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Fabrication of PVDF Hollow Fiber Membranes: Effects of Low-Concentration Pluronic and Spinning Conditions

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Abstract

Due to the unique properties of amphiphilic Pluronic block copolymers, they have been blended with other polymers such as PVDF to prepare membranes. Considering the stability issue, the strong pore-forming ability of Pluronic F127, and the mechanical strength of the resultant membranes, Pluronic/LiCl mixed additive consisting of a very low concentration of Pluronic has been used in this study. The effects of spinning conditions on PVDF hollow fiber fabrication have also been studied. It is found that the use of merely 0.2 wt% of Pluronic is sufficient to impose significant impacts on the morphology, filtration performance, and mechanical properties of the resultant fibers. Hollow fibers spun using higher coagulant temperature, higher take-up speed, and water as the bore fluid exhibit better mechanical properties and filtration performance. PVDF hollow fiber membranes with PWP of 1180 L/m^2 h MPa and MWCO of 5 kDa were obtained when spun with optimized spinning conditions and using 3 wt% of LiCl and 0.2 wt% of Pluronic as the mixed additive. The fibers can withstand a pressure of 0.55 MPa from the lumen.

Keywords: Phase inversion; Poly(vinylidene fluoride); Hollow fiber membrane; Poly(ethylene oxide) – poly(propylene oxide); mechanical strength

1. Introduction

Pluronic is a trade name registered under BASF for amphiphilic triblock copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) PPO [1]. Due to their unique surface activity, reversible thermo-rheological phase behavior, and micellization in water, Pluronic copolymers have been widely used as surfactants, components in drug delivery systems, cell culture media and others for decades [2-5]. In recent years, Pluronic copolymers have also been used in membrane preparation due to their amphiphilic nature that facilitates their segregation to the membrane–water interface and hence changes the surface properties of the membranes. In Wang's study, Pluronic was blended with polyethersulfone (PES) to prepare membranes via nonsolvent-induced phase separation (NIPS) [6]. Significant amount of Pluronic molecules were proven to remain in the resultant membranes despite that they were water-soluble, revealing that the hydrophobic PPO block in the Pluronic interacted with PES and made the Pluronic anchor in the membrane matrix stably.

Since then, a series of studies on PES membrane preparation using Pluronic as an additive have been carried out. It was observed that the hydrophilicity and anti-fouling properties of the resultant membranes were enhanced due to the enrichment of Pluronic molecules on the membrane surface [7-9]. In addition, the pore size and porosity of the membranes were increased when a relatively large amount of Pluronic was used as the additive [8-11]. These observations from various studies reveal that Pluronic has both surface-modifying and pore-forming ability.

In addition to PES, polymer materials including cellulose acetate [12], polyvinyl chloride [13], and poly(vinylidene fluoride) (PVDF) [14-16] has also been blended with Pluronic to prepare

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membranes. Among the different polymers, PVDF has several advantages as the membrane material such as high thermal stability, excellent chemical resistance, and good mechanical properties [17, 18]. In addition, PVDF is a semi-crystalline polymer with typically three different types of crystal phases named α, β, and γ. α- and β-phases have nonpolar and polar (all-trans) conformation, respectively, while γ-phase has an intermediate polar conformation. The electrically active β - and γ-phases of PVDF make it an interesting material in various piezoelectric applications [19].

By far, studies on PVDF membrane preparation using Pluronic as an additive via NIPS are limited. In one of the studies, the polymorphism and thermoresponsive behavior of PVDF/Pluronic membranes were examined [14]. It was observed that the addition of Pluronic in the PVDF dopes facilitated the formation of β and γ crystal phases. Water flux of the resultant membrane was found to be enhanced significantly when the operating temperature was increased during the filtration process. In our previous study, Pluronic and polyethylene glycol, a conventional polymeric additive, were found to behave differently during PVDF membrane formation [16]. Pluronic was observed to be a very strong pore-forming agent even at a concentration as low as 1 wt% due to the interaction between the hydrophobic PPO blocks of Pluronic molecules and the PVDF macromolecular chains. This unique behavior of Pluronic is beneficial to produce highly porous PVDF membranes which are desirable for permeation performance.

