HYDROPHOBIC AND BREATHABLE NANOMEMBRANE FOR FOOD PACKAGE MATERIAL BY MIMICKING COCOON'S STRUCTURE

by

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The aim of this study was to investigate the cross-linked poly(vinyl alcohol) nanofibrous mats treated by flourinated alkane in supercritical carbon dioxide medium. The surface morphology and chemical structure of electrospun mats were analyzed by scanning electron microscopy and Fourier transform infrared. The results showed that the treated mats could maintain their integrity and fibrous morphology as well as their porous structure after being treated. However, the wettability was changed greatly, the average contact angle of treated nanofibrous mats increased from its original value of 28° to 134°, revealing that the treated mats had good water repellent properties. The paper concluded that the hydrophobic and breathable mats with porous structure might be an excellent candidate for food package materials.

Key words: *hydrophobic, breathable, electrospinning, supercritical carbon dioxide*

Introduction

Electrospinning is a relatively simple technical method that produces continuous ultrathin polymer fibers with diameters ranging from micrometers to nanometers [1, 2]. Poly(vinyl alcohol) (PVA) is a water soluble, biocompatible synthetic polymer that can be processed easily, meanwhile, the high water permeability leads to the use of PVA in a wide range of applications in medical, cosmetic, food, and package industries [3-5]. Supercritical fluid has density and solvating power similar to liquid solvent, which allows its application in various fields including polymer modification, formation of polymer composites, polymer blending, microcellular foaming, particle production and polymerization, and has also been proposed as an environmentally friendly replacement of water and organic solvent for many industrial applications [6, 7].

The wettability of a solid surface is an interesting property of a material and is described as the contact angle between a liquid and solid surface [8]. The fabrics treated by common method such as coating can have the performance of hydrophobicity but no air permeability. Islam *et al.* [9] prepared superhydrophobic membranes by electrospinning of fluorinated silane functionalized pullulan, but the electrospun fibers had many beads. Wu *et al.* [10] studied the effect of supercritical carbon dioxide treatment on the structures and proper-

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ties of electrospun poly(vinylidene fluoride) membranes, and results showed that such treatment leads to porous morphology and reduced crystallinity of the nanofibers. Chen *et al.* [11] and Chen [12] studied the cocoon morphology and structure and found that the smaller fiber size would lead to waterproof property. Currently, there is rarely report about electrospinning nanofibers treated in supercritical CO_2 medium to obtain hydrophobicity. The aim of this study was to fabricate nanofibrous membranes to mimic the cocoon. PVA nanofibrous mats were cross-linked and then treated by flourinated alkane in supercritical CO_2 medium. The surface morphology of treated mats and the interaction between PVA and fluorinated alkane were also analyzed.

Experimental

PVA powder was dissolved in distilled water with solution concentration of 0.1 g/ml, and then stirred for 24 hours at temperature of 40 °C. The solution was fed into a plastic syringe controlled by an accurate pump (789100C, Cole-Parmer, USA) and then high voltage of 24 kV was applied at the tip of the syringe needle. A piece of aluminum foil was used to collect the electrospun nanofibers with the distance of 11 cm below the tip. The electrospinning process was conducted under the ambient conditions.

The cross-linking process was carried out by placing the air dried PVA nanofibrous mats supported on the aluminum foil in a sealed desiccator containing 10 ml of 50 % aqueous glutaraldehyde (GTA) solution in a Petri dish. The nanofibrous mats were placed on a holed ceramic shelf in the dessicator and were cross-linked in the GTA vapor for 24 hours at room temperature. The cross-linked membranes were then treated by flourinated alkane in supercritical CO_2 medium for 40 minutes under the pressure of 20 MPa and the temperature of 70 °C. The concentration of the finishing agent is 2.5 mg/ml and the flow velocity of CO_2 was 20 g per minute.

