



High-flux microfiltration filters based on electrospun polyvinylalcohol nanofibrous membranes

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ABSTRACT

A novel class of high-flux microfiltration filters consisting of an electrospun nanofibrous membrane and a conventional non-woven microfibrillar support is being presented. The nanofibrous non-woven layer was fabricated by electrospinning of polyvinylalcohol (PVA) directly onto the microfibrillar support and then followed by chemical cross-linking with glutaraldehyde (GA) in acetone. By altering the processing parameters, such as the applied voltage and the distance between the spinneret and the collector, as well as the concentration of PVA solution, electrospun PVA membranes with an average fiber diameter of 100 ± 19 nm were obtained. Characterizations revealed that the mean pore size of the electrospun PVA membranes ranged from $0.30 \mu\text{m}$ to $0.21 \mu\text{m}$ with the electrospun PVA membrane thickness varying from 10 m to $100 \mu\text{m}$. Due to the high porosity, microfiltration filters based on these electrospun membranes showed 3–7 times higher pure water flux than the Millipore GSWP $0.22 \mu\text{m}$ membrane. The nanofibrous PVA membranes with an average thickness of $20 \mu\text{m}$ could successfully reject more than 98% of the polycarboxylate microsphere particles with a diameter of $0.209 \pm 0.011 \mu\text{m}$, and still maintain 1.5–6 times higher permeate flux than that of the Millipore GSWP $0.22 \mu\text{m}$ membrane.

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1. Introduction

Microfiltration (MF) is an important process in a wide range of water applications, including pretreatment of waste water, clarification of beer and wine, and removal of bacteria, algae or protozoans from surface water or contaminated water [1]. As most water borne microorganisms, such as *Salmonella bacteria*, *Escherichia coli* and *Vibrio cholerae*, have sizes ≥ 0.3 microns [2], it is within reason to expect that we can sterilize contaminated water by filtration using MF membranes with a mean pore size in the 0.2 micron size range and a relatively sharp cutoff. As a result, some commercial sterilizing-grade membranes, such as Millipore MF membranes, with nominal $0.2 \mu\text{m}$ or $0.22 \mu\text{m}$ pore sizes, have been widely used for sterile filtration in a number of biological, medical and industrial applications [2,3].

Electrospinning is a process that can produce continuous polymer fibers with diameters in the sub-micron size range through the application of an external electric field imposed on a spinneret containing the polymer solution [4]. Electrospun membranes

possess some unique structural features, such as good tensile strength, high surface area per unit volume, interconnected open pores and high porosity [5]. Consequently, electrospun membranes have been used successfully in many applications, such as air filtration [6,7], tissue engineering [8], optical and chemical sensors [9,10]. In liquid filtration, we have demonstrated a new type of high-flux thin-film nanofibrous composite (TFNC) membranes, based on electrospun polymeric nanofibers and polyethylene terephthalate (PET) non-woven composite substrates for ultrafiltration (UF) and nanofiltration (NF) [5,11–14]. In this paper, the functions of electrospun polymeric membranes in microfiltration (MF) filters were further investigated.

In electrospinning, the fiber diameter and fiber morphology are tunable by varying processing variables, such as solution concentration, applied voltage, solution feeding rate etc. [15,16]. In electrospun membranes, the pores are created mainly by the entanglement of nanofibers and are highly interconnected. Thus, the mean pore size of electrospun membranes is highly correlated with the fiber diameter. The relationship has been addressed by a number of studies [17–19]. For example, Eichhorn and Sampson applied theoretical models to demonstrate that the fiber diameter plays a dominant role in controlling the pore size of the electrospun nanofibrous network [19]. Li and co-workers also validated the relationship via experiments. Their findings showed that the electrospun membranes with a fiber diameter of $2.58 \mu\text{m}$ exhibited

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mean pore sizes of 3.25–4.38 μm depending on the mass of the membrane, while the membranes with a fiber diameter of 281 nm possessed mean pore sizes of 0.66–0.79 μm , as the membrane mass varied [18]. Thus, there should be an opportunity for the electrospun membranes to be tuned to different pore sizes by changing the fiber diameter so that they can be used to meet different filtration grades than MF filters. Moreover, due to their high porosity and high surface area-to-volume ratio, this new type of microfiltration membrane can overcome the low-flux limitation of conventional porous polymeric membranes manufactured by using the phase inversion method [20–25], yet without compromising the pore sizes.

While most of the materials being used in electrospinning are solution-based polymers, such as polyethersulfone (PES), polyacrylonitrile (PAN) and polyvinylidene fluoride (PVDF), one major issue in the production of these polymers is that the organic solvents used often require solvents recycled from the dilute air stream, making such an operation uneconomical, or the solvent used has to be burned off. Therefore, water-soluble polymers become more desirable candidates for electrospinning in order to achieve a more environmentally friendly and cost effective production process. In this study, we have chosen polyvinylalcohol (PVA) as the electrospinning material, which is relatively inexpensive, chemically and thermally stable, and not degradable under most physiological conditions [11,12,26]. However, the electrospun PVA membranes have to be treated with cross-linking reagents to form a three-dimensional water-resistant network [23,27] before being used as water filters. A variety of multifunctional compounds capable of reacting with hydroxyl groups, including maleic anhydride, glutaraldehyde and glyoxal, have been used for PVA cross-linking [14], and the cross-linking reaction can be performed under different conditions. In industry, Donaldson and American Air Filters International have patented the methods of cross-linking the electrospun PVA nanofibers via heating or UV curing [28,29]. However, cross-linking reactions through these methods may be uneven or incomplete across the membranes, which would make the membranes unsuitable for water filtration as they could suffer from morphology change and structure defects when placed in water. In this study, we utilized a simple immersion method involving the use of GA/acetone/HCl solution to ensure the uniform and sufficient cross-linking of electrospun membranes for water filtration [11].

