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Formation of functional polyethersulfone electrospun membrane for water purification by mixed solvent and oxidation processes

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ABSTRACT

Most water-based filtration applications of electrospun nanofibrous membranes require the substrate to possess suitable strength, wettability and permeability, where the size, inter-fiber adhesion and hydrophilicity of electrospun nanofiber must be carefully controlled in order to meet these criteria. In this study, we demonstrate the fabrication of high quality polyethersulfone (PES) nanofibrous membranes that are particularly useful for water purification. Two treatments were illustrated that can significantly improve the mechanical property and hydrophilicity of the PES membrane without compromising its porosity and water permeance. The first treatment involves the use of mixed solvents (DMF/NMP), containing a high vapor pressure component (NMP), where the mechanical properties (e.g. modulus and strength) of the membrane are improved by solvent-induced fusion of inter-fiber junction points. The second method involves the short time oxidation treatment with a strong oxidant (ammonium persulfate), where the hydrophilicity of the membrane is greatly increased.

1. Introduction

Electrospinning has become a versatile technique that can produce cost-effective, highly porous non-woven membranes with large surface to volume ratios, at a relatively high production rate. Numerous research activities have been explored for possible applications, including biological scaffolds, filtration media, sensors, protective fabrics, and so on [1–3]. In some of these applications, the biomechanical stability of nanofibrous scaffolds with flexibility and resistance to kinking and squashing, as well as sufficiently high tensile and shear strengths to resist fraying at cut edges and tearing out of sutures must be achieved [4]. For typical filtration applications to remove particulates from air stream and gaseous streams, or from liquid streams such as water, hydraulic fluid, lubricant oil or fuel, often requires the membranes to possess sufficient mechanical strength as well as chemical and physical stabilities. This is because the filter media may be exposed to a broad range of temperature, humidity, mechanical vibration, shock, reactive, and abrasive particulates in the fluid flow [5].

The most effective approach to improve the integrity and the mechanical strength of electrospun membrane with a given material selection is to enhance the strength of the junction point within the nanofiber mat, preferably to weld the non-woven fiber structure together forming a "nano-trusses" network. One way to accomplish this goal is to use the thermal treatment above the glass transition temperature of electrospun fiber but below its melting temperature, which can cause inter-fiber fusion [6–9]. The fused nanofibrous structure always showed increased mechanical properties due to welded fiber-fiber junctions [4,9]. A possible drawback of this method is the dimensional shrinkage of heat-treated membranes, when compared with the original membrane dimension. This is because the thermal treatment often induces entropic relaxation of stretched polymer chains, resulting in significant shrinkage along the fiber axis. In this study, we demonstrate a non-invasive method, which will be described later, to enhance the membrane integrity and strength without changing the fiber or membrane dimension.

Most conventional membrane materials, such as polytetrafluoroethylene (PTFE), polypropylene (PP), polyethersulfone (PES), polyvinylidene fluoride (PVDF), are hydrophobic, while for water-based filtration/purification applications, the membranes should be hydrophilic. Hydrophobic polymer surface can be rendered into hydrophilic by various methods, including plasma treatment [10], chemical oxidation and grafting [11–13] and blending with hydrophilic polymers [14–16]. For porous membranes in water applications, the water wetting properties (e.g. hydrophilicity) can be easily adjusted by surface modifications because of the high surface area to volume ratio. Often, only minimal modifications on the surface are required to functionalize these membranes because extensive

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functionalization can also introduce undesirable effects, such as pore blocking/collapsing and unstable post-chemical reactions. For electrospun membranes, the hydrophilicity can be introduced in various ways, which have been demonstrated in the literature. For example, the extraction of the hydrophilic component in polymer blends (e.g. polyethylene oxide (PEO) from polycaprolactone (PCL)/PEO blends) induced porous surface structures in nanofiber, which led to a lower water contact angle (from 124° to 105°, i.e., became more hydrophilic) than that of pure PCL membrane [17]. Poly(lactide-co-glycolide) (PLGA) electrospun membranes were treated with oxygen and ammonia plasma, where the water contact angle was significantly reduced from 112° to 47° after plasma treatments [18]. Polyacrylonitrile (PAN) nanofibrous membranes were also made hydrophilic by alkaline hydrolysis [19], where the water contact angle decreased from 88° to 35° when the membrane was hydrolyzed with 2 N NaOH solution at 60 °C for 2 hours.

In this study, we demonstrate two practical approaches to enhance the mechanical properties as well as the hydrophilicity of electrospun PES membranes. The first method involves the use of mixed solvents to induce fiber–fiber infusion during electrospinning of PES. The method can significantly improve the mechanical integrity (as shown by tensile testing results) of electrospun membranes without compromise the fiber size and morphology. The second method involves the use of a simple oxidative reaction that can produce highly water wettable (hydrophilic) PES electrospun membranes. The surface functionality of the membrane was characterized by infrared (IR) spectroscopy. Finally, the pure water permeant test of the PES electrospun membranes, prepared by the two combined methods, was carried out and the results were compared with those of conventional filtration media. Without question, PES electrospun membranes show much higher flux than conventional filter and will be very useful for water filtration applications.

