

Preparation of Polyvinylidene Fluoride Membrane via Dual Coagulation Bath System and Its Wettability Study

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ABSTRACT: Hydrophobic polyvinylidene fluoride (PVDF) membrane has been successfully developed using dual coagulation bath system in which first coagulation bath produced membrane with nodular structure whereas second water coagulation bath provided membrane with porous structure. The effects of coagulation time, polymer concentration, and isopropanol/water ratio in first coagulation bath on membrane wettability were studied. The membrane surface morphology such as pore size and porosity were studied using field emission scanning electron microscope and porosimeter. The wettability

of the membrane was determined using sessile drop contact angle measurement. Using dual-coagulation bath system, it was found that membrane with bicontinuous structure tends to have higher water contact angles. This membrane could be produced through short immersion time of 18 wt % PVDF solution in soft nonsolvent bath followed by coagulation in water nonsolvent bath. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: E225–E232, 2012

Key words: membrane; contact angle; phase separation; structure–property relations; wettability

INTRODUCTION

In membrane distillation (MD) process, a porous hydrophobic membrane is employed as a barrier for vapor–liquid interface which allows penetration of hydrophobic vapor and prevents the infiltration of the nonwetted compounds into the membrane pores.¹ Therefore, excellent mechanical properties and hydrophobicity of microporous membrane are necessary to ensure the high permeate flux and rejection coefficient in MD process.²

Among the hydrophobic materials applied in fabrication of direct contact membrane distillation (DCMD) membranes, polyvinylidene fluoride (PVDF) is getting more attention due to its unique properties such as excellent chemical resistance and ease of processing through phase inversion.³ Preparation and characterization of PVDF flat-sheet ultrafiltration and microfiltration membranes by dry/wet phase inversion processes were studied extensively.⁴ The hydrophobic property of PVDF membrane is

important to ensure nonwettability of the membrane surface. Besides the material properties of membrane, hydrophobicity could be enhanced through preparation of membrane with different porosity since the surface chemical feature is not the only factor influencing the surface contact angle.⁵

It was commonly accepted that, in order to achieve higher permeate flux in MD process, the surface porosity and pore size of hydrophobic membrane must be as large as possible² (10–30 nm) without exceeding the liquid entry pressure (LEP_w). Tomaszewska fabricated flat sheet PVDF membranes using lithium chloride (LiCl) and found that additive could increase the porosity and pore size of the fabricated membranes.⁶ This led to some flux enhancement in the consequent MD experiments. In a similar study, Khayet et al. found that the pore size and porosity of PVDF membranes increased with increasing concentrations of pure water as a nonsolvent added into the dope solution.⁷ They found that the MD flux increases exponentially with the water content in the PVDF casting solution. Kuo et al. prepared a PVDF microporous membrane by using alcohol as nonsolvent (coagulant)⁸ and a porous membrane with high hydrophobic surface (water contact angle ~ 148°) was produced using phase inversion method in single and dual bath system.

Dual bath system is necessary to produce membrane with finger-like substructure to enhance water vapour permeability; moreover, it is an effective way

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of controlling membrane porosity. Li et al. also improved PVDF membrane hydrophobicity using a dual coagulation process using mixed solvent of triethyl phosphate (TEP) and *N,N*-dimethylacetamide (DMAc) in first coagulation bath,⁹ the highest achievable water contact angle is 136.6°. In another work, Peng et al. prepared PVDF membranes using two methods. In the first method, water/DMAc mixture instead of pure water was used as a soft precipitation bath. In the second method, the PVDF/DMAc casting solution underwent gelation in the open air instead of being immersed into a precipitation bath. The highest contact angles could be achieved is around 141° and 150°, respectively.¹⁰ Feng et al. studied the factors affecting pore structure and performance of poly(vinylidene fluoride-co-hexafluoro propylene) for direct contact MD.¹¹ It was found that the material could provide higher distilled flux compared to that of PVDF; however, the membrane exhibits very low water contact angle (<90°), indicated that the membrane is relatively hydrophilic.

In this work, we would like to show that membrane wettability to a great extent is affected by the morphology (cellular, bicontinuous, and nodular) of the membrane surface. The studied parameters that affect the membrane morphology include the effect of polymer concentration, effect of immerse time in isopropanol (IPA), and the effect of nonsolvent ratio (IPA : Water) in first coagulation bath.

EXPERIMENTAL

Materials

PVDF (Solef 6010/1001) was purchased from Solvay Solexis (France). Anhydrous *N*-methyl-2-pyrrolidone (NMP) supplied from Merck (Darmstadt, Germany) was used as solvent without any further purification. IPA (Merck, Germany) was used as nonsolvent in coagulation bath.