In the present work, cross-linked PVA electrospun membranes with fine nanofibers were prepared. The membrane properties, such as pure water flux, mean pore size and pore size distribution, rejection ratio to latex beads were thoroughly investigated to evaluate the capability and performance of the membranes to be used as MF filters. Properties of a commercial sterilizing-grade MF membrane were also studied for comparison purposes.

2. Experimental

2.1. Materials

PVA powder (Grade CM-318, polymerization degree ~ 1700 , $M_v \sim 1.5 \times 10^5$ g/mol from viscosity experiments, 86–91 mol% hydrolyzed) was purchased from Kuraray Co. Ltd, Japan. The viscosity experiments were carried out by a rheometer (Physica MCR 301, Anton Paar USA Inc., VA, USA) using PVA solutions with concentrations of 0.01, 0.008, 0.006, 0.004, and 0.002 g/mL. Final molecular weight was calculated using the Mark–Houwink equation ($K = 0.0666$ mL/g, $\alpha = 0.64$ at 30 °C) [30]. Glutaraldehyde (GA) (50% aqueous solution), hydrochloric acid (36.5% aqueous solution) and acetone (99.8%) were obtained from Aldrich and used as received. The non-woven polyethylene terephthalate with an

average fiber diameter of around 10 μm (PET No. 16-1) was provided from Sanko Ltd, Japan, and was used as the substrate. The commercial Millipore microfiltration membrane GSWP02500 with a nominal pore size of 0.22 μm was purchased from Millipore Corporation. A Milli-Q water purification system (Millipore Corporation) was used to generate purified water. Polycarboxylate microspheres with diameters of 0.209 ± 0.011 μm used for the rejection test were purchased from Polysciences Inc.

2.2. Preparation of electrospun PVA membranes

PVA was dissolved in distilled water and was stirred at 90 °C for 1 day. Four different concentrations (6, 8, 10 and 12 wt%) of PVA solutions were prepared. The viscosity of the polymer solution was determined by using a Brookfield digital viscometer (model LVTDCP) at 24 °C.

PVA nanofibers were electrospun at voltages ranging from 24 to 32 kV. The diameter of the spinneret was 1 mm, and the flow rate was controlled at 10 $\mu\text{L}/\text{min}$ by a programmable pump (Model M061-FD08, Superior Electric Company, USA). A grounded metal drum (diameter: 10 cm, rotating speed: 300 rpm) with the PET substrate taped on it was used as the collector and was placed 10 cm below the tip of the spinneret. A stepping motor was used to control the oscillatory translational motion, perpendicular to the drum rotation direction to ensure the production of uniform electrospun membranes with sufficient membrane area. The process was operated in a closed chamber, with a relative humidity measured at $55 \pm 5\%$ and temperature of 24 ± 1 °C during the electrospinning process. The electrospun PVA membrane together with the PET substrate was then immersed in 0.15 M GA and 0.05 M HCl in acetone solution for 1 h to ensure completion of the cross-linking reaction [12]. The whole membrane was taken out and washed in water, and then dried in vacuum before use.

2.3. Characterization of nanofiber diameter

The thickness of the electrospun PVA membrane was measured using a micrometer. Electrospun nanofibers were imaged using a scanning electron microscope (SEM) (Phenom, FEI Company, USA) after gold-sputter coating (SC7620 Sputter Coater, Quorum Technologies). Samples were coated at a current of 18 mA and under vacuum of 0.1 mbar for 30 s. The average nanofiber diameter and diameter distribution were analyzed from the SEM images using the LeicaIMGRead software (<http://dell.chem.sunysb.edu>).

2.4. Membrane characterizations

2.4.1. Differential scanning calorimetry

A PerkinElmer DSC7 instrument was used for the melting point measurements of the PVA powder, electrospun PVA membrane and cross-linked PVA membrane (both without the PET substrate). The samples were heated from 50 to 250 °C at a rate of 10 °C/min under nitrogen atmosphere.

2.4.2. Pore size distribution

The mean pore size, the maximum pore size, and the pore size distribution of the electrospun PVA membranes were determined by using a capillary flow porometer (Porous Materials Inc., USA). A wetting fluid Galwick™ (Porous Materials Inc., USA) with a surface tension of 15.9 dyn/cm was used to wet the membrane and fill the pores spontaneously. Under differential pressures of compressed air, the wetting liquid was gradually removed and the pores were successively opened. The air flow rates through the dry and wet membranes were recorded at different pressures. The pore size distribution, the maximum pore size and the mean pore size of the

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