2. Experimental

2.1. Materials

Polyethersulfone (PES) (Radel A-100, M_w: 53,500 g/mol, polydispersity index (PDI): 2.88) was obtained from Solvay Membranes, Inc. Dimethylformamide (DMF) and N-methyl-pyrrolidinone (NMP) were obtained from Sigma–Aldrich, and they were used to prepare the solvent mixtures for PES electrospinning. Ammonium persulfate (APS) was also obtained from Sigma–Aldrich and used as received. The non-woven polyethylene terephthalate (PET) substrate (Hollytex 3242) was obtained from Ahlstrom Mount Holly Springs. A Milli-Q water purification system was used to produce purified water for sample preparation and membrane test.

2.2. Polyethersulfone (PES) nanofibrous membrane fabrication by electrospinning

PES was dissolved in DMF or DMF/NMP mixture at 60 °C for 1 day until it became a homogeneous solution. Five different concentrations (i.e., 24, 26, 28, 30, and 32 w/w%) of PES solutions were prepared. For preparation of mixed solvents (DMF/NMP), 4 different ratios of NMP (i.e., 25, 40, 50, 75 wt% of NMP in total solvent amount) were used. All PES solutions were electrospun onto aluminum foil or non-woven PET support at a high voltage of 15 kV. During electrospinning, the flow rate was 10 μl/min and the spinneret diameter was 0.7 mm. The distance between the collector and the spinneret was 10 cm. In the electrospinning setup, a rotating metal drum (diameter: 9 cm, rotating speed: 300 rpm) was used to collect the deposited nanofibers. A stepping motor was used to control the oscillatory translational motion perpendicular to the drum rotation direction (the oscillation distance was about 12 cm) to ensure the production of uniform electrospun membrane with sufficient area (i.e. larger than $7.6 \times 10.2\ \mathrm{cm}^2$) for measurements.

2.3. Scanning electron microscopy

The morphology of electrospun PES nanofibrous membranes was investigated by scanning electron microscopy (SEM, LEO 1550) equipped with Schottky field emission gun (10 kV) and Robinson backscatter detector. All specimens received 24 s of gold coating to minimize the charging effect. The fiber diameter and pore area were measured by the Scion® image analysis program after calibration with standards.

2.4. Mechanical property and porosity measurements

The mechanical properties of electrospun PES membranes were measured by using Instron (Model 4442) tensile testing machine at ambient temperature. The gauge length was 25 mm and the width at the center of the specimen was 4 mm. The specimen thickness was about 40 μm. The cross-head speed was 10 mm/min. The porosities were determined by using the bulk density of PES pellet and the membrane density ($1 - \rho_{\text{e-spun}}/\rho_{\text{pellet}}$). The bulk density value ($1.37\ \mathrm{g/cm^3}$) of PES pellet used in this experiment was obtained from Solvay Membranes (based on the ASTM D792 method). The electrospun membrane density was calculated by measuring the membrane size, thickness, and the mass of the membrane. Before any measurements, all samples were dried *in vacuo* for several days till the masses become constant.

2.5. Oxidation of electrospun PES membrane by ammonium persulfate (APS)

The oxidation procedures were as follows. Electrospun PES membrane (about $25\ \mathrm{cm}^2$) was pre-wetted in isopropyl alcohol (IPA) and then washed thoroughly with deionized (DI) water. The membrane coupon was kept in 3 w/v% ammonium persulfate solution at 90–95 °C for 15 min. After the reaction, the membrane was washed with a copious amount of DI water. The sample was dried *in vacuo* at 70 °C for 40 min.

2.6. Infrared spectroscopy and contact angle goniometry

Fourier transform infrared (FT-IR) spectroscopy (Nicolet 380 spectrophotometer, Thermo Scientific, Inc.) was used for characterizing oxidized electrospun PES membranes. All samples were scanned 32 times from $650\ \mathrm{cm}^{-1}$ to $4000\ \mathrm{cm}^{-1}$. The initial hydrophilicity of the nanofibrous membranes was checked before and after the oxidation reaction by using contact angle goniometry (CAM200 Optical Contact Angle Meter, KSV Instruments, LTD), where 10 μl of Milli-Q water was used as the probe liquid. At least 3 different places were tested for consistent results throughout the sample.