Preparation of PVDF casting solutions

PVDF with predetermined concentration was dissolved in NMP in a sealed glass flask under continuous agitation. During dissolution, the solution temperature was well controlled at 65°C for 4 h. After 4 h, the temperature was decreased to 40°C and left it for 1 day. Before casting, all the PVDF solution was cooled to room temperature in the incubator.

Preparation of PVDF membrane

The PVDF solution was cast on a glass plate with a thickness of 400 μm using automatic thin film applicator (Elcometer 4340). The nascent membrane was immersed into a first coagulation bath consisting of

solvent mixture (IPA and water) at predetermined time, followed by the immersion in second water coagulation bath (called dual coagulation method) for 24 h. After that, the membranes were immersed in ethanol for 24 h (exchange bath). The formed membranes were removed from the ethanol bath and further dried in air for 2 days.⁸

Water contact angle measurement

Water contact angle of membrane surface was measured by Ramehart instrument Co. (Model 200) using sessile drop method. All the contact angle data were averaged from ten measurements on different locations of membrane surface. A water droplet was introduced on the surface of membranes, and the contour of the water drop was recorded.

Scanning electron microscopy

The morphology of the top surface of membrane was characterized by using field emission scanning electron microscope (SEM), model JEOL JSM 6460 LA. Prior to scanning, membrane was coated with Au using Auto Fine Coater, model JEOL JFC 1600.

Atomic force microscopy

Atomic force microscopy (AFM), model XE 100 was employed to study the surface roughness of the membranes. The membrane surface roughness and topography was obtained through noncontact mode. The scan size (10 μm × 10 μm) was used to evaluate the roughness parameter, R_q of the membrane surfaces.

Liquid entry pressure determination

To determine the LEP_w of the membranes, Porolux 1000 (Beneflux Scientific, Belgium) was used based on the bubble point method. In this method, each membrane samples was cut into 2.5 cm disc and placed in the sample holder with water covering the membrane surface. The sample analysis was started by applying nitrogen gas under increasing step pressure of 0.1 bar until maximum pressure of 5 bars. The LEP_w value is detected at the pressure whereby the first flow of liquid was noticed.

Pore size determination

The pore sizes of the membrane were determined by gas flow/liquid displacement method using the Capillary Flow Porometer Porolux 1000 (CNG Instruments). The membrane samples with diameter of 10 mm were characterized by using the “dry up-wet up” method. Through this method, the gas flow was measured as a function of the transmembrane pressure, first through the wetting of membrane

