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ELECTROSPUN POLYSTYRENE SULFONIC ACID-CO-MALEIC ACID/ POLYVINYL ALCOHOL BLEND ION EXCHANGE FIBERS

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KEYWORDS: Crosslink, nanofibers, PSSA-MA, ion exchange fibers

INTRODUCTION

Ion exchange membranes and resins are applied widely in various fields^{1, 2)}. In pharmaceutical, ion exchange resins are extensively studied in various drug delivery systems³⁾. Recently, increasing attention has been focused on the ion exchange fibers due to many advantages of them over the ion exchange resins⁴⁾. Electrospinning is a simple and easy way to control the morphology of ultrafine fibers. The fibers produced by this method have shown amazing characteristics, such as a very large surface-to-volume ratio and a high porosity with a small pore size. Many polymers are used to produce nanofibers by electrospinning⁵⁾. Some polymer nanofibers can be convert into an ion exchange fibers by chemical reaction such as polystyrene (PS) nanofibers⁶⁾, polytetrafluoroethylene (PTFE) fibers⁷⁾, etc. However, these ion exchange polymers do not have the biodegradable property and their preparation often proceeds via the chemical treatment using toxic media which are very dangerous for environment. Therefore, biodegradable ion exchange fibers prepared by the physical treatment using no toxic media is an interesting and promising approach. Many ionic polymers such as poly (styrene sulfonic acid) (PSSH), poly (sodium styrene sulfonate) (PSSNa), poly (acrylic acid) (PAA), poly (dimethyl dimethylene piperidinium chloride) (PDMeDMPCl)⁸⁾, poly (acrylic acid-co-maleic acid) (PAM)⁹⁾ and poly (styrene sulfonic acid-co-maleic acid) (PSSA-MA) were widely blended with polyvinyl alcohol (PVA) to prepare ion exchange membranes by film casting method¹⁰⁻¹²⁾. Crosslinking the ion exchange membranes is required to improve the ion exchange membranes properties. There are various methods to crosslink the ion exchange membranes depending on the structure properties of polymer. Due to the simple and environmental friendliness of thermally crosslinking method, therefore, the aim of this study was to prepare ion exchange fibers from PSSA-MA, an ionic polymer, blended with PVA by using the electrospinning technique and then thermally crosslinked. The factors such as the PSSA-MA/PVA ratios, crosslinking time and crosslinking temperature affecting the morphology and ion exchange capacity (IEC) were investigated.

MATERIALS AND METHODS

Material: The PSSA-MA (sodium salt, styrene sulfonic acid: maleic acid = 3:1, average Mw=20,000 g/mol). Polyvinyl alcohol (PVA) (degree of polymerization \approx 1600, degree of hydrolysis \approx 97.5-99.5 mol%) was purchased from Fluka, Switzerland. Deionized water was used in this work.

Preparation of PSSA-MA/PVA ion exchange nanofibers

Electrospinning process: The PSSA-MA and PVA aqueous solutions were prepared at 20% and 10% w/w, respectively, and then mixed at the solid polymer weight ratio of 0.2/1, 0.3/1, 0.4/1, 0.5/1, 0.6/1, 0.7/1, 0.8/1, 0.9/1 and 1/1. The polymer solution was taken up in a 5-mL glass syringe equipped with a 20-gauge, stainless steel needle (diameter = 0.9 mm) at the nozzle. The needle was connected to the emitting electrode of positive polarity of a Gamma High Voltage Research device. The electrospinning process was conducted at 25 °C with the fix applied voltage, the distance between the tip and the collector, and the feeding rate as 15 kV, 15 cm and 0.4 ml/h, respectively.

Crosslinking process: The PSSA-MA/PVA nanofibers were thermally crosslinked by placing in a hot air oven at 80-150 °C for 0.25-7 h.

Characterization: Morphology and diameter were investigated using a scanning electron microscope (SEM) and a Fourier Transform Infrared spectrophotometer (FT-IR). Water insolubilization, ion exchange capacity (IEC) and water uptake was determined.