2.7. Pure water permeance of PES nanofibrous membranes

The pure water permeance of oxidized electrospun PES membranes was measured by dead-end filtration at ambient temperature using Milli-Q water. An ultrafiltration cell (Advantec MFS, Inc.: model UHP-43) with active filtration area of $11.5\ \mathrm{cm}^2$ under a feed pressure of 18 psig was used to determine the flux, where the amount of permeate was measured by using a graduated cylinder.

3. Results and discussion

The morphology of electrospun PES membranes prepared from different concentrations was investigated using SEM. In Fig. 1(a),

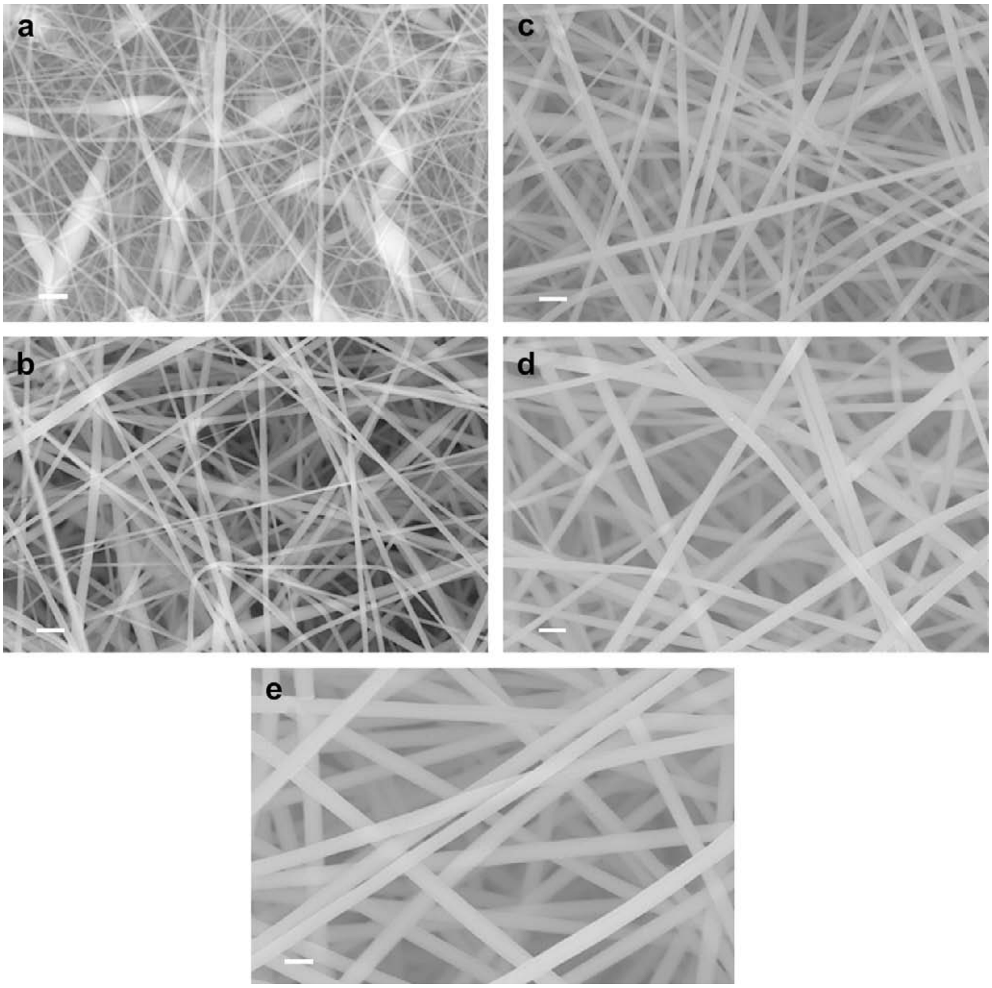

Fig. 1. SEM images of electrospun PES membranes from different PES/DMF concentrations: (a) 24 wt%, (b) 26 wt%, (c) 28 wt%, (d) 30 wt%, (e) 32 wt% (the scale bar is 2 μm).

the mixed bead–fiber morphology was seen from the membrane fabricated by the 24 wt% PES/DMF solution. In contrast, the uniform fiber morphology was found in membranes from 26 to 32 wt% PES/DMF solutions (Fig. 1(b)–(e)). The average fiber diameter increased from 550 nm to 1300 nm as the solution concentration was increased from 26 wt% to 32 wt% (Fig. 2).

The same experimental conditions (electric field strength, flow rate and humidity) for processing of 26 wt% PES/DMF solution, in which the homogeneous fiber morphology was produced, were used to fabricate electrospun PES membranes with mixed solvents (DMF and NMP). Fig. 3 illustrates SEM images of electrospun PES membranes fabricated from mix solvents with different NMP concentrations (the polymer solution concentration was fixed at 26 wt%). When the NMP concentration increased to 75 wt% in the mixed solvent, all electrospun fibers became fused together, forming the porous film-like structure only with a trace of the fiber morphology (Fig. 3(e)). This was probably due to the slow evaporation of the high boiling point component (i.e. NMP) in the mixed solvent during the electrospinning process. From SEM images of electrospun PES membranes prepared from DMF or mixed DMF/NMP solvents (Figs. 1 and 3), the fiber junction points in the membranes prepared from the DMF/NMP solvents appeared to be jointed more closely with some even slightly fused together, when compared to those in the membranes prepared from PES/DMF solutions.