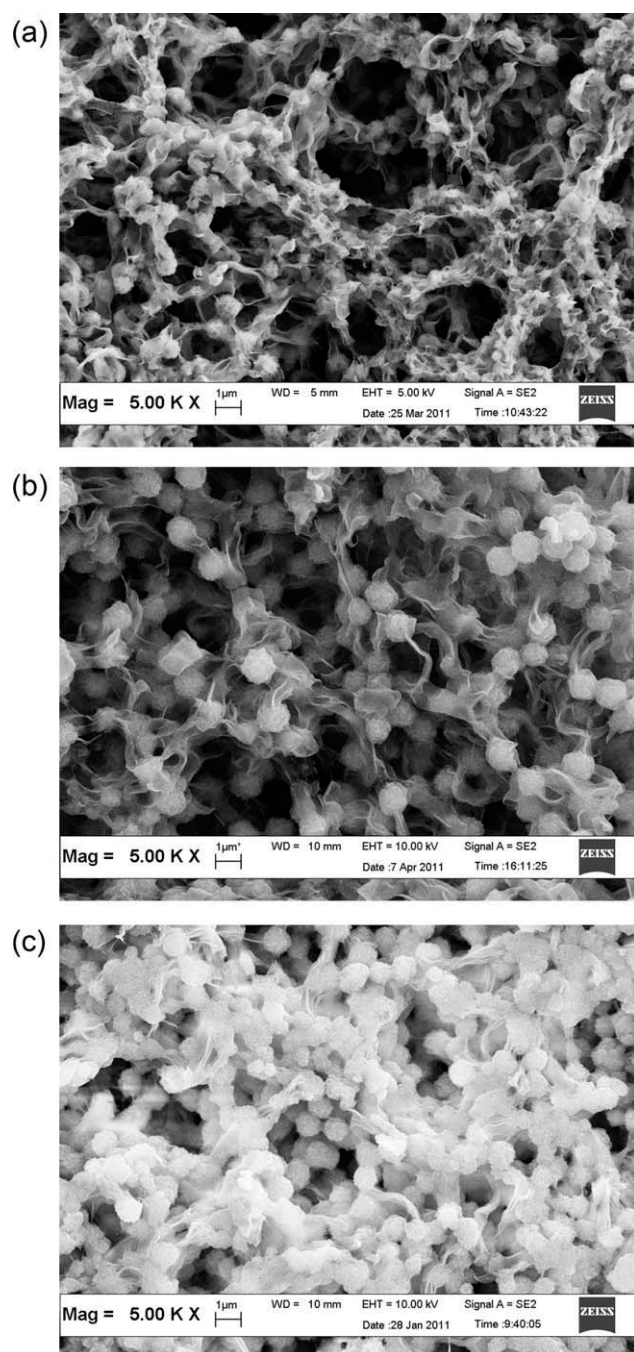


Figure 1 Membrane prepared under different immersion time in IPA: (a) 2 sec in IPA, (b) 1 min in IPA, and (c) 1 day in IPA.

with 1,1,2,3,3,3-hexafluoropropene and then the drying of the membrane. The pore size distribution was estimated using the PMI software.

RESULTS AND DISCUSSION

Effect of immersion time in first coagulation bath with pure isopropanol

System with a rapid phase inversion rate tends to form macrovoids with finger-like structure, whereas

systems with slow phase inversion rate result in a sponge-like structure. So, the system had the potential for instability with respect to both liquid–liquid demixing and solid–liquid demixing (crystallization).¹² In general, the liquid–liquid demixing process creates cellular pores whereas the crystallization forms inter-linked crystalline particles.¹³ Cellular structures are expected morphology for the system with hard nonsolvent; however, for IPA as nonsolvent, the above mentioned structure disappears and replaced with the bicontinuous and nodular structure.⁸

Figure 1 shows the morphology of PVDF membrane which were prepared by immersing the 15% PVDF cast film into (i) IPA bath for 2 sec and then was introduced into water bath (1 day); (ii) IPA bath for 1 min and then was introduced into water bath (1 day); and (iii) directly into IPA bath for 1 day followed by water bath for another day. It could be observed from the SEM images that at longer immersion time in the first coagulation bath, the bicontinuous structure disappeared and membrane was replaced with bigger and closely packed nodular structure. The transition from bicontinuous structure to nodular structure could be explained through combined effect of crystallization (solid–liquid demixing) and binodal decomposition (liquid–liquid demixing). Figure 1(a) shows the bicontinuous structure which was obtained through the crystallization process that occurs almost instantaneously within 2 sec of IPA immersion, followed by binodal decomposition of the crystallite polymer in the second water bath. Conversely, for the full IPA solution bath [Fig. 1(c)], crystallization occurs at prolonged period which provide sufficient time for solidification of the crystallite structure that avoid binodal decomposition,¹⁴ as a result, nodular structure was formed.

Figure 2 shows that the contact angles of membrane decreased drastically from 135° to less than 100° at prolonged immersion time. At shorter immersion time, bicontinuous structure with higher surface porosity will be produced whereas at longer

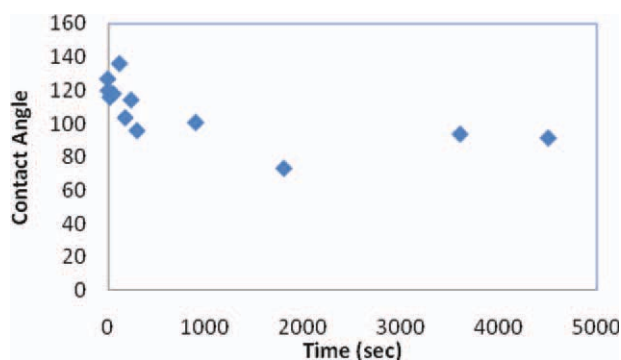


Figure 2 Effect of immersion time in first IPA bath on membrane contact angle. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

