

## POST-ELECTROSPINNING CROSSLINKING OF GUAR/POLYVINYL ALCOHOL MEMBRANE

by

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*The present study reports post-electrospinning crosslinking of guar/polyvinyl alcohol/citric acid nanofiber membranes by heat treatment. Porous, interconnected non-woven nanofiber membranes (average diameter  $194 \pm 23$  nm) were electrospun from a homogeneous blend of 1 wt.% guar gum and 8 wt.% polyvinyl alcohol solution (3:7 weight ratio) containing 5 wt.% (by the total weight of the solution) citric acid. The electrospun nanofiber membranes were then cured at 140 °C for 2 hours. The crosslinked nanofiber membranes were insoluble in water, while the non-crosslinked membranes dissolved instantaneously. The Fourier transform infrared spectrum investigates that crosslinking of guar/polyvinyl alcohol occurred through esterification reaction during heat treatment.*

Key words: guar, post-electrospinning, crosslinking, nanofiber membrane, heat treatment

### Introduction

Electrospun natural polysaccharides nanofiber membranes have been used for drug release, tissue engineer, wound dressing, etc., recently [1, 2]. Guar gum is a natural polysaccharides widely used for thickener, emulsifier, stabilizing agent, etc. Guar composed of a mannose backbone with galactose side groups that are suitable for human colon enzyme degradation, which can be developed for targeted drug delivery material [3]. Fiber homogeneity of electrospun guar gum can be enhanced by solution filtration with a sequence of membrane [4], but viscosity of guar gum solutions were too high due to high molar weight even at 1 wt.% and could not form a stable jet [5]. Polyvinyl alcohol (PVA) is used in biomedical industries due to its biocompatibility, high permeability to small molecules and low toxicity [6]. The PVA produced a stable jet and uniform, bead-free nanofiber during electrospinning [7]. The electrospun fiber properties were controlled based on PVA/guar mass ratio. Electrospun PVA/guar nanofibers immediately dissolve in the water. In order to use PVA/guar nanofibers for drug delivery, the nanofibers should be crosslinked to create water resistant membranes. The PVA nanofibers can be crosslinked either in situ [8, 9] or post-electrospinning [10]. But the crosslinkers was toxic so that we could not produce completely natural or benign crosslinked nanofibers. Citric acid is a non-toxic metabolic product of the body. Citric acid was used to crosslink hydroxyl bearing monomers such as starch [11] and silk [12] at relatively mild condi-

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tions. In this work, citric acid was added into PVA/guar blend solutions. The electrospun membranes were cured at 140 °C for 2 hours. The post-electrospinning crosslinked membranes were insoluble in water.

## Experimental section

### Materials

The PVA (Mw 88000 g/mol, 88% hydrolyzed) was purchased from J & K Chemical®, guar gum powder and citric acid were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). The distilled water was purchased from Pinjiang Chemical Co., Ltd.

### Guar purification

The purification of guar gum was: 1 wt.% guar solution was prepared by adding guar powder slowly into deionized water. The solution was mixed rapidly for 2 hours and then was mixed slowly overnight. The prepared solution was centrifuged at 10,000 rpm for 45 minutes. The supernatant liquid was gathered and poured into two volumes of ethanol. The flocculent of guar precipitates in the bottom of ethanol/water solution, and the sediment was gathered and vacuum dried at 60 °C for 24 hours. The dried guar was ground into powder. The guar powder was preserved in a drier until used [4].

### Electrospinning solution preparation

It was fabricated 1 wt.% solution of the purified guar with deionized water. The solution was stirred constantly over night at room temperature. A 8 wt.% PVA solutions were fabricated with PVA powder and distilled water. The PVA powder was added into distilled water bit by bit at room temperature. The solution was mixed at 80 °C for 3 hours. Then, 1 wt.% guar solution was mixed with 8 wt.% PVA solution in a 3:7 mass ratio. The mixture was stirred for one hour to obtain well-distributed solution. Finally, citric acid powder was added into the solution at 5 wt.% by the total weight of the solution, and the mixture was stirred constantly for 2 hours.