Fig. 4 illustrates the electrospun PES fiber diameter as a function of NMP concentration in the mixed solvent. It was seen that as the amount of NMP in the solvent mixture increased to 50 wt%, the fiber diameter was increased from 550 nm (pure DMF) to 760 nm. Since the factors related to control the fiber diameter are quite complex and they are difficult to be isolated [20], we hypothesize the slight increase of the fiber diameter can be mainly due to two possibilities:

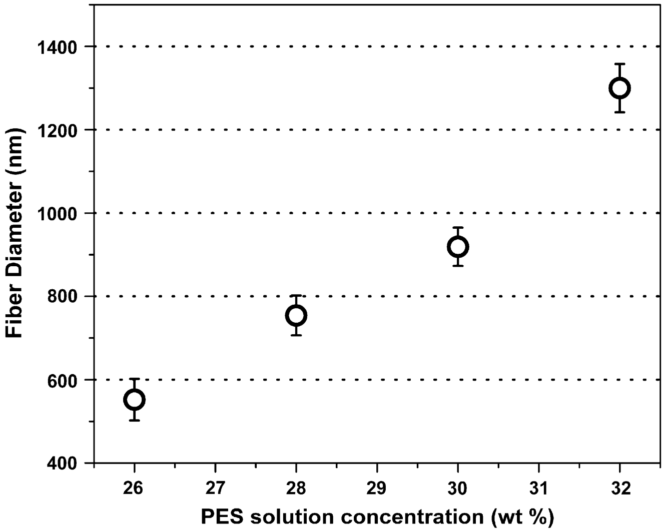

Fig. 2. The effect of solution concentration on the PES diameter of electrospun fiber fabricated from the PES/DMF solution.