However, the strong effect of Pluronic on pore formation is also accompanied with the enhancement of macrovoid growth and the formation of loose micro-structural morphology, which deteriorates the mechanical strength of the membranes [20]. Therefore, there is a need to

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control the membrane morphology while maintaining high porosity of the membrane during fabrication process, in order to obtain strong and highly permeable membranes. One possible strategy is to utilize the synergetic effect of mixed additives while keeping the Pluronic concentration low. The use of a mixture of two compounds as the additive has been found to produce membranes with higher performance than using single additive [21, 22]. It has been shown in previous studies that PVDF membranes with smaller macrovoids, higher permeability, and higher selectivity could be obtained when a mixed additive consisting of Pluronic and LiCl was used [15, 16]. On the other hand, considering that the pore-forming effect of Pluronic is tremendously strong in PVDF system, it is anticipated that high-porosity membranes could still be obtained with the use of low-concentration Pluronic.

Another issue that can arise for PVDF/Pluronic membranes is the stability of Pluronic in the membrane matrix. Despite the strong interaction between PVDF and Pluronic, Pluronic molecules might still be able to leach out from the membrane matrix since they are highly soluble in water [23]. An increase in surface contact angle for PVDF/Pluronic membranes after soaking the membranes in water was reported, indicating that Pluronic may not be completely stable in the PVDF membrane matrix [16]. The loss of Pluronic from the PVDF/Pluronic membranes can change their filtration performance and hence causes an inconsistent long-term performance. Therefore, the use of low Pluronic concentration in PVDF membrane fabrication is also beneficial to long-term stability of the resultant membranes since they contain little or no Pluronic.

For hollow fiber spinning, the membrane morphology can also be controlled by adjusting the spinning conditions. For instance, PVDF hollow fibers with interconnected-globule structure

were obtained when a mixture of alcohols and water was used as the coagulant [24]. The mechanical properties of these hollow fibers were deteriorated because the interconnection between the globules was relatively weak. Wongchitphimon *et al.* reported that PVDF hollow fibers with smaller macrovoids and improved molecular-weight cut-off (MWCO) were obtained when a higher coagulant temperature was employed [25]. Wang *et al.* reported a complete elimination of macrovoids in hollow fiber by employing high take-up speed [26]. Therefore, it is possible to improve the mechanical strength and the separation performance of PVDF/Pluronic membranes by optimizing the spinning conditions.

In this study, spinning of PVDF hollow fibers using the mixed additives of Pluronic/LiCl has been carried out by varying Pluronic amount at constant LiCl concentration. Low Pluronic concentrations ranging from 0 to 0.5 wt% were used in this study due to the above-mentioned reasons. The effects of spinning conditions including air gap, bore fluid composition, coagulant temperature, and take-up speed on the properties of as-spun fibers has also been studied. The objective of this study is to fabricate high-performance PVDF UF hollow fibers with good mechanical strength through the synergetic effects of Pluronic/LiCl and the optimization of spinning conditions.

2. Experimental

2.1 Membrane material and chemicals

PVDF (Kynar 761, MW = 444,000, Arkema) was dried at 323 K under vacuum for at least 1 day before use. N-methyl-2-pyrrolidone (NMP) purchased from Merck was used as the solvent. Pluronic F127 (MW = 12,600, PEO_{100}-PPO_{65}-PEO_{100}, Sigma-Aldrich) and lithium chloride

(LiCl, anhydrous, Merck) were used as the nonsolvent additives in hollow fiber preparation. Dextran with different molecular weights ranging from 6,000 to 500,000 Da (Sigma-Aldrich) was used to determine the molecular weight cut-off (MWCO) of prepared fibers. In addition to dextran, bovine serum albumin (BSA, MW = 67,000 Da) obtained from Sigma-Aldrich was also used to assess the selectivity of as-spun fibers. All the reagents were used as received.

