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Water Filtration Properties of Novel Composite Membranes Combining Solution Electrospinning and Needleless Melt Electrospinning Methods

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ABSTRACT: New composite polyvinyl alcohol (PVA)/polypropylene (PP) membranes were prepared by combining both solution electrospinning and melt electrospinning methods. Self-designed and made needleless melt electrospinning device was used to fabricate PP membranes which acted as the support layer. PVA membrane on the surface was fabricated via solution electrospinning. The electrospun PVA/PP composite membranes were characterized by the pore size distribution, pure water flux, and rejection ratio, then compared with general composite membranes. Characterizations revealed that the fiber diameter of solution electrospun PVA membrane and melt electrospun PP membrane were 0.171 ± 0.027 and 2.24 ± 0.33 μm, respectively, and the average pore size was 0.832 μm and 27.29 μm, which was much smaller than the nonwoven membrane. The rejection ratio to the 500 nm particles of the PVA/PP composite membrane could reach more than 96%, which was much larger than that of the PVA/non-woven substrate of 90%, and the melt electrospun PP membrane of 80%, and still maintained high permeate flux of 32,346 L/m^{2}h under the pressure of 0.24 bar. This approach of compositing the solution electrospun membranes and melt electrospun membranes could be useful in designing novel microfiltration membrane owning both higher flux and higher rejection ratio. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41601.

KEYWORDS: electrospinning; membranes; separation techniques

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INTRODUCTION

The advantages of high filtration efficiency and low resistance provided by the fibrous membranes have attracted much attention.[1,2] As a valuable way, their applications have spread to various areas such as blood dialysis, respiratory protection, test-tube cleaning, filtering material, processing of nuclear and hazardous materials, particle collection in clean rooms, and so on.[3] Among the usual manufacturing methods of fibers, such as wet-laid, melt-blown template synthesis, and electrospinning,[4,5] electrospinning is one of the simplest methods for preparing ultrafine fibers.[3,6,7] Now, electrospun nanofibers have been widely used in many applications, such as sensors,[8] tissue engineering scaffolds,[9] wound dressings,[10] filters[11] for its large specific surface area, high fiber aspect ratio, and high porosity.[12] A simple basic electrospinning apparatus consists of a syringe pump, high voltage supply, and a collector. A polymer solution or melt in high-voltage electrostatic field overcomes the surface tension arising charged jet, resulting in jet solidified on the receiving electrode and form fibers.[6]

PVA has been proved to be widely used for cell and enzyme immobilization.[13,14] As a synthetic hydrophilic polymer, it has been investigated as a material for electrospinning by many researchers for its chemically and thermally stable, and the capability to be easily modified through its hydroxylic groups.[15,16] Many researchers have done a lot of work to investigate the specific effect of PVA membranes.[17,18] Through adding the LiCl to the solution polyvinylalcohol (PVA), Li et al. found that the addition of LiCl significantly accelerated jet thinning and solidification, and the average diameter of smooth jets decreased with increasing LiCl concentration.[19] Koski et al. investigated the effect of polymer weight average molecular weight (MW) on the electrospun PVA fiber structure and found that the fiber diameter increased with increase of MW and concentration.[18]

Generally, electrospinning includes solution electrospinning and melt electrospinning. Since Formhals invented the Electrospinning technique in 1934, the research of solution electrospinning had received much attention from the researchers.[20] In 2012, there were 3,041 articles about the solution electrospinning, while only 32 articles about the melt electrospinning based on "SciFinder" retrieval. In recent years, with the rising of public awareness for environment protection, more researchers focus on the melt electrospinning for its advantages, such as solvent free, safe, environmental friendly technique with high production, and