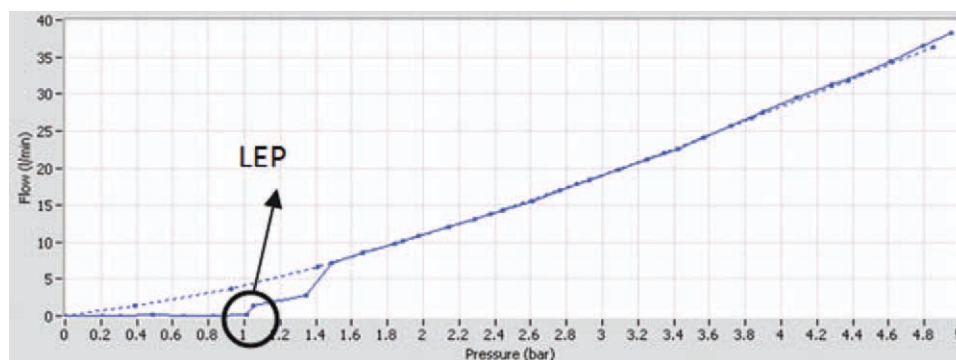


Figure 3 LEPw determination through bubble point method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

immersion time in the first IPA bath, expected crystallite growth will occur and resulted in bigger nodular size and reduced porosity. These results dictate that in order to prepare high contact angle membrane, bicontinuous structure is more favorable compared to the nodular structure. By using dual bath system, optimum membrane could be produced. The first soft nonsolvent bath helps to produce the hydrophobic membrane with the second bath functions as liquid–liquid demixing promoters to create the porous substructure.

As mentioned in the methodology, the LEPw of the membrane could be determined using bubble point method. LEPw is an important criterion for DCMD performance. LEPw is a function of membrane wettability, connectivity, and surface pore size. The higher the LEPw value, the lower the flux will be. On the other hand, too low LEPw will enable the permeation of the liquid together with the retentate which resulted in lower rejection. Figure 3 shows the water flow profile for increasing pressure. LEPw is the point whereby, water flow is first detected. The LEPw for the membranes prepared at 2 sec, 1 min, and 1 day in first coagulation bath are 0.2 bar, 0.65 bar, and 1 bar, respectively. Although membrane prepared at 1 day has lower contact angle, its LEPw value is relatively higher. The increasing LEPw value for the nodular structure is contributed by the closely packed nodules structure. This structure will increase the tortuosity of the membrane for water permeation. It is interesting to note that at a very short contact of IPA in the first bath, membrane with higher surface porosity and bigger pore size could be obtained. Figure 4 shows that the pore sizes of membranes were widely distributed especially at the shorter immersion time. However, the maximum pore size ($r_{p,max}$) of the membranes was able to be identified distinctively. $r_{p,max}$ for membrane prepared at 2 sec, 1 min, and 1 day immersion time were 1 μm , 0.65 μm , and 0.3 μm , respectively. From the pore size distribution,

it could be deduced that the lower LEPw of 2 sec membrane is most likely attributed to its bigger pore size.

Effect of polymer concentration

In phase inversion process, polymer concentration is one of the important factors that affect membrane structure. The effects of polymer concentration on the physical properties of the membrane are presented in Figure 5. The membranes underwent two coagulation processes in which the first bath consists of pure IPA (soft nonsolvent) whereas the second bath consists of pure water (hard nonsolvent). The periods of coagulation were 2 sec and 1 day for first and second bath, respectively.

It could be observed from the SEM images (Fig. 5) and Figure 6 that at higher polymer concentration, membrane pore sizes tend to be decreased. The pore size was reduced from $r_{p,max}$ of 0.25–0.1 μm with the increase of the polymer concentration from 12% to 18%. The pore size for 12% and 15% PVDF were

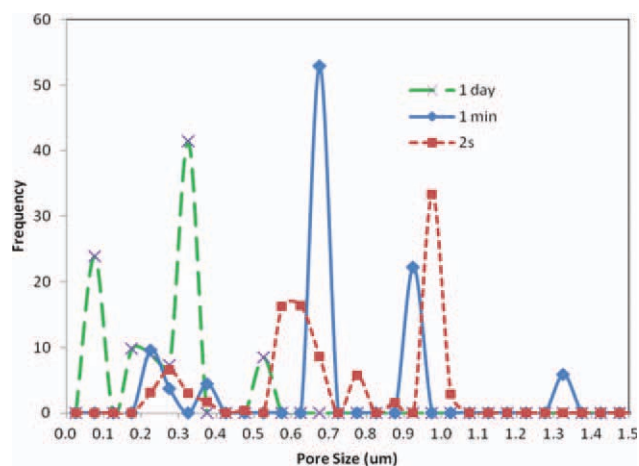


Figure 4 Effect of immersion time in IPA on pore size distribution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