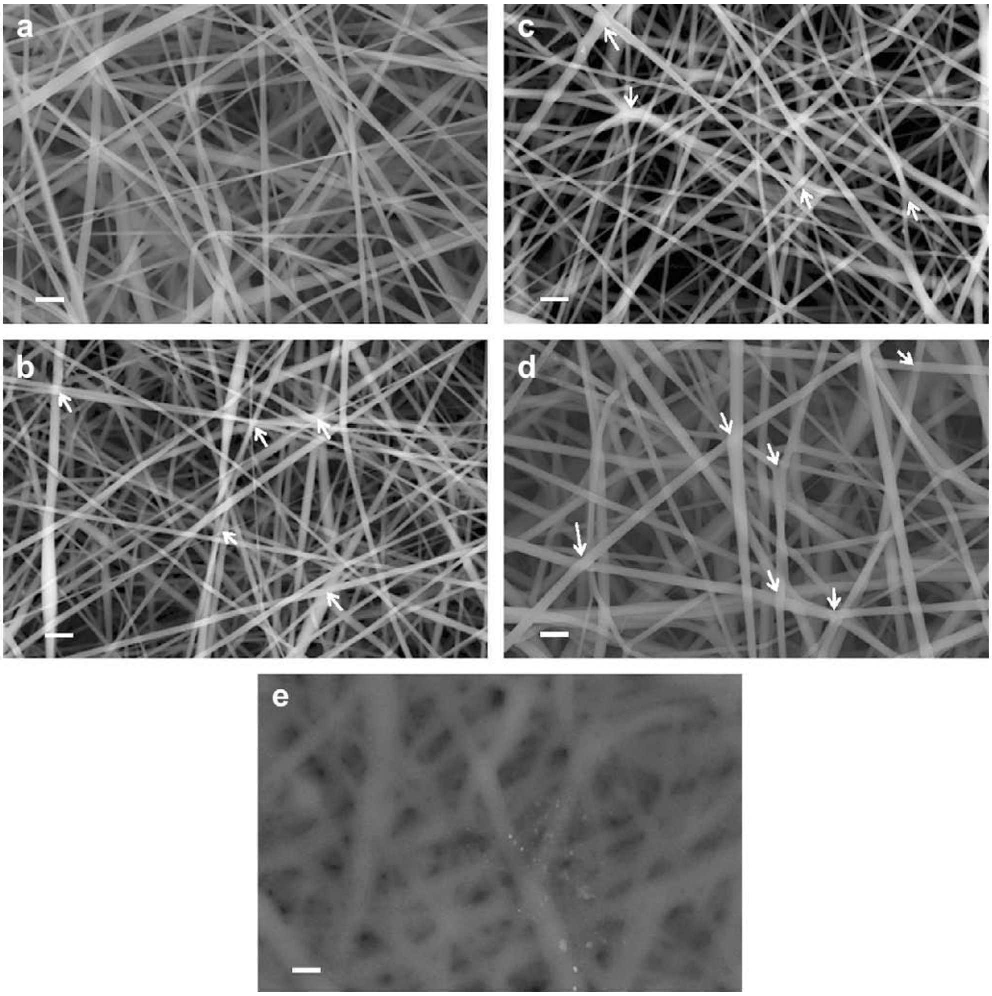

Fig. 3. SEM images of electrospun PES membranes fabricated from mix DMF/NMP solvents with different NMP concentrations (i.e., weight % vs. total solvent, where the polymer solution concentration was fixed at 26 w/w%): (a) 0 wt%, (b) 25 wt%, (c) 40 wt%, (d) 50 wt%, (e) 75 wt% (the scale bar is 2 μm).

(1) the increase in the viscosity of the mixed solvents (DMF: 0.92 cps, NMP: 1.7 cps), which can lead to the higher solution viscosity of the polymer solution in electrospinning, and (2) the decrease in the vapor pressure of the mixed solvents (DMF: 2.7 torr, NMP: 1.7 torr).

The mechanical properties of electrospun PES membranes, such as Young's modulus, ultimate tensile strength and strain at break, as a function of the NMP concentration in solvent mixture are shown in Fig. 5. The electrospun PES membrane prepared by using the 50 wt% of NMP (i.e., DMF/NMP ratio = 50/50 by weight) exhibited the maximum modulus and tensile strength. The ultimate tensile strength was found to gradually increase with increasing NMP concentration, while the modulus showed an abrupt increase near the 50 wt% NMP concentration. Overall, the modulus and ultimate tensile strength were improved by 570% and 360%, respectively, from electrospinning of PES solution using the 50/50 DMF/NMP solvent when compared to those of from PES/DMF solution. The maximum strain at break was seen in the electrospun PES membrane prepared at 25 wt% NMP. The mechanical property results can be correlated to the SEM observations in Fig. 3, where the significant improvement in modulus and tensile property in membranes from the 50/50 NMP/DMF mixed solvent can be attributed to solvent-induced fusion at the fiber junction points. In other words, the slow evaporation of NMP (with higher boiling point and less vapor pressure than those of DMF) during electrospinning could keep the deposited fibers relatively 'wet', resulting in a slight fusion between the contacts of inter-fibers. The residual NMP could also play a plasticization role in making the electrospun membrane to be more stretchable as indicated by the increased strain at break values at higher NMP concentration. However, the strain at break value of the membrane from the 50 wt% NMP

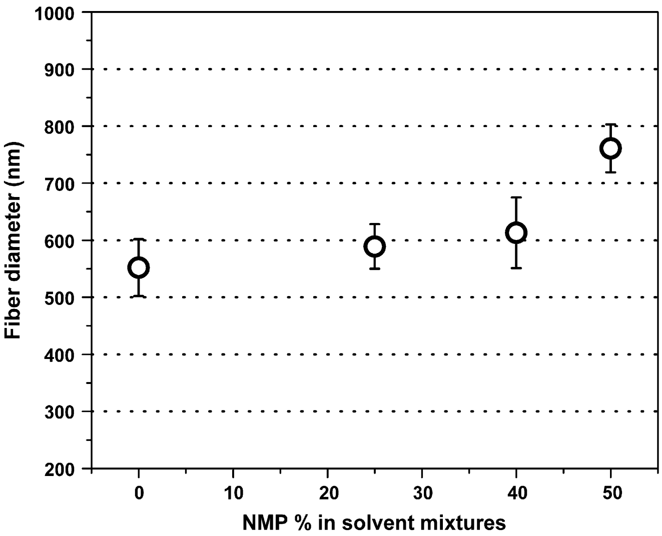

Fig. 4. The effect of mixed solvent on the electrospun PES fiber diameter.

