



# High stability under extreme condition of the poly(vinyl alcohol) nanofibers crosslinked by glutaraldehyde in organic medium



Yanbao Li<sup>\*</sup>, Song Yao

College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, PR China

## ARTICLE INFO

### Article history:

Received 16 October 2016

Received in revised form

22 January 2017

Accepted 28 January 2017

Available online 1 February 2017

### Keywords:

Crosslinking

High performance polymers

Water-soluble polymers

Morphology

## ABSTRACT

Water-soluble poly(vinyl alcohol) (PVA) nanofibers cannot be applied in aqueous condition. Fortunately, the PVA nanofibers can become stable in aqueous condition after physically or chemically crosslinked. However, these crosslinking methods require some harsh experimental conditions. In this article, organic solvents were introduced as the media to crosslink PVA nanofibers with glutaraldehyde, which is different from the conventional crosslinking method. The results of the field emission scanning electron microscopy (FESEM) show that the crosslinked PVA nanofibers can maintain the morphology not only in water but also in extreme solutions (such as hot water for 2 d, strong acid/alkaline solutions at 95 °C for 2 h). The tensile strength of the crosslinked PVA nanofiber mats can maintain more than  $12.1 \pm 1.1$  MPa after soaked into these extreme solutions. The crosslinked PVA nanofiber mats with high stability and porous morphology have potential applications as filter membrane and adsorbing material.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Poly(vinyl alcohol) (PVA), which is obtained by the hydrolysis of poly(vinyl acetate), has attracted considerable attention due to its favorable properties such as excellent biocompatibility [1], non-toxicity [2], good film-forming properties [3] and high hydrophilicity [4]. So PVA has been actively explored for different applications such as food packaging, drug carrier, biomaterials and so on [5–7]. On electrospinning, the PVA solutions are stretched to form micrometer- or nanometer-sized fibers with extraordinary structures that have attracted significant interest [8–11]. However, PVA nanofibers are dissolved in aqueous solution rapidly because PVA is a hydrophilic polymer [12] and the PVA nanofibers own high specific surface area [13]. This disadvantage greatly limits the application of PVA nanofibers in many fields. Many researches have been reported to improve the stability of the PVA nanofibers in aqueous solution [14–17]. These reported methods can mainly be divided into physical and chemical crosslinking. Physical crosslinking of PVA nanofibers can be obtained when the hydrogen bond between PVA chains and water are replaced by the intermolecular hydrogen bonds of PVA after treatment. For example, Li et al. [14] obtained the stabilized nanofibers without disintegration in

aqueous solution after treatment of PVA nanofibers with methanol for 24 h (hours). Kang et al. [17] improved the water-resistance of PVA nanofibers by heat treatment at 150 °C for 10 min. Chemical crosslinking of PVA nanofibers is the formation of chemical bond between PVA and other polymers. For example, Yan et al. [16] obtained water-insoluble nanofibers after crosslinking in situ through interaction between PVA and poly(acrylic acid) (PAA) in nanofibers at 120 °C for 3 h. Although these treatments can improve the stability of PVA nanofibers in aqueous condition, they need a complex experimental process and/or a harsh experimental condition.

It is worth pointing out that glutaraldehyde (GA) has been used to crosslink the PVA nanofiber mat recently. Destaye et al. [15] got the crosslinked PVA nanofibers through crosslinking the PVA nanofibers (pH = 3) with the GA vapor for 48 h at room temperature. Naebe et al. [18] obtained crosslinked PVA nanofibers after the PVA nanofiber mat was soaked in an acid GA-acetone solution for 4 h, and then treated at 150 °C for 10 min. However, the use of GA aqueous solution introduces water in the crosslinked environment [19]. So the existing water may influence seriously the stability of the PVA nanofibers. And the morphologies of these GA-crosslinking nanofibers change obviously after immersion in aqueous condition [14,17]. So these obtained crosslinked PVA nanofibers can not be applied in the water condition.

In this article, we have used hydrophobic organic solvents as the media of the crosslinked reaction. The crosslinking process only required a mild experimental condition at a relatively short time. At

<sup>\*</sup> Corresponding author.

E-mail addresses: [lyanbao@163.com](mailto:lyanbao@163.com), [ybli@njtech.edu.cn](mailto:ybli@njtech.edu.cn) (Y. Li).

the same time, the crosslinked PVA nanofibers treated by this method are completely stable in some extreme solutions (such as hot water for 2 d, strong acid/alkaline solutions at 95 °C for 2 h). And the tensile strength of the crosslinked PVA can maintain more than  $12.1 \pm 1.1$  MPa even if it is soaked in extreme solutions.

## 2. Experimental

### 2.1. Materials

PVA was purchased from Shanghai Yingjia Industrial Development Co., Ltd (degree of polymerization  $2400 \pm 50$ ; degree of hydrolysis 88%). Glutaraldehyde (GA, 25% aqueous solution), petroleum ether and tris(hydroxymethyl) aminomethane (Tris) were obtained from Sinopharm Chemical Reagent Co., Ltd. Methylbenzene and hydrochloric acid (HCl, 37.0%) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. *n*-hexane was obtained from Shanghai No.4 Regent & H.V. Chemical Co. Ltd. All reagents are of analytical grade without further purification. Dopamine was obtained from the Aladdin industrial Co. Ltd.