2.2 Spinning of PVDF hollow fiber membranes

A polymer dope solution for spinning was prepared by dissolving desired amount of PVDF and additives in NMP using a jacket flask. the concentrations of PVDF and LiCl were kept constant at 18 wt% and 3 wt%, respectively. The dope solution was mechanically stirred for at least 2 d at 333 K. The homogenous dope prepared was then cooled down to room temperature and subsequently degassed under vacuum for overnight before spinning.

The PVDF hollow fiber membranes were fabricated via dry-jet wet spinning process as described in literature [27]. Tap water was used as the external coagulant while the bore fluid was varied from water to a mixture of NMP/water. Various other spinning conditions including air gap, take-up speed, and coagulant temperature were changed to study their effects on membrane properties and performance. In order to obtain fibers with circular inner contour and desirable dimensions, the dope and bore fluid flow rates were also adjusted for different cases. The detailed dope composition and spinning conditions for each membrane are listed in Table 1.

The as-spun fibers were soaked in water for at least 2 d before use to wash out any remaining solvent. Freeze drying was then carried out using Martin Christ Freeze dryer (Alpha 2-4 LD) for characterizations that required the use of dry membranes.

2.3 Membranes Characterizations

The cross-sectional and surface morphologies of hollow fiber membranes were observed using a field emission scanning electron microscope (FE-SEM, JEOL JSM-7600F). The membranes were broken in liquid nitrogen and sputtered with platinum prior to the test. To determine the overall porosity of membranes, the gravimetric method with the following equation was employed [28]:

$$\varepsilon = 1 - \frac{\rho_{membrane}}{\rho_{PVDF}} = 1 - \frac{W/V_{membrane}}{\rho_{PVDF}} \tag{1}$$

where ε is the membrane porosity; $\rho_{membrane}$ the membrane density; W the weight of dry membrane; $V_{membrane}$ the volume of membrane which can be determined based on its inner/outer diameter (ID/OD); ρ_{PVDF} the specific gravity of PVDF which has a value of 1.78 according to the Kynar product information. It should be noted that deviation of ID/OD along the length of hollow fiber may lead to some uncertainty on this membrane porosity measurement.

The crystallinity of as-spun hollow fibers was measured by differential scanning calorimetry (DSC, TA Instruments, Q10). Appropriate amount of dried membranes sealed in an aluminum pan was heated from 323 to 463 K at a heating rate of 10 K/min. The membrane crystallinity in percentage (X_c) can be calculated based on the following equation [29]:

$$X_c = \frac{\Delta H_f}{\Delta H_f^*} \times 100\% \qquad (2)$$

where ΔH_f is the melting enthalpy of as-spun membranes and ΔH_f^* is the melting enthalpy for PVDF with 100% crystallinity (104.5 J/g). To assess the chemistry information of the as-spun fibers, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was carried out by IRPrestige-21 spectrophotometer from Shimadzu. The surface of dried membranes was directly analyzed and the IR spectra were obtained by 45 scans at a resolution of 4 cm^{-1}. The hydrophilicity of the hollow fiber membranes was examined by dynamic contact angle using a tensiometer (DCAT11 Dataphysics) according to Wilhelmy method. Three immersion-emersion cycles in Mili-Q water were carried out for each specimen with a repetition of 5 times for all the samples. The advancing contact angle of the second cycle was recorded.

The mechanical properties of the membranes were measured using a Zwick Roell BT1-FR0.5TN.D14 tensile tester. A hollow fiber was clamped at the both ends with an effective length of 25 mm and was pulled at a constant elongation velocity of 50 mm/min. The Young's modulus was determined at strain of 0.05 to 0.25%. Young's modulus, tensile stress at break, and elongation at break were obtained by averaging five times of measurement results. The calculation of mechanical properties involves membrane ID and OD. Therefore, there exists some uncertainty on the measurement due to the deviation of ID/OD along the length of hollow fiber.