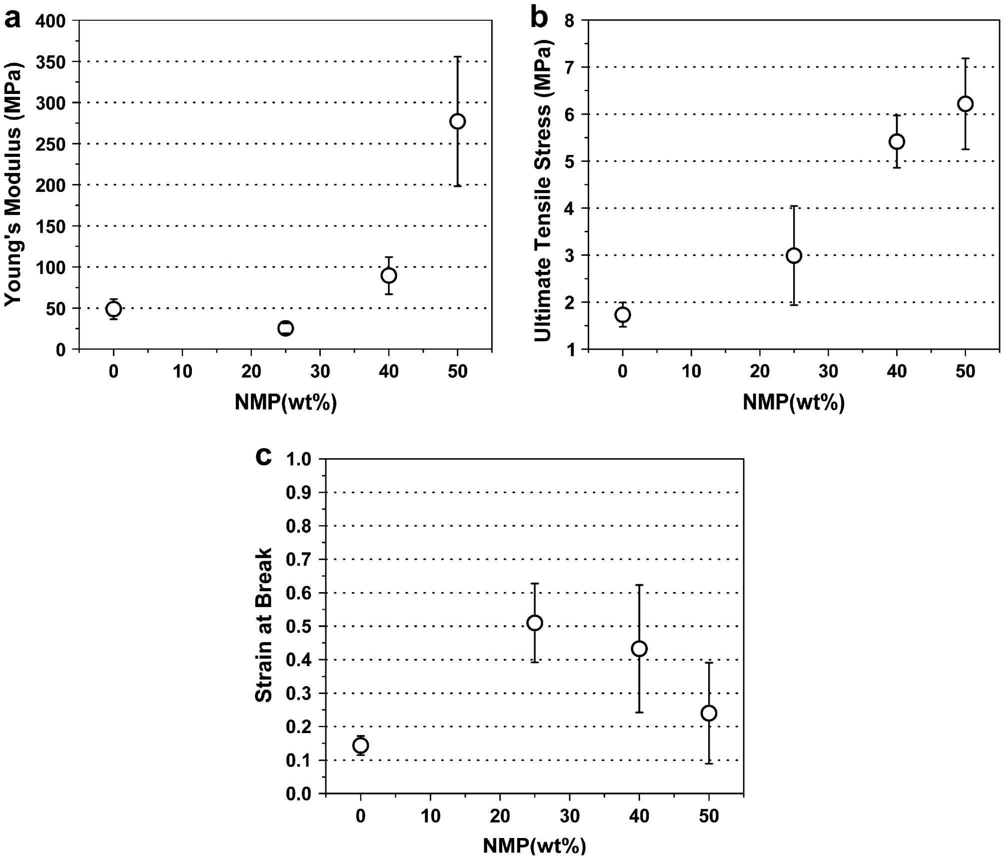

Fig. 5. Mechanical properties of electrospun PES membranes as a function of the mixed solvent: (a) Young's modulus, (b) ultimate tensile strength, and (c) strain at break.

solution became less than that from the 25 wt% NMP solution. This is probably because the enhanced fusion at fiber junction points in fact limited the stretchability of the membrane, even containing higher content of residual NMP.

The porosity of electrospun PES membranes as a function of the NMP concentration in the mixed solvent is shown in Fig. 6. It was found that the membrane porosity decreased slightly with increasing NMP content from 84% (in pure DMF) to 76% (in 50 wt% of NMP). The lower porosity of the electrospun membrane made from the higher NMP content can be explained by the enhanced fusion of junction points. Even though the porosity was slightly reduced, the porosity of the membranes fabricated with the mixed solvents was still in the typical range for electrospun mats [21].

Ammonium persulfate (APS) was used to modify the hydrophilicity of electrospun PES membrane fabricated from the DMF/NMP = 50/50 mixed solvent. The IR spectra of APS (3 w/v% in water) treated membrane and untreated membranes are shown in Fig. 7. Under the chosen oxidization conditions (90 °C for 10–15 min), the amount of oxidized groups seemed to be too small to exhibit a clear

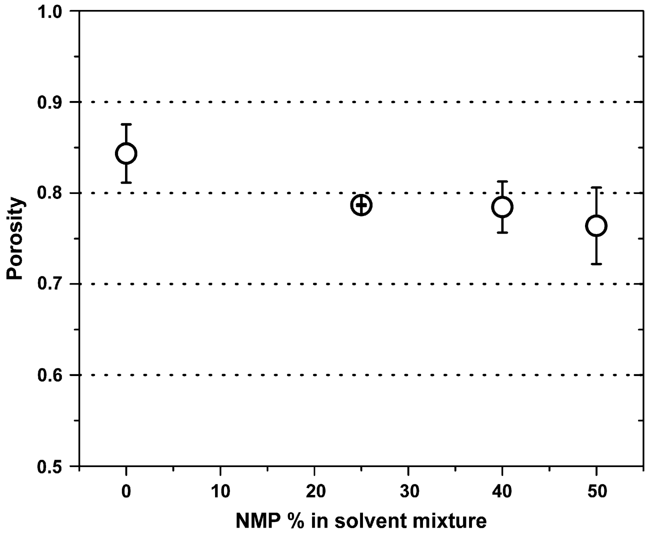

Fig. 6. Porosity of the electrospun PES membrane as a function of the mixed solvent.

