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Increasing strength of electrospun nanofiber membranes for water filtration using solvent vapor

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A B S T R A C T

Electrospun nanofibrous membranes (ENMs) are an emerging material in the filtration space. However, widespread adoption of these materials has been hindered by poor mechanical strength thus necessitating the use of an additional support layer which can add to membrane thickness and resistance. The poor mechanical strength of ENMs are mostly due to their high porosity compounded with weak bonding at fiber junctions. In this study, we demonstrate a post-treatment approach to improve the mechanical properties of two commonly used membrane polymers: polyacylonitrile (PAN) and polysulfone (PSu). This post-treatment involves exposing ENMs to the solvent vapor where the mechanical strength is improved by the solvent-induced fusion of inter-fiber junction points. The treated membranes showed significant enhancement on tensile strength and Young's Modulus while high porosity and water permeability were retained.

1. Introduction

Eletrospinning has become a versatile technique that can create sub-micron scale fibers. Recent studies have focussed on using this technique to fabricate nanofibers for various applications ranging from membrane filtration to tissue engineering and electrodes [1–3]. Electrospun nanofibrous membranes (ENMs) have a great potential in membrane filtration technology because they possess several attractive attributes, such as high porosity and interconnected open pore structure, submicron pore sizes, and a large surface area to volume ratio. ENMs have already been successfully commercialized in air filtration [4] and have shown promise as high efficiency pre-filters for liquid separation [1,5]. In addition, ENMs can be served as a mid-layer over a non-woven fabric support and coated with a barrier layer. This novel three-tier structure has recently been developed for ultrafiltration [6,7], nanofiltration [8], and forward osmosis [9].

Typical membrane filtration, especially pressure-driven liquid filtration, requires membranes to possess sufficient mechanical strength in addition to chemical and thermal stability. These processes will often expose the membrane to a broad range of temperature, humidity, hydraulic pressure, mechanical vibration, and abrasive particulates in the fluid flow [10]. ENMs have often been avoided largely due to their poor mechanical strength attributed to their small fiber diameters, non-woven and highly porous structure, and weak bonding between the fibers. For instance, the tensile strength of the polyacrylontrile (PAN) ENM is about 10–100 times lower than that of the traditional fiber [11], limiting their use in filtration. For instance, Kaur observed that the thin film composite nanofiltration membrane using PAN ENM as the mid-layer cannot withstand the impact of high pressure greater than 130 psig [12].

Previous studies have reported several methods to improve the mechanical strength of ENMs. These methods can fall into three categories. Some studies attempt to change the nonwoven fiber mats into self-bundled fiber yarns [13]. These structures, however, have lower porosity than the traditional nonwoven structure and are less suitable for use in filtration. Another method involves reinforcing the single nanofiber strength by adding carbon nanotubes [13,14], layered silicate [15] or graphite nanoplatelets [16] into polymer solution for electrospinning. The composite electrospun nanofibers usually show enhanced Young's Modulus. However, synthesizing these nanocomposite nanofibers is complicated and costly. Probably the most effective approach is to enhance the bonding at junction points in the fiber mat by welding or soldering the fibers together [17]. One way to achieve this goal is to heat the mat above the glass transition temperature of electrospun polymer but below its melting temperature, which can cause inter-fiber fusion [1,18–20]. A possible drawback of this approach is the axial shrinkage of heat-treated membranes caused by entropic relaxation of stretched polymer chains [17].

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In this study, we demonstrate a less invasive post-treatment approach to weld the fibers and enhance the strength of junction points without greatly changing the membrane morphology and dimension. This post-treatment involves the use of solvent vapor. Solvent plays an important role in determining mechanical properties of electrospun fiber mats. After spinning some solvent may reside on the fiber in its nonwoven structure. This solvent will facilitate fusion between fibers at their junction points [21]. In this case, polymer solutions containing solvents of high boiling points are often used to achieve better adhesion between fibers [22]. For instance, Yoon et al. used a mixture of a solvent with lower boiling point: Dimethylformamide (DMF) and a solvent with higher boiling point: N-methyl-pyrrolidone to induce fiber–fiber fusion during electrospinning of polyethersulfone and found significant improvements in mechanical strength [8]. In this study, we hope to increase the amount of solvent in the electrospun network by exposing the spun ENMs to the DMF vapor for different periods of time. Scanning electron microcopy and mercury intrusion porosimetry were used to determine the membrane morphology and pore structure change after vapor treatment. Finally, the pure water permeability test of the treated PAN and PSu ENMs was carried out to see whether the treatment impacted membrane performance.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, Mw=150,000) was purchased from Scientific Polymer Products (Ontario, NY). Polysulfone (PSu, UDEL 3500, Mw=80,000–86,000) was obtained from Solvay Specialty Polymers (Alpharetta, GA). N, N-Dimethylformamide (DMF) was acquired from Acros Organics (Geel, Belgium) as the solvent. The water used for membrane tests was ultrapure Milli-Q water produced by a Millipore Integral 10 water system (Millipore Corporation Billerica, MA).