### Electrospinning

The electrospinning apparatus equipped with a precision injection pump (KDS100 by KD Scientific), a high voltage DC power supply (Tianjing Dongwen High Voltage Power Supply Co., Ltd), and a collector plate. Newly fabricated guar/PVA solution was added into a 20 mL plastic injector with a 7G stainless needle. The flow of solution was controlled by the injection pump at the rate of 2 mL/min. The stainless needle was connected to the positive electrode of the high voltage DC power supply. An aluminum foil was covered on the grounded collector plate. The tip-to-collector distance was set as 20 cm, and the applied voltage was set as 12 kV. The electrospun membrane was cured in a cabinet drier at 140 °C for 2 hours to initiate chemical crosslinking.

### Stability test

The water solubility of electrospun PVA/guar membrane was tested. The membrane was cut into small pieces, weighed, and then immersed into deionized water at room temperature for 24 hours. The samples were dried in a cabinet drier at 80 °C for 10 hours before scanning electron microscopy (SEM) analysis. The mass loss rate during dissolving in water was calculated as in eq. (1):

$$\text{Mass loss rate} = \frac{W_1 - W_2}{W_1} \quad (1)$$

where  $W_1$  is the initial dry weight of the sample, and  $W_2$  is the dry weight after dissolving in water.

### Characterization

The morphology of electrospun PVA/guar membranes before and after water treatment was observed by Hitachi S4800 SEM. The membranes were cut into small pieces and coated with gold for about 10-20 nm thickness. The average diameters of nanofibers were observed by nano measurer software. The chemical structure of samples was characterized by attenuated total reflectance mode Fourier Transform Infrared spectrophotometer (ATR-FTIR) (Equinox55, Bruker). The samples were thoroughly washed in water to remove unattached citric acid. The washed samples were placed on a germanium plate and 100 scans were collected for each sample.

## Results and discussion

### Fiber morphology

The SEM images of electrospun PVA/guar membranes are shown in fig. 1. Electrospinning of PVA/guar/citric acid aqueous solution resulted in randomly oriented continuous nanofibers (average diameter  $194 \pm 23$  nm) with porous interconnected non-woven membrane, fig. 1(a). Nanotechnology links classical mechanics and the chaos of quantum mechanics. There is a grey area between the two classical and quantum scale. In the process of electrospinning, fiber is closer to the size of quantum than to the ordinary world. They often show quantum-like properties, and there are many fascinating nanoeffects [13]. Adding guar in the electrospun PVA nanofibers leads to high surface reactivity and biocompatibility. Using the properties raises the potential of electrospinning to make things possible at drug release [14]. Electrospun nanofibers had smooth surfaces with a circular cross-section and bead free morphology. The PVA/guar micro fibrous membrane pass heat flow obviously, however, when the fibers tend to be nanoscale, the membrane has excellent heat insulating property [15]. The heat treatment at  $140^\circ\text{C}$  for 2 hours caused shrinking of the nanofibers (aver. diameter  $204 \pm 18$  nm), but the physical integrity of the fibrous structure remained intact, fig. 1(b) [16]. The observed contraction can be ascribed to the conformational transitions of the polymer chains and/or release of water molecules from the matrix upon heat treatment. Electrospun PVA/guar membranes dissolved in aqueous medium immediately before heat treatment, but the mass loss rate of the cured membranes is 0% after one day of water immersion. Although the heat treated nanofibers did not dissolve, it is obviously that they swelled and their morphology changed, fig. 1(c). This can be attributable to the hydrophilicity of PVA and guar. The residual hydroxyl

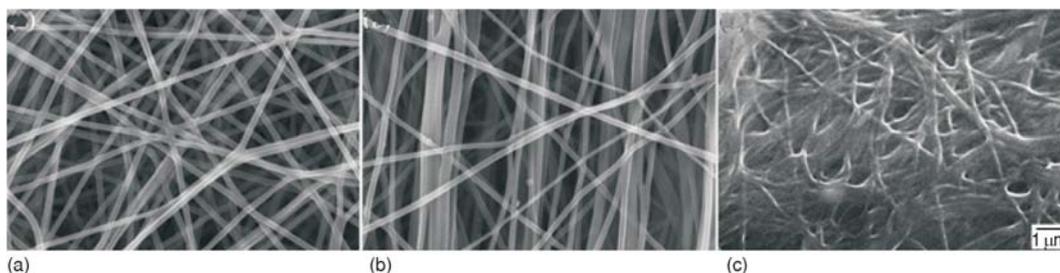


Figure 1. The SEM images of electrospun PVA/guar membranes; (a) before heat treatment, (b) after heat treatment, (c) the cured electrospun membrane immersed into deionized water for 24 hours