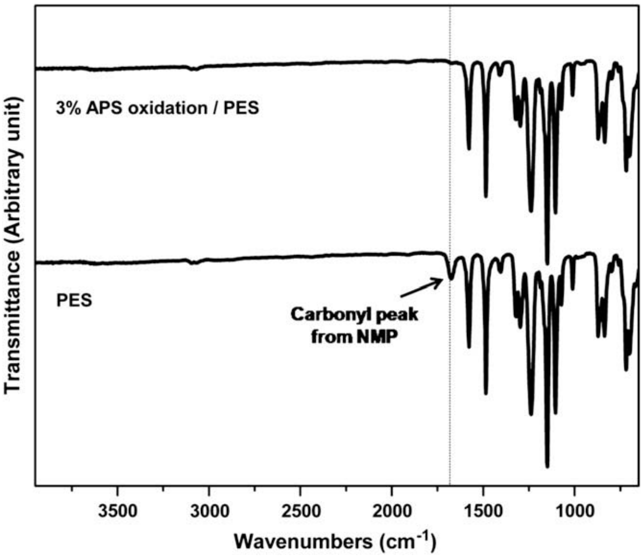

Fig. 7. IR spectra of oxidized and untreated electrospun PES nanofibrous membranes.

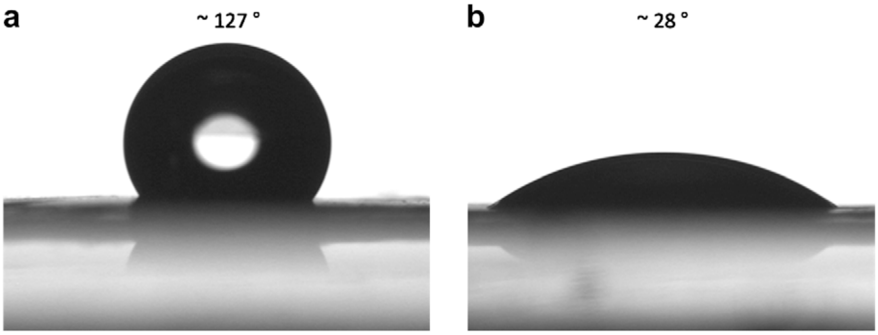

Fig. 8. Water contact angles for oxidized and untreated electrospun PES membranes.

difference in the IR spectra between untreated and treated ones. The only difference indicated that a small amount of the residual NMP in the nanofiber web was eliminated after the oxidation reaction as seen by the disappearance of the absorption peak at 1674 cm^{-1} from NMP. Nevertheless, the images of the water contact angle showed a clear difference between the treated and untreated membranes (Fig. 8). The water contact angle for untreated electrospun PES membrane was 127°, but for APS treated one was only 28°. The treated PES membrane showed the instantaneous wetting by water, suggesting that APS oxidation was taking place at the surface of the nanofiber. However, we note that the improved water wettability of the treated membrane may also be due to the enhanced surface porosity of electrospun fiber, which facilitates the wicking of water droplets into the nanofibrous web, as a result of the remaining solvent removal by the oxidative treatment.

For most water-based filtrations as by depth or surface filters involving thin-film composite (TFC) membranes, the pure water flux of the membrane directly reflects the productivity of the filter. The pure water permeances of several different types of electrospun PES membranes were measured by using a dead-end filtration cell and the results are shown in Fig. 9. It was seen that the PES membrane electrospun from pure DMF showed slightly higher flux (2826 l/m^{2}h psi) than that (2626 l/m^{2}h psi) from the mixed DMF/NMP solvent (50/50). This is probably due to the higher porosity of the electrospun membrane from the PES/DMF solution. The 10% APS treated PES membrane showed the highest value of pure water flux (2913 l/m^{2}h psi), although the increase is relatively small. This may be due to the following reason. The hydrophilicity of the membrane definitely plays a role in the pure water flux. The effect of the membrane hydrophilicity on pure water flux in the initial stage may be pronounced, but the effect in the later stage becomes minimal, where the flux is mainly dependent on the membrane porosity.

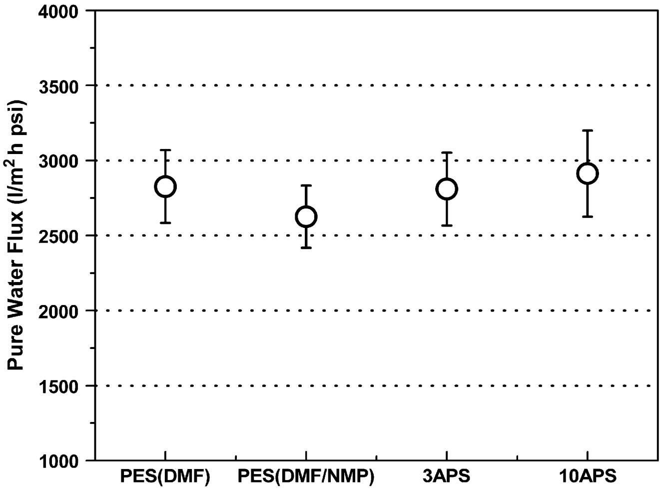

Fig. 9. Pure water fluxes of electrospun PES membranes prepared from 26 wt% PES/DMF solution; 26 wt% PES/(DMF/NMP = 50/50) solution; 3 APS – 3 wt% APS treated PES (DMF/NMP) membrane; 10 APS – 10 wt% APS treated PES (DMF/NMP) membrane.