2.4 Pure water permeation and MWCO measurement of PVDF hollow fiber membranes

To measure the pure water permeation (PWP) of the as-spun fibers, lab-scale hollow fiber module was made by sealing 10 pieces of 20-cm-length hollow fibers in plastic tubing. Two modules were prepared and tested for each batch of the hollow fibers using Mili-Q water as the feed. Compaction on the membranes was done under the pressure of at least 0.1 MPa for 1 h and the permeate was subsequently weighted for calculating the PWP.

The compacted hollow fibers were used for MWCO test in which 1500 ppm of a dextran aqueous solution with a molecular weight distribution ranging from 6,000 to 500,000 Da was used as the feed. The permeate was collected after 30 min of feed circulation under 0.1 MPa to ensure that the system was stabilized. Gel permeation chromatography (GPC, PL-GPC50 Plus, A Varian, Inc.) was used to characterize the dextran molecular weight distribution in the feed and permeate. The molecular weight of dextran at which the rejection is 90% was recorded as the MWCO of the membrane. During BSA rejection test, the BSA aqueous solution with a concentration of 1 g/L was used as the feed. The concentration of BSA in the feed and permeate was determined by measuring their total organic carbon (TOC) using TOC Analyzer (Shimadzu, TOC-V CSH).

3. Results and discussion

3.1 Membrane morphology and porosity

3.1.1 Effects of air gap and bore fluid composition

Figure 1 shows the effect of air gap on the cross-sectional structure of hollow fibers spun with 50 wt% of NMP and water as the bore fluid. Deformation of inner contour is observed for fibers

spun with 50 wt% of NMP and the situation does not improve with increasing air gap up to 20 cm. Similarly, when water is used as the bore fluid, inner contour deformation also exists when the air gap is below or equal to 20 cm. However, the membrane structure becomes more regular when the air gap is increased from 20 cm onwards and a fully circular structure is obtained at an air gap of 25 cm.

Due to the fact that the rate of solvent diffusing out from a polymer dope is always lower than that of nonsolvent diffusing into the dope, shrinkage is always observed in nascent membranes during phase inversion [30]. In hollow fiber spinning process, the shrinkage of nascent fiber in coagulant bath induces inward radial force which in turn deforms the inner contour of the fiber if the lumen skin is not rigid enough [31]. For dry-jet wet spinning, phase inversion has already started at the interface between the bore fluid and the dope before the dope is in contact with the external coagulant. With a larger air gap, there is more sufficient time for the demixing or the solidification of polymer to occur near the lumen of the nascent fiber. As a result, a more rigid lumen skin can be formed before the dope entering the coagulant bath. Therefore, the irregular inner contour of the fiber spun with water as the bore fluid can be eliminated when the air gap is large enough.

For fibers spun with 50 wt% NMP as the bore fluid, a slower demixing process occurs compared with the case using water as the bore fluid. Consequently, the formed lumen skin is still not strong enough to resist the inward radial stress when the dope enters the coagulant bath. However, when the NMP concentration in the bore fluid is further increased to 80 wt%, no solidified skin is formed in the lumen of nascent fibers [31]. As a result, the induced stress can be relaxed and hollow fibers with regular cross-section can be obtained at an air gap as low as 1cm,

as shown in Figure 2 (a1). It should be noted that the spinning using 80 wt% NMP as the bore fluid could only be carried out at a very low air gap because the polymer flow became unstable when the air gap was large. Therefore, the air gap used was different for hollow fibers spun with different bore fluids.

Figure 2 shows the morphology of membranes prepared using the same amount of additives but different bore fluids. The cross-section of membrane P5-80 (80 wt% NMP as the bore fluid) exhibits a structure with macrovoids developed from the shell and sponge-like structure near the lumen, while its outer surface is dense and inner surface is highly porous with big pores. On the other hand, macrovoids are developed from both the shell and lumen in membrane P5-00 (water as the bore fluid) while the outer surface has larger pores than the inner surface, possibly due to the high air gap. The observed structures are in accordance to those in literatures since the instantaneous demixing induced by strong coagulant (water) facilitates the formation of dense skin and macrovoids while delayed demixing causes the formation of sponge-like structure and the elimination of skin layer when a soft coagulant (80 wt% NMP) is used [17].