The surface morphology of the nanofibrous membranes and the atomic composition of chemical element of the treated membranes were analyzed by scanning electron microscopy (SEM) and energy disperse spectroscopy (EDS) after platinum coating. Fourier transform infrared (FTIR) spectrometry was utilized to analyze the cross-linking mechanism of the electrospun PVA fibrous mats. All spectra were recorded in the wavelength range of 4000-500 cm^{-1} wavenumbers. Surface wettability of the electrospun mats were characterized by water contact angle test. The contact angles of electrospun, cross-linked, and functionalized fibrous mats were measured, respectively.

Results and discussion

Figures 1(a) and (b) were the morphologies of electrospun PVA nanofibers before and after being cross-linked, respectively. After being cross-linked, the electrospun PVA mat could keep the fibrous structure, which indicating that being cross-linked in GTA vapor for 24 hours would be an effective method to avoid being dissolved in distilled water. According to Image J analysis, the average diameter of electrospun PVA nanofibers at solution concentration of 0.1 g/ml was 251 nm. Most fibers distributed with diameter ranging from 200 nm to 260 nm.

Figure 2 showed the surface morphology of nanofibers after the electrospun mats had been treated by flourinated alkane. The nanofibrous structure and pores kept almost unchanged.

To confirm that the treated nanofibrous mats contained the fluorine element in their structure, EDS analysis was performed. Table 1 summarized the elemental composition on the surface of the mat. PVA has only oxygen and carbon in its structure. However, the treated

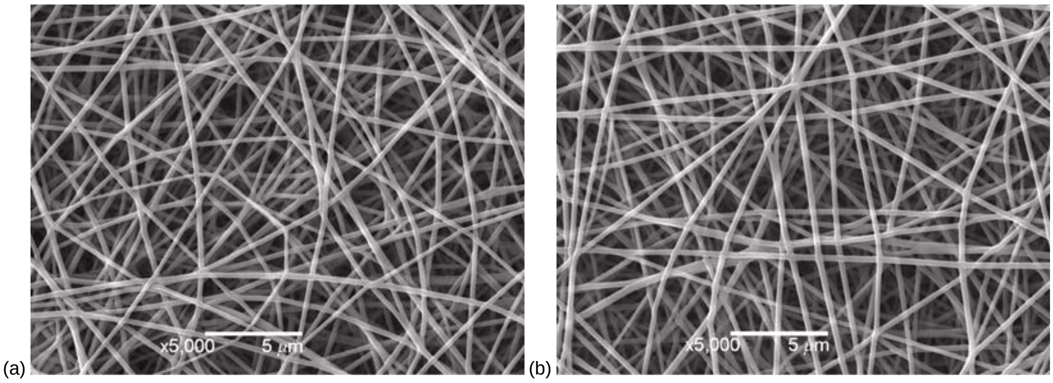

Figure 1. The SEM images of nanofibers (a) before, and (b) after being cross-linked

mats had aluminum (Al), chlorine (Cl), platinum (Pt), and fluorine (F) element. The appearance of aluminum was due to the collecting device covered with aluminum foil, which was then tested together with the electrospun mats by SEM. The introducing of chlorine element was in the process of cross-linking. Hydrochloric acid was used to improve the cross-linking effect by condensation reaction and yield diphenyl ether linkages and carbonyl group. Platinum was due to coating before tested in SEM. The fluorine was from the finishing agent. The existing of fluorine indicated that the finishing agent reached on the surface of the mat. Therefore, both the fluorine element and the kept pores would make the treated mats have hydrophobic and breathability properties.