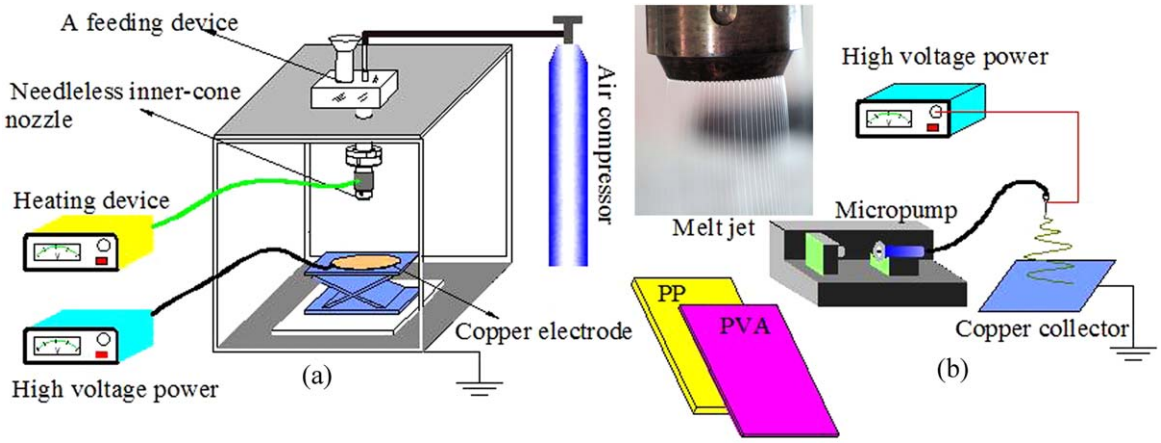

Figure 1. Schematic diagram of electrospinning apparatus. (A) Melt electrospinning; (B) solution electrospinning. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

good materials adaptability compared with the solution electrospinning. Solution electrospinning technique and melt electrospinning technique have their own advantages, combining solution and melt electrospinning will be a major trend in the future. This article introduced a new needleless melt electrospinning device for preparing PP membrane which acted as the support layer, then fabricated PVA membrane as surface membrane via solution electrospinning device. The capability and performance of both membranes were compared by evaluating the membrane properties, such as pure water flux, pore size distribution, and rejection ratio.

EXPERIMENTAL

Materials

Polyvinyl Alcohol (PVA) with 1750 degree of polymerization and 98% degree of hydrolysis was purchased from Shanghai Yingjia Co. Ltd, China.

Polypropylene (PP) with a melt flow rate (MFR) of 2000 g/10 min was purchased from Shanghai Expert Co., China.

Preparation of PVA/PP Composite Filter Membranes

Melt Electrospun PP Fibers. Figure 1(A) shows a schematic diagram of the needleless melt electrospinning apparatus used in this study, which is consisted of five major components: a variable high voltage power supply, a needleless inner-cone nozzle, an air pressure gun, a heating device, and a copper collector. The two attractive advantages of the device: (1) brings forth the new needleless inner-cone nozzle, which can generate multiple Taylor cones; (2) air current can make fiber diameter refined and improve the output by strengthening the stretching force of the jets. The optimal operating parameters of the melt electrospinning have been investigated in our previous work.[21] The PP fibers were electrospun in a humidity of 25% at 24°C, and the nozzle temperature was set at 240°C. The melt feeding rate was adjusted to 15 g/h which was controlled by an adjustable pump. The distance between the nozzle and electrode was 12 cm, and the applied voltage of electrode was 50 kV. The fabrication process of the melt electrospun PP fibers is described as follows: the melt was injected from a cylinder into the nozzle; a thin and uniform melt film formed on the umbellate circumferential surface; multiple jets around the rim of the nozzle were drawn to the collector spontaneously under the influence of the electric field.

Solution Electrospun PVA Fibers. PVA was dissolved in distilled water and was stirred at 100°C to obtain the PVA (8 wt %) solution containing surfactant of lauryl sodium sulfate (0.2 wt %). A schematic diagram of the solution electrospinning device is shown in Figure 1(B). Electrospun PVA nanofibers were electrospun at voltages ranging from 15 to 25 kV by using a metal needle of 1 mm inner diameter. The flow rate was controlled at 0.5 mL/h by a microsyringe pump (WZ-50C6, Smiths Medical Instrument Co., Ltd., China). After making a thorough investigation, the favorable conditions of electrospun PVA nanofibers with good morphology could be acquired under 20 kV and 14 cm collecting distance between needle tip and the collector. The process was operated with a relative humidity of 25% and temperature of 24°C during the electrospinning.

Characterization of Morphology

The morphologies of the electrospun fibers were observed using a scanning electron microscopy (SEM, HITACHI S4700, Japan). Before observation, all fibers were coated with an ultrathin electrically-conducting material, commonly gold, deposited on the sample. The solution electrospun fibers were electrospun onto the melt electrospun PP membranes, and the thickness of the PVA membrane was thin of several microns. So the PVA fibers must be placed at the top to avoid being covered by support layer. For the membranes after the particle rejection test, left them to dry naturally, then removed the particles accumulated on the membrane surface carefully. The bottom melt electrospun membranes were separated carefully to prepare SEM sample, and the rest of the membranes were used to prepare another sample. The average fiber diameter was calculated by analyzing the SEM images with the image analysis software (Image J2X). A micrometer was used to measure the thickness of the membranes.