3.1.2 Effects of Pluronic concentration

Figure 3 presents the cross-sectional morphology of hollow fibers spun with different Pluronic concentrations and spinning conditions. Regardless of the spinning conditions, a significant increase in macrovoid size can be observed with the addition of merely 0.2 wt% of Pluronic. Further increase of Pluronic concentration from 0.2 wt% to 0.5 wt% has a smaller impact on the macrovoid size. On the other hand, the overall porosity of the as-spun membranes is also improved significantly with increasing Pluronic concentration, as shown in Figure 4. These

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observations reveal the strong pore-forming ability of Pluronic, which might be attributed to the interruption to the rearrangement between PVDF macromolecules due to the interaction between the hydrophobic PPO blocks in Pluronic molecules and PVDF macromolecules [16]. The above observations also suggest that the interruption is significant enough to possess an impact on the macrovoid formation even with the presence of just 0.2 wt% of Pluronic.

Figure 5 shows the morphology of outer surface for hollow fibers spun with different Pluronic concentrations and spinning conditions. For fibers spun with 80 wt% NMP as the bore fluid, the outer surfaces are dense with no visible pores at 50,000x magnification regardless of the Pluronic concentration. For fibers spun with water as the bore fluid, the membrane surface is not significantly affected with the addition of 0.2 wt% Pluronic (membrane P0-00 and P2-00). Highly porous surface can be observed on membrane P5-00 when the Pluronic concentration is 0.5 wt%.

3.1.3 Effects of take-up speed

When the dope and bore fluid flow rates are kept constant, a higher take-up speed imposes a higher stretching force on the nascent fiber. Therefore, the dimensions of the hollow fibers become smaller. The cross-sections of the fibers are not significantly affected by different take-up speeds, as can be seen in Figure 6. However, the surface of membrane P5-00H-B spun at a take-up speed of 5.7 m/min becomes less porous and the pore size becomes smaller compared with that of membrane P5-00H-A spun with a lower take-up speed.

In literature, the effect of take-up speed on the membrane pore size and the explanations on the phenomenon are diversified. Chou *et al.* reported an increase in pore size with increasing take-up speed possibly due to the expansion of pores under elongation stress [32]. In contrast, Sukitpaneenit *et al.* observed smaller surface pores when a higher take-up speed is used, while the proposed mechanisms were related to the enhanced spinodal decomposition of demixing and rapid shrinkage of the nascent fiber [33]. In this study, the mechanism of liquid-liquid demixing is believed to be nucleation and growth at a higher take-up speed since dispersed pores with continuous PVDF phase is observed. Hence the spinodal decomposition mechanism cannot explain the reduction in surface pore size and porosity in this case. Instead, it is believed that the shear stress caused by the higher take-up speed is responsible for this phenomenon. Under a high shear stress, the orientation of PVDF macromolecular chains is induced and hence a close packing is formed which in turn produce a less porous structure [34].

3.1.4 Effects of coagulant temperature

The effect of coagulant temperature on the morphology of membrane cross-section and the outer surface can be observed in Figure 3 and Figure 5, respectively. It seems that the cross-sectional morphology does not change much with increasing coagulant temperature from 298 to 323 K, except that the size of macrovoids developed from the shell become smaller for membrane P2-00H and P5-00H compared with that of membrane P2-00 and P5-00, respectively. The suppression of macrovoids at higher coagulant temperature has also been observed by Wongchitphimon *et al.* for PVDF/polyethylene glycol/NMP system [25]. At a higher temperature, the thermodynamic stability of a polymer dope system is enhanced which in turn delays the onset of liquid-liquid demixing [25]. When the nascent fibers are immersed into the

coagulant bath with a temperature of 323 K, the temperature of the dope in contact with the water is increased. Therefore, delayed demixing occurs and smaller macrovoids are developed from the shell of fibers compared with the case using a lower coagulant temperature.