### 2.2. Electrospinning of the PVA nanofiber mat

PVA (1.4 g) was dissolved into deionized water (20 mL) under constant stirring at room temperature for 2 d (days). Then the 7% (w/v) PVA solution was loaded into a 5 mL disposable syringe. During the process of electrospinning, the flow rate of PVA solution was controlled at 25  $\mu$ L/min with a syringe pump (Longer Pump Co., Ltd. Baoding, China). The applied voltage and the distance between the tip of the stainless needle (gauge 24) and the grounded aluminum foil were 14 kV and 15 cm, respectively. The voltage was provided with a direct current high-voltage generator (DW Co., Ltd. Tianjing, China).

### 2.3. Crosslinking of the PVA nanofiber mat

The methylbenzene (30 mL) was poured into a separatory funnel. Then the pH value was adjusted to 3 with HCl. Different amounts of aqueous GA solution (the mass ratio of GA/PVA = 2:1, 6:1 and 10:1, respectively) as crosslinking agent was mixed with the acid methylbenzene solution. Then the upper turbid solution (i.e. the acid GA-methylbenzene solution) was collected through the separatory funnel. The PVA nanofiber mat was soaked into the acid GA-methylbenzene solution. Afterwards, the crosslinked nanofiber mat was collected after reaction for different times at room temperature and washed with ethanol and water, alternatively, to remove methylbenzene. Finally, the crosslinked nanofiber mats were dried at room temperature.

### 2.4. Applications of the crosslinked PVA nanofiber mat

Our crosslinked PVA nanofiber mats were applied as a filter membrane to filter aqueous graphene oxide solution (GO, 1 mg/mL), and the commercial cellulose acetate membrane were used as reference. GO was synthesized using the modified Hummers method [20]. We also prepared the crosslinked polydopamine (PDA)-coated PVA (PVA@PDA) nanofiber mat for dye adsorbent. The detailed preparations of PVA@PDA nanofiber mat are described in [Supplementary Data](#).

### 2.5. Material characterization

The morphology of the nanofiber mats was observed under a scanning electron microscope (FESEM, S-4800, Hitachi, Tokyo, Japan) with an acceleration voltage of 5.0 kV after coated by gold.

The contact angles of the nanofiber mats were measured by a contact angle measurement (JC2000CS, Powereach, Shanghai China). All contact angles were measured immediately when the water drop dropping on the nanofiber mats. X-ray diffraction (XRD) measurements of the nanofiber mat were conducted on an ARL X'TRA X-ray diffractometer (SmartLab™ 9 kW, Rigaku, Tokyo, Japan) using Cu K $\alpha$  radiation ( $\lambda = 1.5409$  Å) from 3° to 60° at a scanning rate of 10°/min. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were obtained with a Nexus 670 spectrometer (Nicolet, Massachusetts, USA). The tensile properties were evaluated by a universal testing machine (E44, Sans Company Co. Ltd., Shenzhen, China) with a crosshead speed of 20 mm/min at room temperature. All samples were cut into strips with a size of 30 mm  $\times$  5 mm. At least five samples were tested for each nanofiber mat. UV–vis absorption spectra of the GO filtrate were measured using a UV–vis spectrophotometer (Gold spectrumbab-54, Shanghai Leng-guang Tech. Co., Shanghai, China) in the range of 200–800 nm.

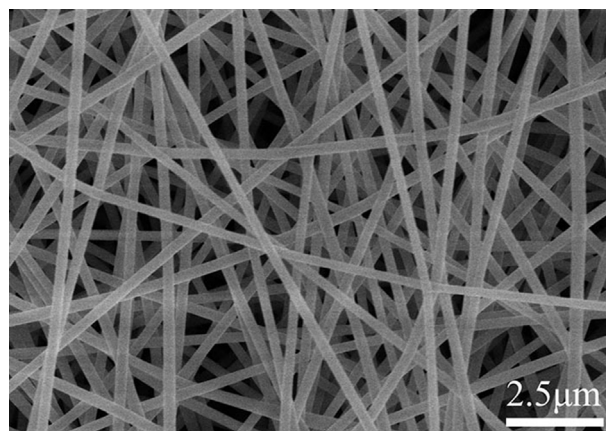
## 3. Results and discussion

### 3.1. Crosslinking of the PVA nanofiber mat

**Fig. 1** shows the FESEM image of the PVA nanofiber mats via electrospinning 7% (w/v) PVA solution under 14 kV with a collection distance of 15 cm. The original PVA nanofibers are smooth without any bead, twining and adhesion. However, due to the hydrophilic property and the high specific surface area of PVA nanofibers, the original PVA nanofiber mat shrinks instantaneously and then dissolves when soaked into water. It limits the application of the water-soluble nanofiber mat under aqueous condition.

It is well-documented that the stability of PVA can be increased after chemically crosslinked [21–23]. However, the stability of PVA will deteriorate and even disappear after soaked into aqueous solution and/or extreme solution [14,17]. In order to improve the durability of the stable PVA nanofiber, organic solvents (methylbenzene, *n*-hexane and/or petroleum ether) were used as reaction media in the crosslinking experiment.

The PVA nanofiber mats were crosslinked by GA after treated in the acid GA-methylbenzene solution with different GA amounts for 1 h. **Fig. 2** shows FESEM images of the crosslinked nanofiber mats before and after soaked into distilled water at room temperature for 2 h. Before soaked into distilled water at room temperature, all these crosslinked PVA nanofibers show smooth morphologies without any bead, twining and adhesion (**Fig. 2A, 2B and 2C**), which



**Fig. 1.** FESEM image of electrospinning 7% (w/v) PVA nanofibers prepared under 14 kV with a collection distance of 15 cm.

Download English Version:

<https://daneshyari.com/en/article/5200820>

Download Persian Version:

<https://daneshyari.com/article/5200820>

[Daneshyari.com](https://daneshyari.com)