2.2. Fabrication of PAN and PSu ENMs.

PAN and PSu ENMs were prepared using a custom-built electrospinning setup. Details for the electrospinning system were described elsewhere [23]. These mats were spun from solutions consisting of 10% PAN and 26% PSu (both by mass) in DMF. These concentrations were chosen based on previous studies (not shown) which yielded relatively uniform fibers with fewer beads and reasonable mechanical strength. The solutions were first prepared by stirring at 60 °C for 24 h. The chosen spinning parameters for this study are listed in Table 1. The electrospinning took place at room temperature and the spinning relative humidity was controlled at 5–10% to maintain fiber uniformity [23]. The mat thickness was in the range of 50–100 μm. All mats were spun onto aluminium foil.

Table 1
Electrospinning conditions used for this study.

Polymer	Solvent	Concentration (wt%)	Voltage (kV)	Flow rate (ml/h)	Rotating rate (rpm)
PAN	DMF	10	28	1	70
PSu	DMF	26	28	1	70

2.3. Solvent vapor post-treatment

Once spun, the PAN and PSu ENMs were immediately cut into smaller coupons (about 8 cm × 8 cm) and sealed in a glass dessicator saturated with DMF vapor. The coupons were exposed to solvent vapor for different period of times (6, 9 and 18 h for PAN; 1, 3, and 6 h for PSu) and then air dried in fume hood for 24 h to let most of the residual DMF evaporate before further characterization. During exposure, the fiber was left on the aluminum foil for some tests (Method A) and removed from the foil for others (Method B).

2.4. Surface morphology characterization and property measurements

Changes in surface morphology between the ENMs and treated membranes using both methods were observed by FEI PHENOM tabletop scanning electron microscope (SEM) (FEI Company, USA) and field emission scanning electron microscopy (FESEM) (JEOL 6335F). The samples were first sputter-coated with gold or platinum prior to obtaining SEM or FESEM images.

The mechanical properties of all the PAN and PSu ENMs were measured by using TA instrument Dynamic Mechanical Analysis at 25 °C. A minimum of three strips of length 40 mm × 5.5 mm were cut from each type of membrane.

2.5. Membrane characterization

A mercury intrusion porosimeter (PoreMaster, Quantachrome) was used to characterize the pore structure (porosity and pore size) before and after DMF vapor treatment. The porosity was calculated by using the following equation, where V_p is the cumulative pore volume measured by the porosimeter, m is the mass of the sample and ρ is the density of the sample obtained by measuring the mass and dimension of the sample.

$$\%\,Porosity = \frac{V_p \times m}{m/\rho} \times 100 \tag{1}$$

The Washburn equation was used to calculate the pore diameter distribution from the intrusion pressure, P

$$P \cdot d = -4\gamma \cdot \cos\theta \tag{2}$$

In Eq. (2), P is the intrusion pressure in MPa, d is the pore diameter in μm, γ is the surface tension of mercury (480 dynes/cm) and θ is the contact angle of mercury (a value of 140° was assumed) with the sample. The sample was tested in the pressure range of 0–60,000 psi. This instrument provides an equivalent pore diameter based on the assumption of cylindrical pores. It is also to be noted that the intrusion technique can detect both through and blind pores but not closed pores.

A Millipore Amicon bioseparations stirred cell (model 8200, Fisher scientific, Pittsburgh, PA) with active filtration area of 28.7 cm^2 was used to evaluate the pure water flux performance. The tested membrane was placed in the filtration cell which was then filled with 120 ml of DI water. The applied pressure was increased in increments of 2 or 3 psi and water permeability was measured.

3. Results and discussion

3.1. Influence of solvent vapor treatment on membrane surface morphology.

Figs. 1 and 2 illustrate SEM images of PAN and PSu ENMs treated with DMF vapor under different exposure time