The pore size and pore size distribution of membranes are very important factors which can influence the quality of membranes,

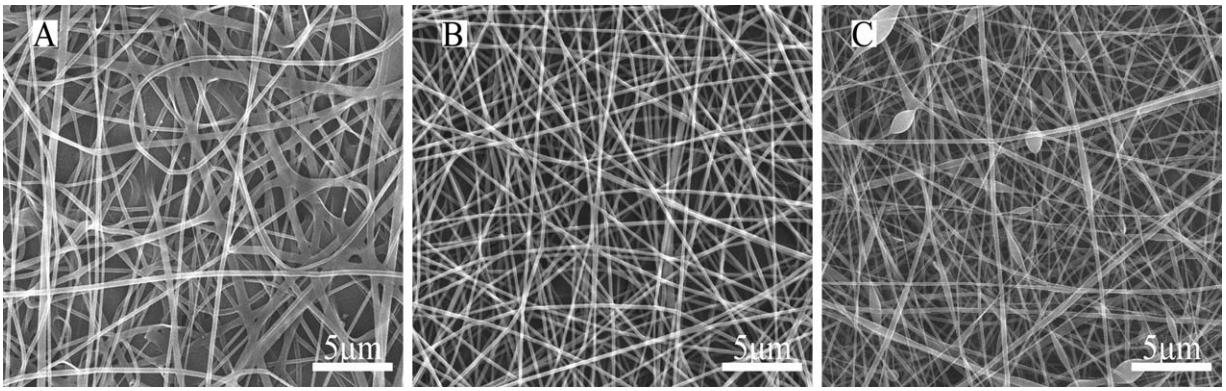

Figure 2. SEM images of different solution electrospun PVA fibers: (A) pure PVA solution; (B) PVA solution containing 0.2 wt % lauryl sodium sulfate; (C) PVA solution containing 2 wt % lauryl sodium sulfate.

such as the air and water permeability and retention rate.[22] The pore size and pore size distribution of the membranes were determined by a pore size analyzer (3H-2000PB, BeShiDe Inc., China) using the bubble-point method. The pores of the sample were filled with a wetting liquid, and the filter holder was connected to a source of a regulated pressure. The air pressure was gradually increased and the formation of bubbles on the liquid side was noted. The pressure required to force an air bubble through the