The measured Flux values are all in the flux range of microfiltration (MF) membranes having a nominal pore size of 0.5 μm [21]. A preliminary microfiltration test indicated that the effective pore size of these electrospun PES membranes may be much smaller than 0.5 μm, which will be the subject of a future study. Without question, the electrospun PES membranes will be valuable for many microfiltration applications; they are also useful as scaffolds to support thin barrier layers to produce thin-film nanofibrous composite (TFNC) membranes for ultrafiltration and nanofiltration applications, which have been recently demonstrated by us [22–25].

4. Conclusions

High quality electrospun polyethersulfone (PES) membranes could be fabricated by using DMF or mixed DMF/NMP as solvents. Uniform fiber morphology (diameter: 550–1300 nm) was obtained at PES concentrations from 26 to 32 wt% in DMF. With the addition of less-volatile NMP, the average fiber diameter was slightly increased from 550 nm (pure DMF) to 761 nm (50 wt% NMP in the solvent mixture), but the corresponding mechanical properties (e.g. modulus and tensile strength) were significantly improved. The enhanced mechanical properties were caused by the fusion of inter-fiber junction points. The short period of oxidation treatment using ammonium persulfate (APS) could make electrospun PES membranes hydrophilic (contact angle $\sim$ 28°), having instant water wettability. Finally, the pure water flux was tested for all electrospun PES membranes fabricated by mixed solvents or modified by oxidation. Their flux performance was in the range of microfiltration (MF), probably with smaller effective pore size that will be evaluated later.

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References

[1] Greiner A, Wendorff JH. Angew Chem Int Ed 2007;46:5670.
[2] Schreuder-Gibson HL, Gibson P. ACS Symp Ser 2006;918:121.
[3] Li D, Xia Y. Adv Mater 2004;16:115.
[4] Lee SJ, Oh SH, Liu J, Soker S, Atala A, Yoo JJ. Biomaterials 2008;29:1422.
[5] Chung HY, Hall JRB, Gogins MA, Crofoot DG, Weik TM. US Patent Application, 20070271891.
[6] Choi SS, Lee SG, Joo CW, Im SS, Kim SH. J Mater Sci 2004;39:1511.

[7] Gopal R, Kaur S, Ma Z, Chan C, Ramakrishna S, Matsuura T. J Membr Sci 2006;281:581.
[8] Ma Z, Masaya K, Ramakrishna S. J Membr Sci 2005;265:115.
[9] Ma Z, Masaya K, Ramakrishna S. J Membr Sci 2006;272:179.
[10] Denes FS, Manolache S. Prog Polym Sci 2004;29:815.
[11] Bamford CH, Al-Lamee KG. Macromol Rapid Commun 1994;15:379.
[12] Bamford CH, Al-Lamee KG. Polymer 1996;37:4885.
[13] Gang DH, Lenk W, Berwald S, Lunkwitz K, Simon F, Eichhorn KJ. J Appl Polym Sci 1996;60:1087.
[14] Hayama M, Yamamoto K, Kohori F, Uesaka T, Ueno Y, Sugaya H, et al. Biomaterials 2004;25:1019.
[15] Sun S, Yue Y, Huang X, Meng D. J Membr Sci 2003;222:3.
[16] Hamza A, Pham VA, Matsuura T, Santerre JP. J Membr Sci 1997;131:217.
[17] Kim G, Park J, Park S. J Polym Sci Part B Polym Phys 2007;45:2038.
[18] Park KE, Lee KY, Lee SJ, Park WH. Macromol Symp 2007;249/250:103.
[19] Liu H, Hsieh YL. Macromol Rapid Commun 2006;27:142.
[20] Thompson CJ, Chase GG, Yarin AL, Reneker DH. Polymer 2007;48:6913.
[21] Ramakrishna S. An introduction to electrospinning and nanofibers. World Scientific; 2005.
[22] Wang X, Chen X, Yoon K, Fang D, Hsiao BS, Chu B. Environ Sci Technol 2005;39(19):7684–91.
[23] Yoon K, Wang X, Fang D, Hsiao BS, Chu B. Polymer 2006;47:2434–41.
[24] Wang X, Fang D, Yoon K, Hsiao BS, Chu B. J Membr Sci 2006;278:261–8.
[25] Yoon K, Hsiao BS, Chu B. J Membr Sci 2009;326:484–92.