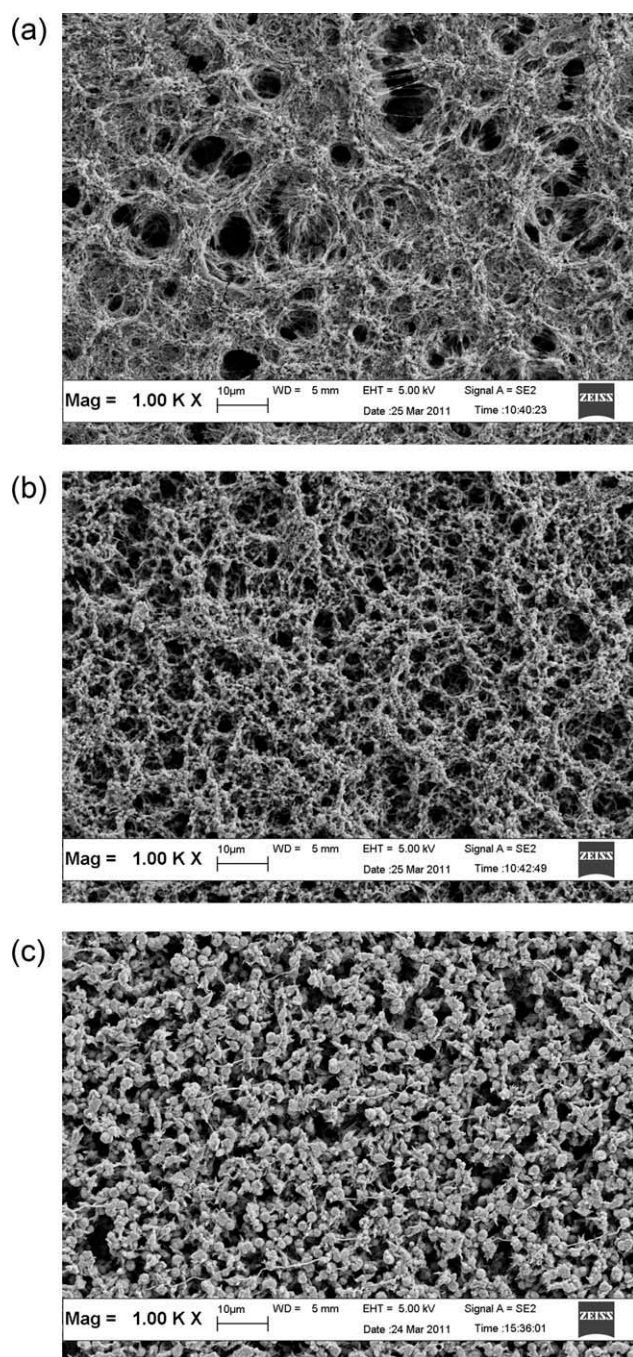


Figure 5 SEM image of membrane with different PVDF concentration: (a) 12% PVDF, (b) 15% PVDF, and (c) 18% PVDF.

having quite similar distribution except that 12% PVDF had more random pores compared to 15% PVDF. The cellular pore structure as shown for 12% PVDF membrane disappeared at higher polymer concentration and replaced with the pores contributed by nodular packing. This phenomenon could be understood based on the thermodynamic behavior of the solution system. Within 2 sec of immersion time in IPA, the solution with 18% poly-

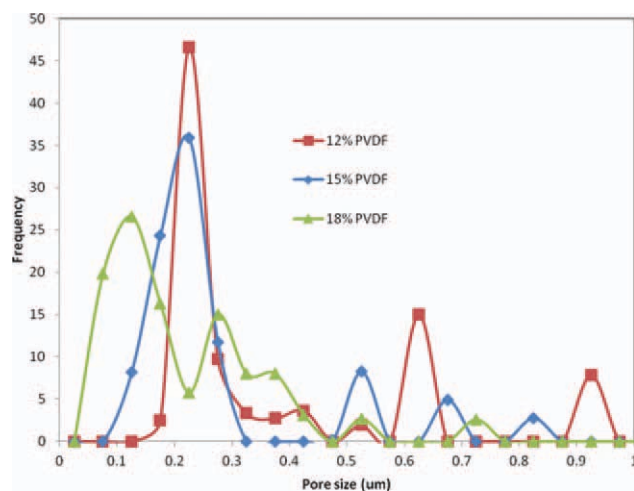


Figure 6 Pore size distribution of membranes prepared using different polymer concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mer concentration develops into morphology composed of spherical nodules. These nodules depicted the circumstance where solid-liquid demixing occurred through crystallization process. On the other hand, lower polymer concentration (12% and 15% PVDF), when first immersed in pure IPA, underwent a crystallization process but upon immersion in pure water yields binodal liquid-liquid demixing dominated morphology. Solution with 12% PVDF shows a significant binodal decomposition phenomenon in which the surface consists of the cellular structure. The cellular structure is a typical phenomenon of nucleation and growth for polymer poor phase.¹⁴ The transition structure (bicontinuous) is clearly seen for 15% PVDF polymer concentration. For 18% PVDF, such structure represents a crystallization dominated precipitation situation, wherein all crystalline particles were