RESULTS AND DISCUSSION

The PSSA-MA/PVA nanofibers were prepared by various PSSA-MA/PVA ratios including 0.2/1, 0.3/1, 0.4/1, 0.5/1, 0.6/1, 0.7/1, 0.8/1, 0.9/1 and 1/1 (g/g). Figure 1 showed the SEM images, the visual appearance and the diameter of fibers. The bead-free uniform fibers were observed at PSSA-MA/PVA ratios of 0.2/1, 0.3/1 and 0.4/1 whereas the bead-on-string fibers occurred in other ratios. As the higher PSSA-MA/PVA ratios (0.5/1-1/1) were used, the more beads in fibers were occurred. The visual appearance of the PSSA-MA/PVA nanofibers was similar in each ratio, except the color intensity of fibers that was more intense when increasing the PSSA-MA/PVA ratio. The diameter of fibers was

slightly decreased with increasing the PSSA-MA/PVA ratio due to the lower viscous solutions. Thus, there was lower resistance for fibers to be stretched with electrostatic force in the electrospinning process. This result was in accordance with a previous study in which the diameter of PVA nanofibers prepared from the low PVA concentration (low viscosity) was smaller than the PVA nanofibers prepared from high PVA concentration (high viscosity)¹³. From this experiment, the smooth bead-free nanofibers were successfully received from the PSSA-MA/PVA ratios up to 0.4/1; therefore, it was chosen to crosslink by thermal treatment.

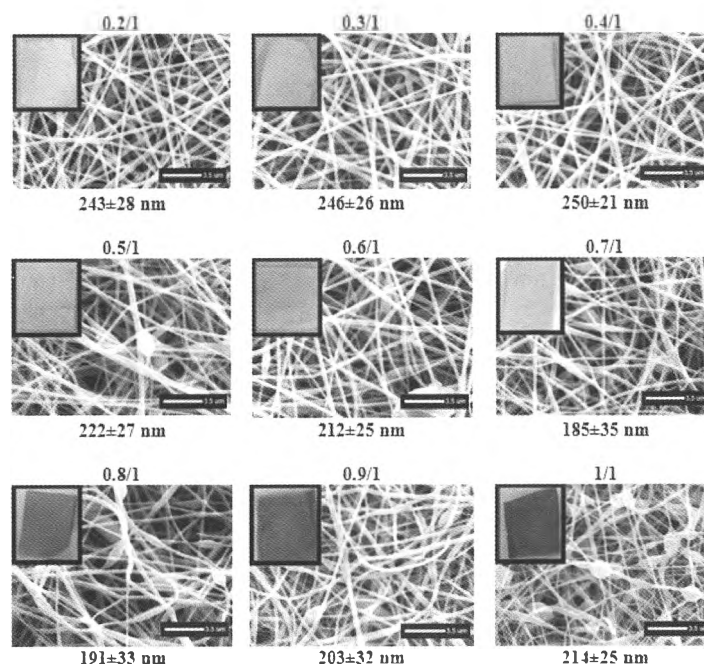


Figure 1 Morphology of the nanofibers at various PSSA-MA/PVA ratios

The PSSA-MA/PVA fibers were crosslinked at 80-150 °C for 0.25-7 h. The success of crosslinking fibers was confirmed by determining water insolubilization and FTIR. The crosslinking time and temperature significantly affected on water insolubilization of fibers. The PSSA-MA/PVA fibers were not successfully crosslinked at the temperature of 80 and 100 °C. At 120 °C, the significantly higher water insolubilization was observed as 68.2, 90.2, 97 and 98% when the crosslinking time was 1, 3, 5 and 7 h, respectively. This result was in accordance with the SEM images of the crosslinked fibers after water insolubilization testing (Table 1). The SEM images at 0.5 h showed the fiber was mostly dissolved in water. At the crosslinking time increased, the fibers persisted but they shrank and moved into closer proximity. From the water insolubilization and SEM images, it indicated that the appropriate crosslinking time was 5-7 h at 120 °C and 1 to 7 h at 130, 140 and 150 °C. The water insolubilization was 95-99%. Although at 150 °C the fastest and the percentage of water insolubilization were increased significantly, the appearance of crosslinked fibers was burnt, crispy and very inflexible. Therefore, the optimum temperature and time for crosslinked PSSA-MA/PVA nanofibers were 120-140 °C for 1-7 h.