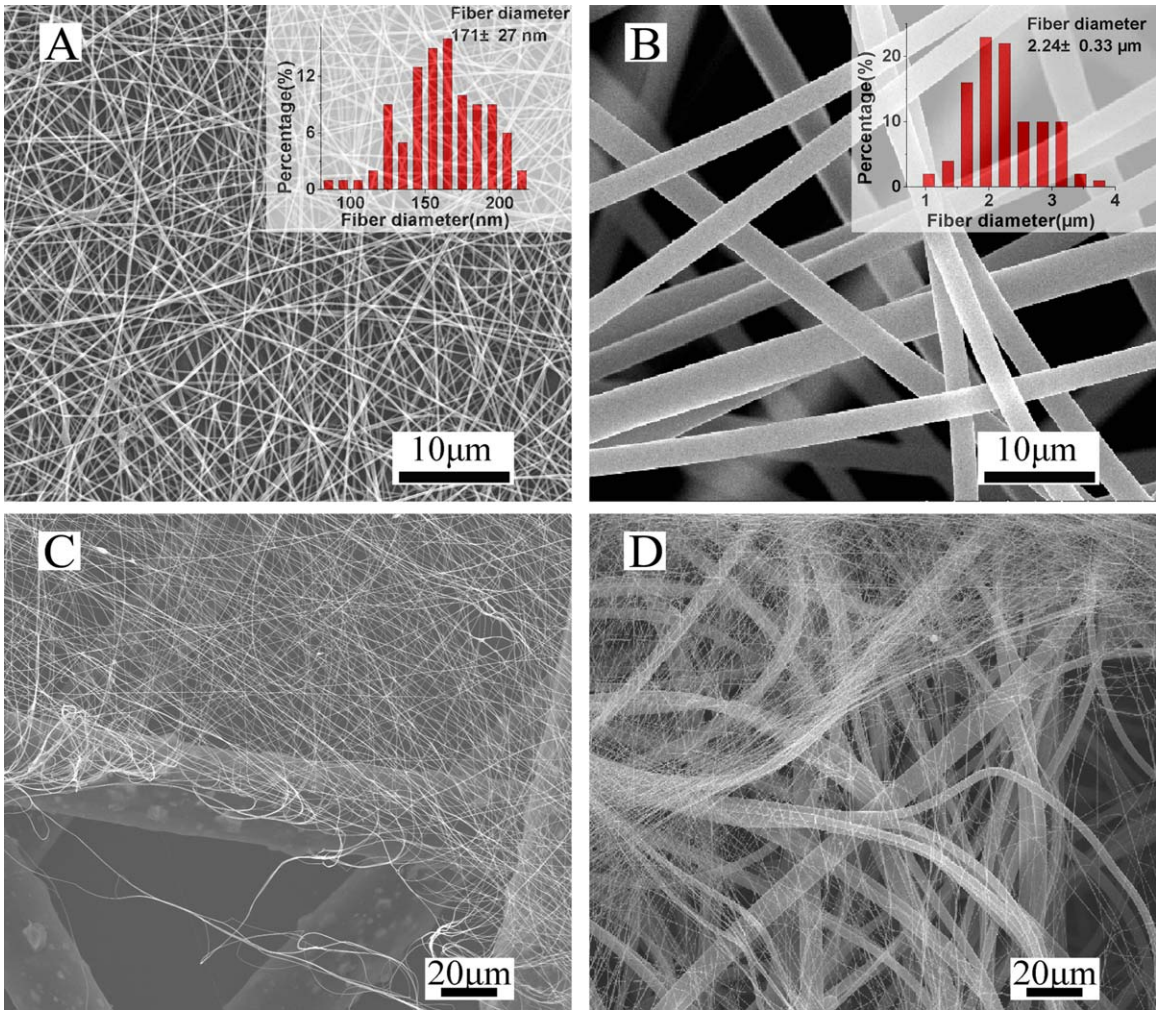

Figure 3. SEM images of electrospun membranes: (A) solution electrospun PVA membrane; (B) melt electrospun PP membrane; (C) electrospun PVA membrane fabricated on the PP non-woven substrate; (D) electrospun PVA/PP composite membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

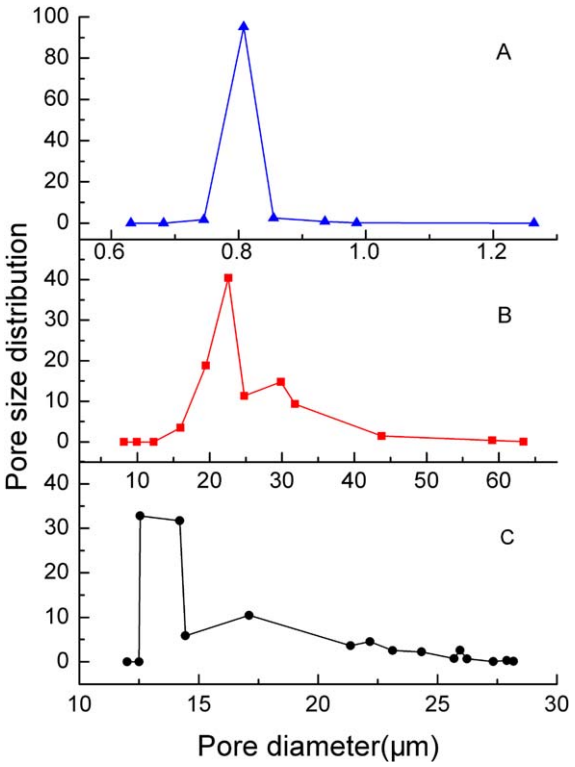

Figure 4. Pore size distributions of the solution electrospun PVA membrane (A), the melt electrospun PP membrane (B), and the electrospun PVA/PP composite membrane (C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pore was inverse proportion to the size of the hole. Thus by determining the pressure necessary to force water out of the capillary, the diameter of the capillary could be calculated. The theoretical relation between this transition pressure and the pore size is:

$$D=\frac{4\gamma\cdot\cos\theta}{P} \quad (1)$$

where P is the bubble-point pressure, γ is the surface tension of the liquid, θ is liquid-solid contact angle, and D is diameter of the pore.

Filtration Efficiency Evaluation

Contact Angle and Water Permeate Flux. The hydrophobicity of membranes was evaluated by water contact angle using a contact angle system (OCA20, Dataphysics, Germany). Two microliters of deionized water were dropped on the surface of samples. Image of solid/liquid interface was captured by a charge-coupled device camera.

The pure water flux test was performed using the dead-end filtration. All membranes used on this test were 10 cm in diameter. Before the test, each membrane was flushed with distilled water for 2 min to open the possible closed pores. The flux of membrane, J (L/m^2 h), is calculated according to formula (2):

$$J=\frac{V}{A\cdot t} \quad (2)$$

where V is the liquid volume through the filter (L), A is the effective area of membrane (m^2).