groups after crosslinking absorb water molecules easily and the nanofibers swell enormously in water. The SEM images of the water treated PVA/guar nanofibers show a 17% increase in the size (average diameter  $240 \pm 45$  nm) [17]. Nanoeffect have demonstrated unusual strength, high surface energy, surface reactivity, high temperature, and electrical conductivity. The strength and surface energy of nanofiber depend on the fiber diameter at the nanoscale (from several to tens of nanometers):

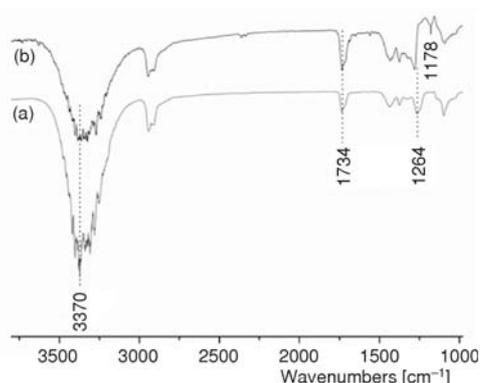
$$\tau = \tau_0 + \frac{k_\tau}{d^\alpha} \quad (2)$$

$$E = E_0 + \frac{k_E}{d^\beta} \quad (3)$$

where  $k_\tau$  and  $k_E$  are the fitting parameters (material constants),  $t_0$  and  $E_0$  – the strength and surface energy of the bulk material, respectively,  $d$  – the fiber diameter, and  $\alpha > 0$  and  $\beta > 0$  are scaling exponents [18-20].

#### The FT-IR spectroscopy

The FT-IR spectra of electrospun PVA/guar membranes before and after heat treatment are shown in fig. 2. It can be seen from figs. 2(a) and 2(b) that the large bands observed around  $3370 \text{ cm}^{-1}$  are linked to the O-H stretching from the intermolecular and intramolecular hydrogen bonds present in guar and PVA. The small bands at around  $1099 \text{ cm}^{-1}$  correspond to O-H stretch



**Figure 2. The FT-IR spectra of electrospun PVA/guar membranes; (a) before heat treatment, (b) after heat treatment**

in-plane bending vibration. The bands at around  $2941$  and  $850 \text{ cm}^{-1}$  correspond to the backbone  $\text{CH}_2$  symmetric stretching vibration and out-of-plane twisting. The bands at around  $1328 \text{ cm}^{-1}$  correspond to the backbone CH bending vibration. The band at around  $1734 \text{ cm}^{-1}$  correspond to residual  $\text{C} = \text{O}$  stretching vibration in fig. 2(a), while the band is comparatively larger after heat treatment in fig. 2(b). The O-H stretching band around  $3370 \text{ cm}^{-1}$  is relatively smaller and C-O-C asymmetric stretching vibration is comparatively larger in fig. 2(b). The results show that ester structure increases after heat treatment. The C-O stretching vibration at around  $1178 \text{ cm}^{-1}$  in fig. 2(b) shows that citric acid was bonded to hydroxyl bearing monomers [21].

#### Conclusions

We have proved that citric acid, a non-toxic polycarboxylic acid, can crosslink PVA/guar nanofiber membranes post-electrospinning. The crosslinked PVA/guar nanofiber membranes were insoluble in water which may have important implications for drug release application. This is compared to the non-crosslinked PVA/guar nanofiber membranes that dissolved immediately in water. The FT-IR spectrum indicates that esterification crosslinking reaction occurred during heat treatment. This kind of simple, efficient, and environmentally friendly crosslinking technique may realize industrialization of guar-based electrospun membranes in drug delivery and tissue engineering.

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