The FTIR spectra of the pure PVA, the PSSA-MA, the PSSA-MA/PVA nanofibers and the crosslinked PSSA-MA/PVA nanofibers (140 °C, 5 h) are shown in Fig.2. The PSSA-MA/PVA nanofibers's spectrum showed the sulfonic acid peak of PSSA at 1186, 1121 and 671 cm^{-1} , the O-H stretching vibration peak at 3438 cm^{-1} which shifted to the higher wavelength region compared with the O-H peak of pure PVA. It might be due to the formation of hydrogen bonds between O-H groups of the PVA and SO_3H groups of the PSSA¹⁰⁻¹². The C=O vibration peak and the O-H peak of maleic acid at 1716 and 915 cm^{-1} respectively. The crosslinked PSSA-MA/PVA nanofibers showed the different peak compared with the un-crosslinked nanofibers. The O-H peak of maleic acid at 915 cm^{-1} disappeared because the COOH groups of maleic acid were interacted with the OH groups of PVA to create ester bond. The C=O peak of ester bond occurred at 1716 cm^{-1} but the C-O peak of ester bond at 1200 cm^{-1} was hidden by the sulfonic acid peak. Therefore, the PSSA-MA/PVA nanofibers were crosslinked with the ester bond by thermal treatment.

Table 1 The scanning electron microscopy (SEM) images (3000x) of crosslinked fibers at various crosslinking times and temperatures after the water insolubilization testing.

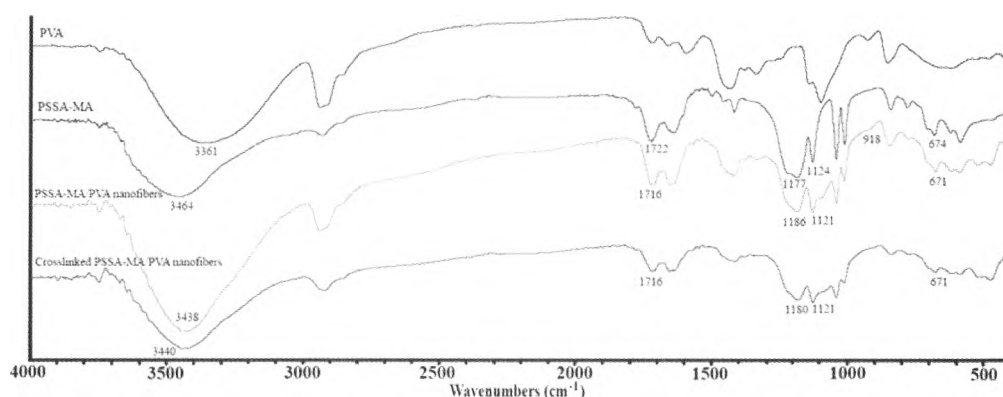
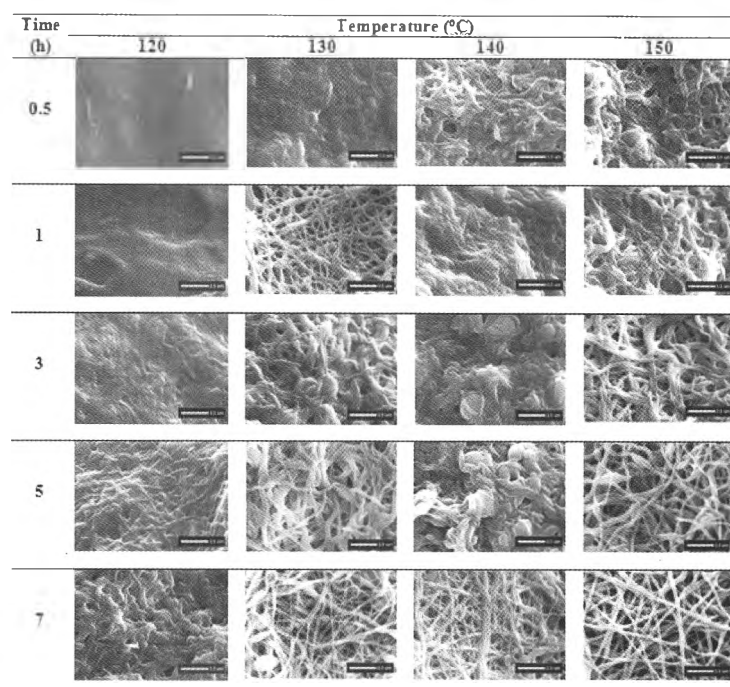


