 70:30, and 50:50. The voltage is specified as 15kV.

Fig. 2 shows that when applying a voltage of 20kV, PEO solution and PEO/WSC mixtures can result in nanofibers. In comparison to SEM images using 15kV, the nanofibers made by using 20kV have a smaller diameter: 252.8nm for PEO nanofibers and 297.3nm for PEO/WSC nanofiber. The diameter is decreased by 71.3nm (PEO) and by 20.4nm (PEO/WSC). A high voltage results in a high drawing force to electrospin the solution, thereby decreasing the diameter of the nanofibers. However, at a high voltage, a PEO/WSC ratio of 50:50 still results in bead-shaped nanofibers, as the viscosity of the mixture is lower than 1000cP. With a low viscosity, it is difficult to form a Taylor cone, and causes discontinuous jet flows and eventually beads in the nanofibers.

Figure 2. SEM images of PEO/WSC electrospun nanofiber membranes in relation to blending ratios of 100:0, 70:30, and 50:50. The voltage is specified as 20kV.

**FT-IR Analyses**

Fig. 3 shows that for PEO, the characterization peak with corresponding frequency are C-O-C (1144 cm\(^{-1}\)), CH\(_2\) (1461 cm\(^{-1}\)), and C-H (2876 cm\(^{-1}\)), while for WSC, the absorption at 1650 cm\(^{-1}\) is amide bond I, and that at 1540 cm\(^{-1}\) is amide bond II. Amide bond I has the characterization peak of C=O, and amide bond II has characterization peaks of N-H and C-N. The characterization peaks of WSC
are present in FT-IR analyses of PEO/WSC mixtures, indicating that the two materials have been successfully combined. Moreover, the comparison of absorption peaks in terms of pure PEO solution, pure WSC solution, and PEO/WSC mixtures also indicate that PEO and WSC are evenly blended in the mixture.

![Figure 3. FT-IR spectrum of PEO/WSC electrospun nanofiber membranes in relation to PEO/WSC ratios of 100:0, 70:30, and 0:100.](image)

**CONCLUSION**

This study successfully produces PEO/WSC electrospun nanofibers. The test results suggest that viscosity and electrospinning voltage are highly associated with the formation of the nanofibers. In particular, a PEO/WSC ratio of 70:30 results in optimal fiber formation, and FT-IR spectrum also indicates that PEO and WSC are evenly blended. According to the test results, the combination of a voltage of 20kV and a PEO/WSC ratio of 70:30 can effectively produce nanofibers with lower amounts of beads and small diameter size. With a voltage of 20kV and a 70:30 ratio, the diameter is decreased by 20.4nm, which significantly improves the electrospinning of water-soluble chitosan.

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