Particle Rejection Test. The rejection performance of membrane was evaluated by the retention rate of one particle. The micron particles with a diameter of 0.5 μm were diluted in distilled water to prepare 1% wt of the original solution. The rejection ratio was calculated by using the following equation:

$$\eta=\left(1-\frac{C_{\text{down}}}{C_{\text{up}}}\right)\cdot 100\% \quad (3)$$

where C_{up} and C_{down} represent the concentration of the feed solution and that of the filtrate solution, respectively.

RESULTS AND DISCUSSION

Characterizations of Electrospun Membranes

Quality of PVA Fibers. In course of exploring the preparation condition of electrospun PVA fibers, three kinds of PVA solutions were prepared: the pure PVA solution, PVA solution containing 0.2 wt % surfactant of lauryl sodium sulfate, and PVA solution containing 2 wt % surfactant of lauryl sodium sulfate. They were all electrospun at the condition of 20 kV voltage and 14 cm collecting distance, the SEM images of the PVA fibers are shown in Figure 2. When pure PVA solution was used to prepare fibers, the process was very unstable and the jet was discontinuous, sometimes higher voltage of 30 kV was needed. However, when 0.2 wt % lauryl sodium sulfate was added to the PVA solution, the electrospinning process became stable. From Figure 2, it could be seen that the quality of fibers was very poor and the fiber diameter was not uniform at the condition of pure PVA solution. While the morphology of fibers was very perfect after 0.2 wt % lauryl sodium sulfate was added to the PVA solution. As the concentration of the surfactant

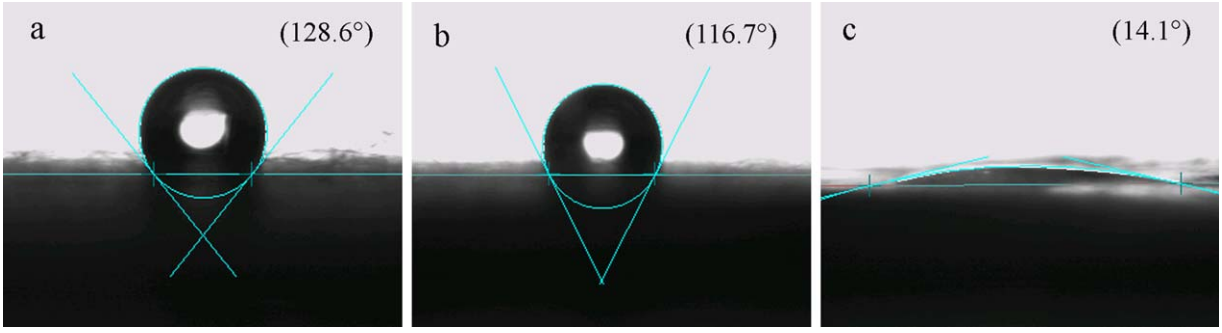

Figure 5. Contact angle of membranes. (a) Melt electrospun PP membrane; (b) electrospun PVA/PP composite membrane; (c) solution electrospun PVA membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

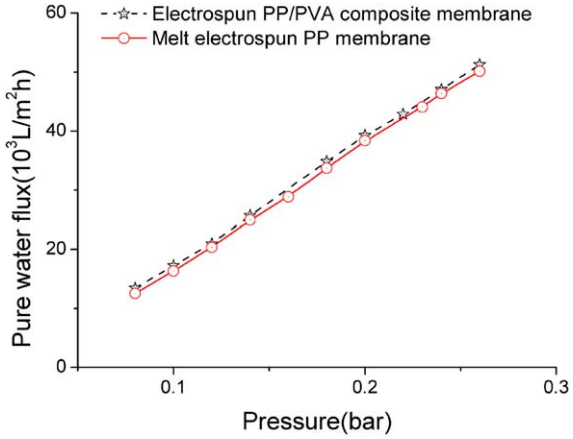

Figure 6. Pure water flux of elctrosoun PVA/PP composite membrane and melt PP membrane at different pressures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increased to 2 wt %, the fiber quality would become erratic again and many beads emerged.

As PVA is water-soluble, PVA membranes must be crosslinked to form water-resistant groups before being used as water filter membrane in practical applications. PVA can be crosslinked through the reaction with hydroxy groups using a wide range of chemicals. The research effort focused on the fabrication of composite membranes which combined the two electrospinning techniques and filtration efficiency evaluation of the composite membranes. So the crosslinking of the PVA membranes was not investigated. However, the conclusions could be justified by the experiment and results. The PVA1799 used in this experiment was only swelled in water at room temperature and dissolved at high temperature of more than 90°C, so the PVA fibers in this study could support the new idea and conclusions. The PVA fiber was one common example of the solution electrospun fibers in this system, it could be replaced by other solution electrospun fibers which have fine diameter, for example, we have also prepared the cellulose acetate (CA) fibers which have the similar fiber size as the PVA fibers.