On the other hand, the pore size of membrane surface becomes significantly larger when the coagulant temperature is increased to 323 K, especially for membrane P2-00H and P5-00H which is spun with the addition of 0.2 wt% and 0.5 wt% Pluronic, respectively. This phenomenon is in contrast with the study reported by Choi *et al.* in which the pore size of PVDF membranes (without any additive) was observed to decrease significantly with increasing coagulant temperature [35]. The difference might be aroused due to the use of LiCl and Pluronic as the additives in this study:

(1) With the presence of LiCl, the suppression of nucleus growth induced by the high dope viscosity is the dominating factors of pore formation. The viscosity of polymer dope decreases with increasing temperature. As a result, the effect of nucleus-growth suppression becomes less pronounced at a higher temperature and larger pores are formed.

(2) Water solubility of the center PPO block in Pluronic decreases significantly at elevated temperatures [1]. In other words, PPO is much more hydrophobic at higher temperature. When the outer surface of nascent fiber is in contact with hotter water, it is possible that the hydrophobic-hydrophobic interaction between PPO and PVDF becomes stronger. This leads to a more pronounced disruption on the rearrangement of PVDF macromolecules, which facilitates the formation of larger pores.

3.2 Filtration performance

As can be seen in Figure 2, it is noticed that when 80 wt% NMP is used as the bore fluid, the membrane outer surface is much denser than the inner surface. This indicates that the selective layer is located at the shell side of the as-spun fibers. However, relatively dense skins are formed at both the shell and lumen side of the fibers when water is used as the bore fluid. In order to determine the location of the selective skin, filtration tests operated under outside-in (feed at shell side) and inside-out (feed at lumen side) modes were carried out for membrane P5-00 and P5-00H which are spun using water as the bore fluid.

Table 2 presents the PWP and MWCO of membranes P5-00 and P5-00H tested under outside-in and inside-out modes. It is observed that the PWP is higher for the inside-out mode when the area of surface that is directly in contact with the feed is taken for calculation. However, the absolute flux is similar when the fibers are tested under both modes. On the other hand, the MWCO is much smaller when the feed is located at the lumen side, indicating that the surface pore size at the lumen is smaller. The higher MWCO tested under outside-in mode is attributed to the concentration polarization in the membrane matrix, since some dextran molecules that has passed through the outer skin are accumulated near the inner skin.

Figure 7 presents the PWP and MWCO of PVDF hollow fibers spun with different conditions. According to the location of the selective skin, the feed was run at the shell side and the lumen side for the fibers spun with 80 wt% NMP and water as the bore fluid, respectively. The PWP is calculated based on the surface area that is directly in contact with the feed. It can be seen that the PWP increases with increasing Pluronic concentration in the spinning dope. For the fibers

spun with 80 wt% NMP as the bore fluid, the PWP increases tremendously by about 190% from 250 to 720 L/m^2 h bar with the addition of merely 0.2 wt% of Pluronic. For the fibers spun with water as the bore fluid, the presence of 0.2 wt% Pluronic also enhances the PWP significantly by 46% and 39% when the coagulant temperature is 298 K and 323 K, respectively. Despite the pronounced enhancement in PWP, the MWCO of the fibers is not affected much by the low concentration of Pluronic.

The PWP is further enhanced significantly at 0.5 wt% of Pluronic concentration. A remarkable increase in MWCO is also observed when the Pluronic concentration is increased from 0.2 to 0.5 wt%. For instance, The PWP increases from 870 to 2090 L/m^2 h bar and the MWCO changes from 4 to 65 kDa, when comparing membranes P2-00 and P5-00. The increase in PWP and MWCO is due to the enhancement in membrane surface and overall porosity as discussed in Section 3.1.