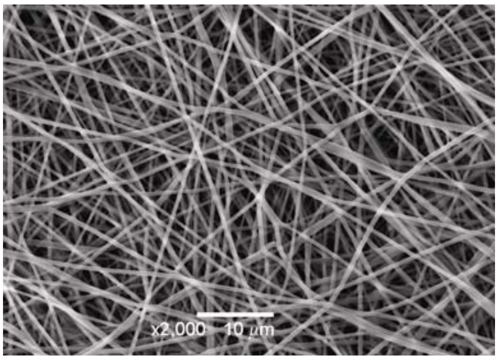

Figure 2. The SEM morphology of cross-linked PVA nanofibers after treated by flourinated alkane

Table 1. Weight and atomic percentages of the atoms in the electrospun nanofibers

Element	C	O	F	Al	Cl	Pt
Weight (%)	55.67	33.22	4.85	0.36	3.27	2.62
Atomic (%)	65.41	29.3	3.6	0.19	1.3	0.19

GTA has been applied to cross-link chitosan and gelatin materials. FTIR spectras give information about the chemical structure of the membranes. In fig. 3, the illustrations of spectra of PVA and the cross-linked PVA membranes ranging from 4000 cm^{-1} to 500 cm^{-1} were showed. In fig. 3, curve *a* represents the electrospun PVA membrane. The strong absorption band in 1090 cm^{-1} indicates the presence of C-O. Band at 2939 cm^{-1} is due to the stretching vibration of CH_2 groups. The absorption band in 3330 cm^{-1} is the hydrogen band formed by O-H. Curve *b* was the treated PVA membrane by flourinated alkane. Comparing the spectra (a) and (b), the band of PVA in 3330 cm^{-1} and 835 cm^{-1} shifted to 3323 cm^{-1} and 846 cm^{-1} after being cross-linked which represented the reaction of aldolization between PVA and GTA reacting in the process of cross-linking.

The wettability depends on the surface composition and also the morphology of fibrous mats. The wettability of PVA including electrospun fibrous mats, cross-linked mats and treated by flourinated alkane was measured, and the results were shown in fig. 4. The average water contact angles of the nanofibrous membranes decreased from 54° to 28° after being

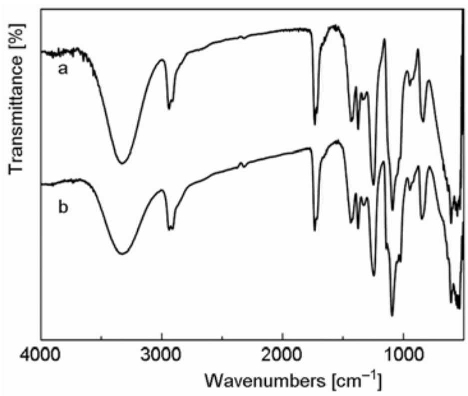

Figure 3. FTIR spectra of membranes of (a) PVA and (b) cross-linked PVA

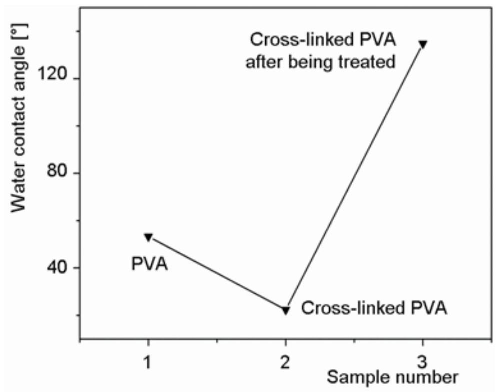

Figure 4. The average water contact angles of the membranes

cross-linked, which demonstrates the process of cross-linking increasing the surface energy of the membranes. In addition, the average water contact angle of the treated mats by flourinated alkane could reach to 134° which displayed highly hydrophobic properties. The hydrophobicity of the treated mats could be due the presentence of fluorine element.

Conclusions

Crosslinking in GTA vapor is an effective way to improve the stability of electrospun PVA fibrous mat. The average water contact angle of the treated mats could reach to 134° after the cross-linked fibrous mats were treated by flourinated alkane in supercritical carbon dioxide medium. The fibrous morphology and porous structure of treated mats was preserved after being treated which indicated that the membranes had breathable property besides excellent water repellent property. Therefore, the hydrophobic and breathable membranes with porous structure can be potential in food package materials.

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