Surface Morphology of PVA/PP Composite Membrane. Based on the optimal conditions of the melt electrospun PP fibers and solution electrospun PVA fibers, PVA/PP composite membranes at the thickness of 0.2 mm and 10 μm, respectively have been obtained. Figure 3 shows the morphologies of the electrospun membranes and general non-woven fabrics. As shown in Figure 3, we can see that the average fiber diameter of the solution electrospun PVA membrane and melt electrospun PP membrane was 0.171 ± 0.027 and 2.24 ± 0.33 μm, respectively. And the fiber diameter of general non-woven fabrics was 28.46 ± 4.30 μm, which was much larger than the melt electrospun PP fibers. The quality of non-woven fabrics was lower and much poor than the electrospun membranes, thus the filtration properties of the PVA membrane coated on the PP nonwoven substrate would be also lower than the composite electrospun PVA/PP membranes.

Pore Size and Distribution. Figure 4 shows the pore size distribution of the solution electrospun PVA membrane, melt electrospun PP membrane, and electrospun PVA/PP composite membrane. The average pore size and the maximum pore size of the virgin melt electrospun PP membrane were 27.29 μm and 86.34 μm, respectively. For the solution electrospun membrane, the average pore size was 0.832 μm and the maximum pore size was 1.283 μm. As depicted in Figure 4, the solution electrospun PVA membrane showed smaller pore size than the melt electrospun membrane, this mainly because the PVA membrane had smaller fiber diameter. The pore size of the melt electrospun PP substrate webs was considerably larger than the ones covered with solution electrospun PVA fibers with average pore size of 15.61 μm.

Contact Angle and Pure Water Flux of Membranes

Contact Angles. The membrane wettability was examined on the basis of water contact angle. Compared with the melt electrospun PP membrane, the electrospun PVA/PP composite membrane was shown to be more hydrophilic, making it favorable for applications in water purification. The experimental results showed that the PVA/PP composite membrane had a smaller contact angle of 116.7° than the melt electrospun PP membrane of 128.6°. That could be due to the surface PVA membrane, it was found that the water droplet was spread out instantaneously and immediately penetrated into the pure PVA membrane, as shown in Figure 5(c).

Pure Water Flux. Each membrane was flushed with the distilled water for 2 min to open all pores before the pure water flux test. The flux rate of the electrospun PVA/PP composite membrane and the melt electrospun PP membrane under different pressures were investigated. The result of that comparison is shown in Figure 6. It was found that the initial pressure of the PVA/PP composite membrane which made water pass through the membrane was a little smaller than that of the PP membrane. This subtle difference was caused by the higher hydrophilic of solution electrospun PVA membrane. From Figure 6, it can be seen that when the pure water flux was completely stable, the difference of the water flux for the two kinds of electrospun membranes was smaller. The reason to cause this phenomenon was that the solution electrospun PVA membrane

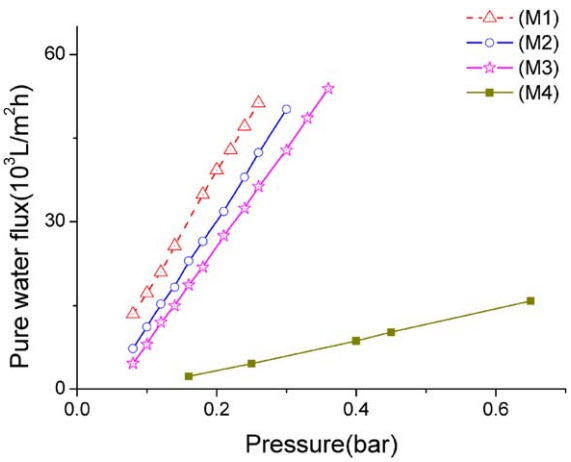

Figure 7. Pure water flux of the electrospun PP membranes at different thicknesses. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