Figure 2 The FTIR spectra of the pure PVA, PSSA-MA, PSSA-MA/PVA and crosslinked PSSA-MA/PVA nanofibers (140°C, 5 h)

The PSSA-MA/PVA ratios and crosslinking time clearly affected the IEC values of the crosslinked PSSA-MA/PVA nanofibers. The IEC value increased significantly from 1.54 to 2.51 meq/g-dry the crosslinked PSSA-MA/PVA nanofibers with an increase of the amount of the PSSA-MA parts from 0.2 to 1 (Table 2). It might be due to the more cation-exchangeable sites from the sulfonic acid groups of the PSSA and the carboxylic acid groups of the MA^{12,13}. A decrease of the IEC value was significantly occurred when crosslinking time was longer. It might be due to increasing the esterification between OH groups of the PVA and COOH groups of the MA from the thermal treatment, causing a decrease of the cation-exchangeable sites from COOH groups of the MA. Moreover, Water uptake (%) was also affected by changing the PSSA-MA/PVA ratios, crosslinking time and crosslinking temperature. Increasing the PSSA-MA/PVA ratios from 0.2/1 to 1/1, the water uptake (%) decreased significantly from 490% to 307% (Table 2). It might be due to an increase in the esterification reaction, causing the more rigid and compact crosslinked fibers and hence the obstruction of the diffusion of water into the crosslinked one¹⁰. At the same crosslinking time, the water uptake decreased significantly as increasing crosslinking temperature. It might be due to an increase in the degree of crosslinking, thus causing the difficulty of the water uptake into the crosslinked fibers.

Table 2 The IEC values and water uptake (%) of the PSSA-MA/PVA nanofibers at various the PSSA-MA/PVA ratios after crosslinking at 140 °C for 5 h. (*) indicates significant differences between IEC (0.2/1) and another ratio at $p < 0.05$. (**) indicates significant

PSSA-MA/PVA ratios	IEC (meq/g)	Water uptake (%)
0.2/1	1.54	489.9
0.3/1	1.61	442.6**
0.4/1	1.78*	427.8**
0.5/1	2.14*	377.4**
0.6/1	2.15*	337.2**
0.7/1	2.21*	310.5**
0.8/1	2.24*	309.5**
0.9/1	2.39*	308.0**
1/1	2.51*	306.9**

CONCLUSION

PSSA-MA/PVA ion exchange fibers were successfully prepared by the electrospinning method and post thermal treatment. The PSSA-MA/PVA ion exchange fibers without bead structure were obtained from the immediate fibers fabricated from the PSSA-MA/PVA ratios up to 0.4/1. The appropriate temperature for crosslinking was 120-140 °C for 1-7 h. The diameter, IEC value and water uptake (%) of the crosslinked PSSA-MA/PVA nanofibers were about 180 ± 45 - 233 ± 68 nm, 1.6-3.0 meq/g and 232-721%, respectively.

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