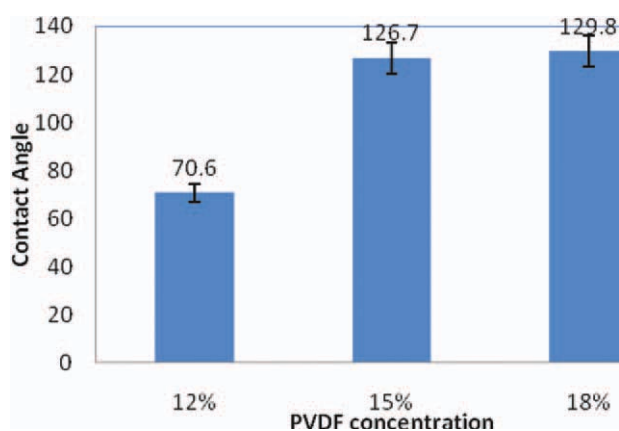


Figure 7 Effect of polymer concentration on contact angle. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

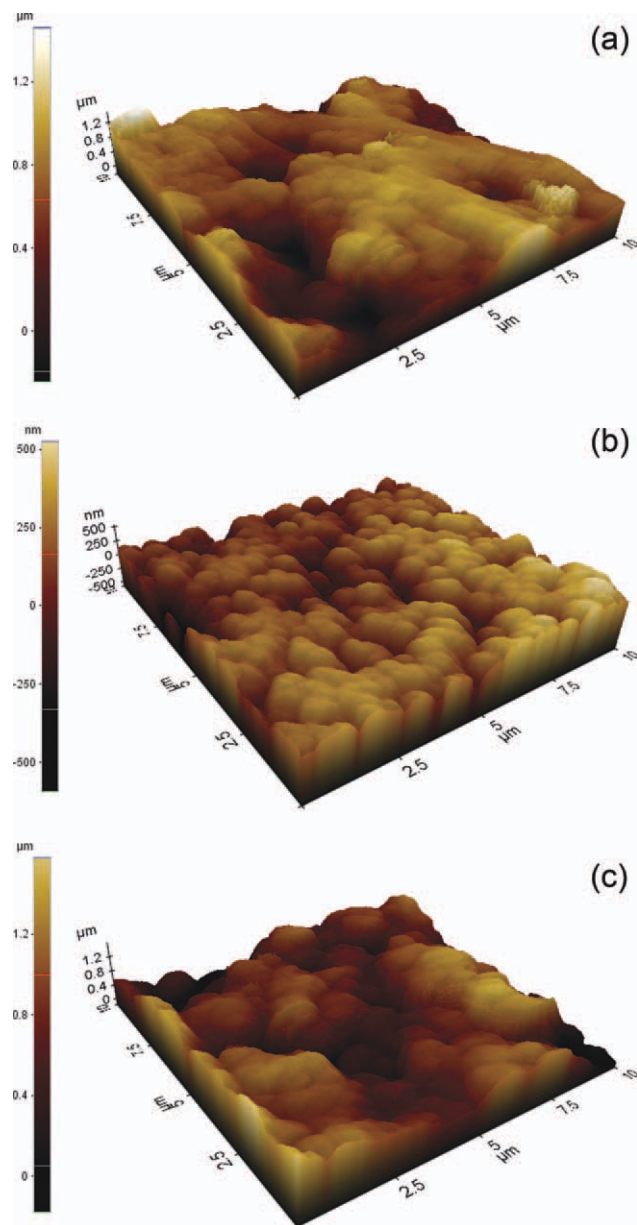


Figure 8 AFM image of membrane with different PVDF concentration: (a) 12% PVDF, (b) 15% PVDF, and (c) 18% PVDF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nucleated and grown in a similar concentration field.¹⁵ According to van de Witte et al., for semi-crystalline polymer such as PVDF, increasing polymer concentrations favored solid-liquid demixing over liquid-liquid demixing.¹⁴ For this rapidly crystallizing polymer, membrane with spherulites structure as shown in Figure 5(c) could be produced.