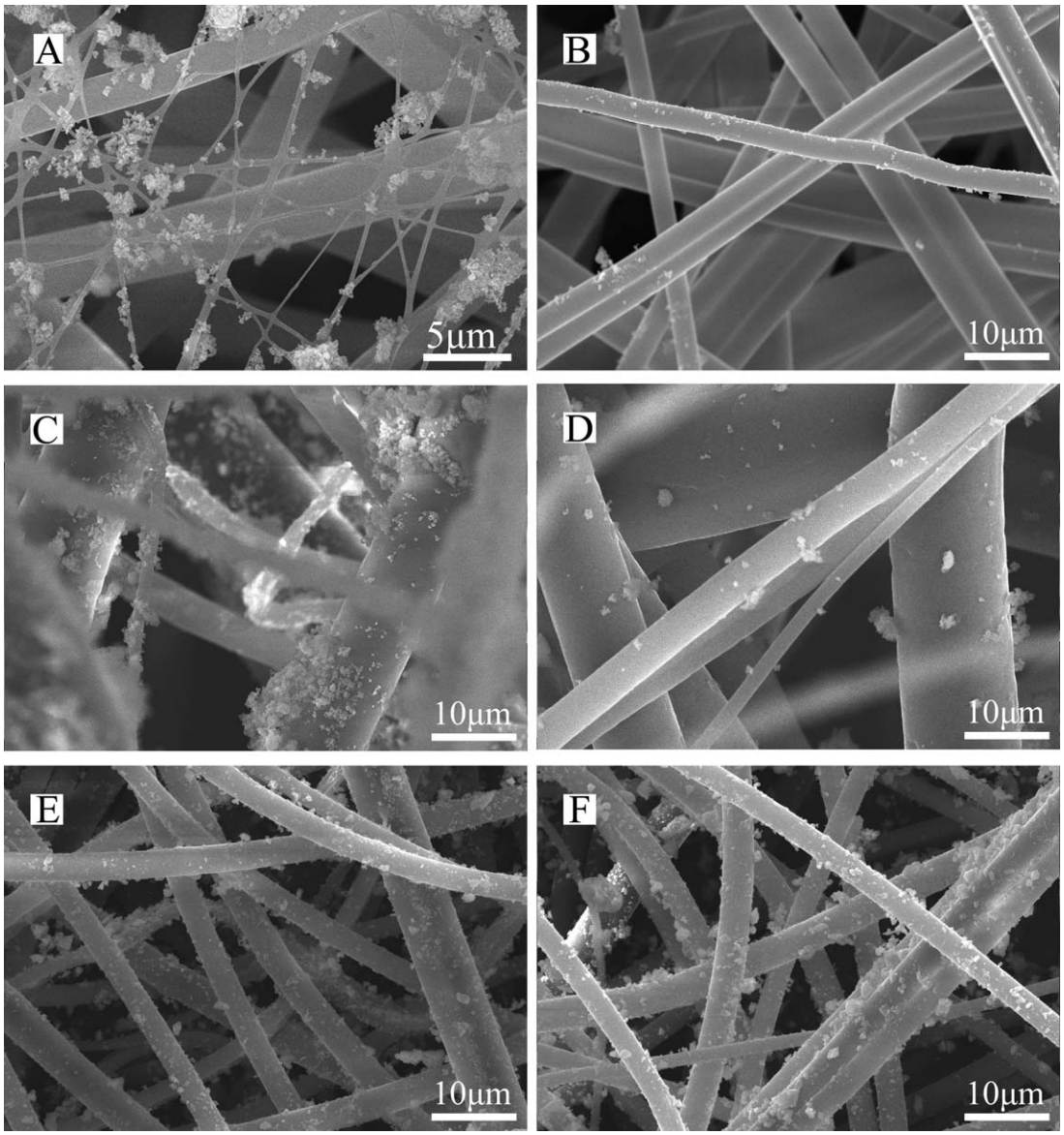

Figure 8. SEM images of membranes in different views: surface layer (A) and bottom layer (B) of the PVA/PP composite membrane; surface layer (C) and bottom layer (D) of the PVA/non-woven substrate membrane; surface layer (E) and bottom layer (F) of the melt electrospun PP membrane.

coated on the melt electrospun PP membrane was very thin of 10 μm, so the change of membrane wettability was very little. After the test lasted for 1 h, the pure water flux still remained about the same, this could prove that the electrospun composite membranes owned good mechanical properties. The yield stress and tensile strength of the melt electrospun membrane were 1.14 and 5.14 MPa, respectively.[21]

The effect of the melt electrospun PP fiber layer thickness on the water flux rate was also evaluated. To ensure that the membranes kept the same packing density, the time of electrospun fibers was controlled to get different thickness. The membranes at three different thicknesses of 0.2 mm, 0.4 mm, and 0.6 mm were fabricated corresponding to the samples M1, M2, and M3. And the membrane M4 was the sample M1 after hot-pressing at 90°C for a moment. The experimental results are shown in Figure 7, we can see that the pure water flux of the melt electrospun virgin membranes was very high. The pure water flux of M1, M2, M3 was 47,064, 37,970, and 32,346 L/m^{2}h, respectively, under the pressure of 0.24 bar, this due to the large membrane pore size of dozens of microns (Figure 4). As the thickness was increased from 0.2 mm to 0.6 mm, the pure water flux was obviously decreased. When the hot-pressing treatment was done, the melt crosslinking of fiber surface would occur, thus the pure water flux was decreased from 47,064 to 4563 L/m^{2}h corresponding to the sample M1 and M4. The influence of the hot-pressing for the virgin electrospun membranes has been investigated before.[21]