The effects of bore fluid composition on PWP and MWCO are not comparable since the location of selective skin is different in the two cases. On the other hand, no obvious trend can be observed for the impacts of the coagulant temperature on the PWP and MWCO: As shown in Figure 7, the PWP increases at a higher coagulant temperature when the Pluronic concentration is 0.2 wt% or less, while the MWCO is not affected much; both PWP and MWCO of the fibers spun with 0.5 wt% of Pluronic decreases at a higher coagulant temperature. The changes in PWP at different coagulant temperatures can be attributed to the different overall porosities of as-spun membranes as shown in Figure 4. As for the MWCO, it is believed that the increasing coagulant temperature does not significantly affect the membrane structure near the lumen side because the inner surface is not in direct contact with the external coagulant. Accordingly, the inner surface

pore size is expected to be similar for hollow fibers spun at different coagulant temperatures. This is true for the as-spun fibers in this study except for the fibers spun with 0.5 wt% of Pluronic, while the reason is unclear.

The impact of take-up speed on the filtration performance of as-spun fibers can be assessed in Table 2. Comparing fibers P5-00H-A and P5-00H-B which are spun with different take-up speeds, the PWP is observed to be similar. However, the MWCO of the fibers becomes smaller when the take-up speed is increased, indicating that hollow fibers with smaller surface pores can be obtained at the presence of elongation stress. This is due to the formation of close-packing structure caused by shear-induced PVDF chain orientation, as discussed in Section 3.1.3.

3.3 Crystallinity and FTIR of PVDF hollow fibers

Table 3 shows the crystallinity of as-spun PVDF hollow fibers. All the membranes show similar crystallinity of 52 to 56 % despite the difference in Pluronic concentration and spinning conditions. This reveals that the addition of Pluronic up to 0.5 wt% does not impose significant impact on PVDF crystallinity under the studied spinning conditions. The crystalline forms of as-spun membranes were assessed by examining the FTIR spectra. As shown in Figure 8, the characteristic peaks of β- and γ-phase PVDF crystalline can be observed at wave numbers of 840 (β and γ), 1234 (γ), and 1277 cm^{-1} (β). Meanwhile, no significant peak is observed at wave numbers of 766 and 976 cm^{-1}, indicating that the presence of α-phase PVDF crystalline is insignificant in the membranes [19]. Regardless of the amount of Pluronic added, all of the as-spun hollow fibers possess both β- and γ-phases and no significant α-phase. The observation is in accordance to the study of Du *et al.* [14].

The presence of Pluronic in as-spun PVDF hollow fibers can also be assessed by their FTIR spectra as shown in Figure 8. No peak can be observed at the wave number of 1107 cm^{-1} for all the fibers spun with different Pluronic content. This reveals that little or no ether group exists in the membranes. In addition, the contact angle of the fibers does not change significantly with increasing Pluronic concentration up to 0.5 wt%, as listed in Table 4. It seems that the chemical properties of the fibers are not affected by the addition of Pluronic in the spinning dopes when its concentration is lower or equal to 0.5 wt%. In other words, Pluronic functions as a pore-former but not surface modifier at low concentration. It is anticipated that the stability of Pluronic in membrane matrix is no longer an issue since the membranes contains very insignificant amount of Pluronic.

3.4 Mechanical Properties

The mechanical properties of as-spun fibers tested under tensile mode are presented in Figure 9. The Young's modulus, tensile stress at break, and elongation at break of all the fibers are observed to be reduced with increasing Pluronic concentration, except for the elongation at break of hollow fibers spun with 80 wt% NMP as the bore fluid. The reason for the reduction in mechanical strength with increasing Pluronic concentration might be attributed to the higher membrane porosity. As discussed in Section 3.1.2, the rearrangement of PVDF chains is disrupted during the membrane formation process due to the interaction between PVDF and Pluronic, causing a looser membrane structure and enhanced overall porosity. This in turn decreases the mechanical strength of the resultant membranes. The Young's modulus and tensile stress of the fibers decrease significantly with the addition of merely 0.2 wt% Pluronic. This reveals that the PVDF-Pluronic interaction is significant enough to impact the mechanical

properties at a very low Pluronic concentration. Similar phenomena have also been observed in previous sections where the addition of 0.2 wt% Pluronic imposes a great impact on membrane structures and filtration performance.