Figure 7 shows the result of water contact angles for membranes prepared under different polymer concentrations. Since the polymer solutions were coagulated under the same nonsolvent environment, the trend of increasing contact angle at higher poly-

mer concentration is mainly contributed by the surface morphology of the membrane. The nodules adhering to each other form a sponge-like structure to provide the hydrophobic property of membrane. The same phenomenon was observed for the bottom surface of PVDF membrane prepared by the phase inversion method¹⁰ in which increasing roughness helps to enhance hydrophobicity for PVDF. AFM images (Fig. 8) shows that membrane with higher

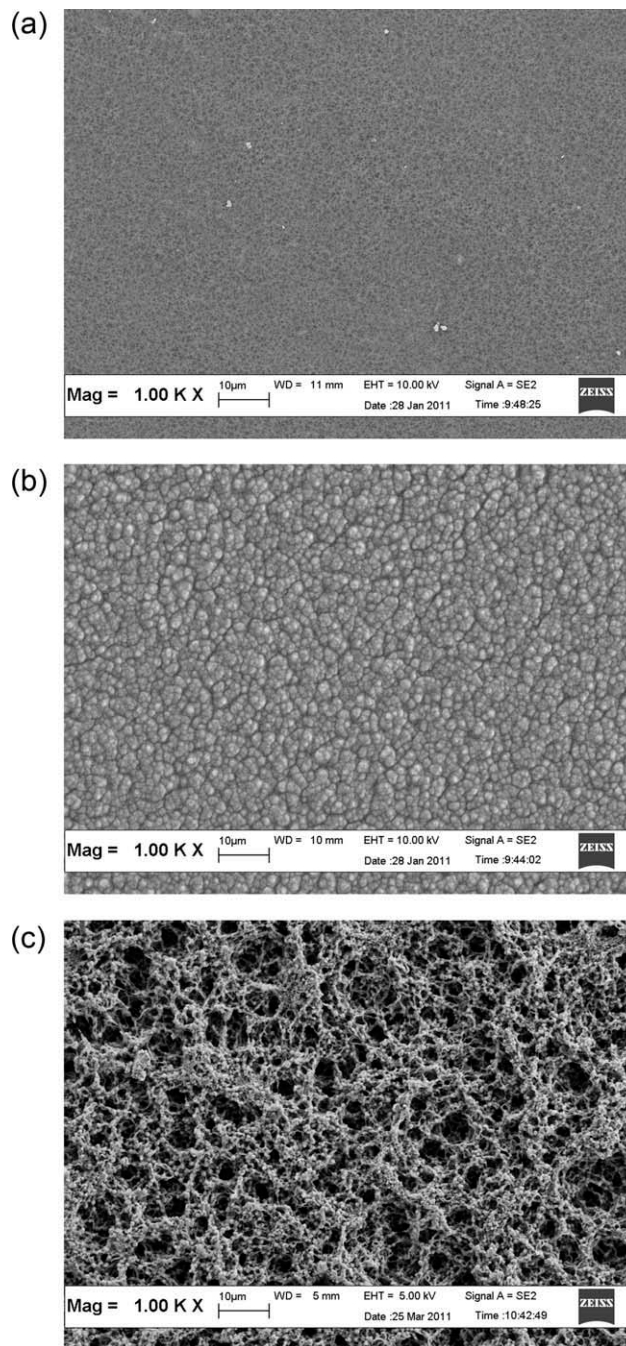


Figure 9 SEM image of membrane prepared under different IPA concentration: (a) pure water, (b) 50% IPA : 50% water, and (c) 100% IPA in first coagulation bath for 2 sec.

concentration of PVDF will give the higher value of mean roughness (R_q). The value of R_q for 18%, 15%, and 12% PVDF are $0.316 \mu\text{m}$, $0.261 \mu\text{m}$, and $0.157 \mu\text{m}$, respectively. It shows that, the nodular structure has higher surface roughness compared to the bicontinuous structure and cellular structure.

The LEPw of the membranes prepared with 12%, 15%, and 18% PVDF concentrations were 0.1, 0.2, and 0.4 bar, respectively. These results showed that membrane with higher polymer concentration is having higher resistance for the water to flow mainly due to the smaller pore size (Fig. 6) as well as increasing higher contact angles (Fig. 7). The nodular packing has relatively poor connectivity compared to the finger-like structure.

Effect of nonsolvent ratio (IPA : water) in the first coagulation bath

The IPA concentration in the first coagulation bath had a considerable effect on the properties of the prepared membrane. Its effects on the membrane morphology were presented in Figure 9. A dramatic change of membrane morphology was observed for membranes prepared using (a) pure water; (b) equal mixture of IPA/water, and (c) pure IPA as nonsolvent bath. By using the pure water only as the first coagulation bath created a dense membrane with very small pore size. By mixing equal volume of IPA and water, the membrane surface structure changed into bicontinuous structure. It could be observed from Figure 10 that membrane prepared using pure water and 50% water + 50% IPA have quite similar pore size distribution and both membranes were having a magnitude of order smaller pores compared to the membrane prepared using pure IPA as nonsolvent.