Evaluation of Particle Rejection

The ability of particle rejection is one of the key factors of the membrane filtration efficiency. To evaluate the retention rate capacity of the electrospun PVA/PP composite membrane, the melt electrospun PP membrane and the electrospun PVA

membrane fabricated on the PP non-woven substrate were tested, and then compared with the PVA/PP composite membrane.

In previous work, we have found that the retention rate of the microparticles was high for the electrospun PP membranes. So we choose the 0.5 μm particles to do the contrast experiments. The particle rejection test was employed at 0.2 bar after that the membranes were flushed with deionized water. The results showed that the retention rate of the PVA/PP composite membrane could reach more than 96%, and the electrospun PVA membrane fabricated on the PP non-woven substrate was 90%, while the melt electrospun PP membrane could only reject 80% of the particles. Through this conclusion, we could assume that the solution electrospun membrane played a very important role in rejecting the particles. Many studies have proved that the fiber diameter of electrospun fibers and pore size of membrane could influence the retention rate. Thus the ability of particle rejection of the membranes coated with the solution electrospun fibers would be more efficient than the single melt electrospun PP membrane. However, when the electrospun PVA membrane were electrospun onto the melt electrospun PP substrate, the rejection efficiency could be improved very highly, and could maintain the same high permeate flux as the melt electrospun membrane.

Figure 8 shows the SEM images of the top and bottom membranes after the particle rejection test. It could be seen that particles were trapped by the upper membrane of the PVA/PP composite membrane, and almost no particle was observed in the bottom of the membrane [Figure 8(A,B)]. For the electrospun PVA membrane fabricated on the PP nonwoven substrate, most of the particles were intercepted on the surface layer and there were a small amount of particles on the bottom layer [Figure 8(C,D)]. As the experimental results showed, the rejection ratio of the single melt electrospun PP membrane was very low, and many particles penetrated into the bottom layer [Figure 8(E,F)]. This conclusion could be explained by the pore size of membranes, the average pore diameter of the single melt electrospun membrane was 27.29 μm, which was much greater than the particle size. Thus, it is conceivable that the electrospun PVA/PP composite membrane can be used to improve the membrane performance of higher flux and higher rejection ratio.

CONCLUSIONS

In this study, a new needleless melt electrospinning device was introduced to fabricate the melt electrospun PP membrane with the average fiber diameter of 2.24 ± 0.33 μm and the mean pore size of 27.29 μm. And the general solution electrospinning was used to fabricate PVA nanofibers. The effects of surfactant on the morphology of solution electrospun PVA fibers have been examined. The electrospinning process became stable and the fiber quality became better when 0.2 wt % lauryl sodium sulfate was added to the PVA solution. As the concentration of surfactant increased to 2 wt %, the fiber quality would become erratic and many beads emerged. The diameter of PVA fibers prepared under the optimal condition (8 wt % solution concentration, 0.2 wt % lauryl sodium sulfate, 20 kV, 14 cm) was 0.171 ± 0.027 μm and its average pore size was 0.832 μm. Novel composite PVA/PP membranes were fabricated by the two electrospinning techniques to combine the beneficial properties of nanofibers and microfibers. Filtration efficiency of membranes, such as the pore size distribution, pure water flux, and the rejection ratio of 0.5 μm particles, were investigated to evaluate the composite membranes. Its average pore size was 15.61 μm, which was much smaller than the melt electrospun PP membrane. Experimental results showed that the solution electrospun PVA membrane played a very important role in rejecting the particles. The PVA/PP composite membrane with the thickness of 0.2 mm and 10 μm could reject more than 96% of the 0.5 μm particles, which was higher than the composite PVA/nonwoven substrate membrane of 90% rejection ratio and the melt electrospun PP membrane of 80% rejection ratio. What's more, the PVA/PP composite membrane still maintained high permeate flux of 32,346 L/m^2 h under the pressure of 0.24 bar as well as the melt electrospun membrane. The PVA fiber was one common example of the solution electrospun fibers in this system, it could be replaced by other solution electrospun fibers which have fine diameter. This study proved that combining the solution electrospun membrane and melt electrospun membrane could be useful in designing novel filter membrane which owned good mechanical properties, higher flux, and higher rejection ratio.

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