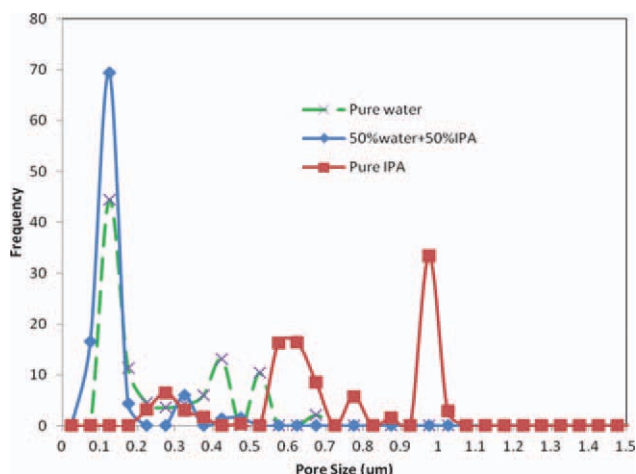


Figure 10 Effect of nonsolvent on pore size distribution of membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

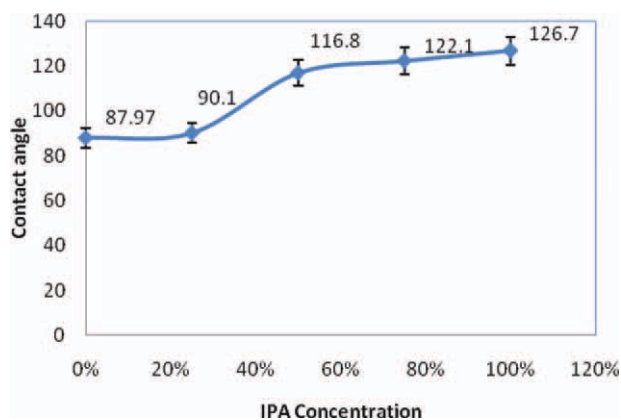


Figure 11 Effect of IPA concentration in first coagulation bath. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The dense surface structure shown in Figure 9(a) is due to the higher solvent outflux compared to the nonsolvent influx which results in the sudden increase of surface polymer concentration. As a result, it underwent a very rapid precipitation process called instantaneous demixing. By increasing the IPA concentration, the rate of precipitation was slowed down so that for pure IPA bath (within 2 sec immersion), the sluggish crystallization process could produce an initial nodular structure which is immediately superceded by the binodal decomposition in the water bath, subsequently, an intermediate structure (bicontinuous to cellular structure) was created.

Figure 11 presents the effect of IPA/water ratio on the surface contact angle. The contact angle was about 88.0° for the dense surface using pure water as coagulation bath and increased drastically to 126.7° using pure IPA as coagulation bath. From the contact angle data, it can be concluded that bicontinuous structure which has highest surface roughness and porosity is the desired morphology for preparing high contact angle membrane (MD). LEPw analysis shows that membrane immersed in pure water shows no resistance to water flow, which is not suitable to be used as membrane distiller because the membrane coagulated using pure water is hydrophilic (contact angle $< 90^\circ$). Increasing the IPA concentration in the coagulation bath to 50% does increase its LEPw to 0.5 bar due to its increasing hydrophobicity but further increase in IPA concentration (100%) reduced its LEPw to 0.45 bar due to the bigger pore structure produced.

CONCLUSIONS

The surface properties of PVDF membrane obtained by the phase inversion process depend on the coagulation time, the polymer concentration, and the IPA/water solvent ratio. The structure of the resultant

membranes changed remarkably from cellular; bicontinuous to nodular structure depends on the two phase separation mechanism namely crystallization and binodal decomposition. The first coagulation bath promotes the crystallization which produce nodular structure whereas binodal decomposition takes place in the second bath.

At longer coagulation time in the first bath, membrane produced is nodular in structure which has lower porosity and low contact angle. On the other hand, lower polymer concentration produced membrane with cellular structure which has lower contact angle compared to the nodular structure of the high polymer concentration. Coagulation in pure water bath produces hydrophilic membrane with dense surface which has lowest contact angle ($<90^\circ$), which is not suitable to be used as membrane distiller. An optimum morphology with high hydrophobicity and optimum pore size was found to be bicontinuous in structure. Bicontinuous structure had both higher contact angle and hydrophobicity and reasonable LEPw around 0.5 bar which is needed for MD application.

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