In Figure 9, it seems that the increase in coagulant temperature does not impose significant impact on the mechanical properties of the as-spun fibers. Similarly, the effect of take-up speed on the mechanical properties of membranes is also observed to be insignificant (data not shown). However, when comparing the fibers spun using different bore fluid, the fibers spun with 80 wt% NMP as the bore fluid were observed to have a significantly lower value of Young's modulus, tensile stress, and elongation than the fibers spun with water as the bore fluid. For both of the bore fluids, the resultant fibers consist of both macrovoids and sponge-like structures (Figure 3) and the region with sponge-like structure acts as the mechanical support. A closer look at the sponge-like structure located at the middle of the cross-section for hollow fibers P5-80 and P5-00 is presented in Figure 10 (A) and (B), respectively. One can clearly see that membrane P5-00, which is spun using water as the bore fluid, has a more compact structure compared with its counterpart. The difference in the "packing density" of sponge-like region between the two fibers is even more obvious near the lumen side, as shown in Figure 10 (a) and (b). Although the region near the lumen of membrane P5-80 is fully sponge-like while that of membrane P5-00 is mainly occupied by macrovoids, the latter consists of a much denser sponge-like structure in between the macrovoids. The tighter packing observed in the sponge-like region of the hollow fibers spun with water as the bore fluid is believed to be the reason for its higher mechanical strength.

The collapsing pressure of as-spun hollow fibers has also been tested to reflect the actual tolerance of the membranes towards hydrostatic pressure during applications. As listed in Table

4, the collapsing pressure of fibers decreases significantly with increasing Pluronic concentration, which is in accordance with the observed trend in the tensile properties. Interestingly, it is observed that the hollow fibers spun at a higher coagulant temperature can tolerate a higher pressure than their counterparts, regardless of the Pluronic concentration. One of the reasons may be due to the smaller macrovoids developing from the shell side of the fibers.

According to the collapsing pressure listed in Table 4, the hollow fibers spun with 0.2 wt% of Pluronic are rigid enough for UF applications as they can tolerate a pressure of at least 0.3 MPa. Selected membranes with a selective skin located at the lumen side have also been tested for the burst pressure, which indicates the tolerance of the fibers towards pressure acting from the lumen. The burst pressure was taken at the pressure at which the PWP appears to continuously increase over time because it indicates the emergence of defects. Membranes P2-00 and P2-00H are observed to exhibit a burst pressure of 0.45 and 0.55 MPa, respectively, which are greater than their collapsing pressure. For the fibers spun with 0.5 wt% of Pluronic, the collapsing pressures are relatively low (0.15 – 0.25 MPa), indicating that they are more suitable for low-pressure applications.

The performance of PVDF hollow fiber membranes prepared in this study has been compared with those in literature as listed in Table 5. It can be seen that the hollow fiber P2-00H prepared in this study exhibit a very low MWCO and very high BSA rejection, while its PWP is reasonably high. In addition, hollow fiber P2-00H is also stronger than most of the other membranes in terms of tensile stress and elongation at break.

4. Conclusions

It is found that the use of merely 0.2 wt% of Pluronic is sufficient to impose significant impacts on the morphology, filtration performance, and mechanical properties of the resultant fibers. The observations reveal the extremely strong pore-forming ability of Pluronic in PVDF system. The long-term performance of PVDF/Pluronic hollow fibers spun with low concentration of Pluronic is believed to be stable since there is no or very little amount of Pluronic in the resultant membranes.

By using the mixture of Pluronic and LiCl as the additives and adjusting the spinning conditions, PVDF hollow fibers with high performance have been obtained. The effects of spinning conditions on the membrane properties include:

(1) Spinning at high air-gap can help to eliminate the irregular inner contour of hollow fibers.

(2) The inner skin layer is removed when 80 wt% NMP is used as the bore fluid, while relatively dense skins are formed at both the shell and lumen side of the fibers when water is used as the bore fluid. The mechanical strength is better for the fibers spun with water as the bore fluid, probably due to the closer packing of sponge-like region.

(3) At a higher coagulant temperature, the macrovoids developed from the shell side of the fibers become smaller while the surface pores are larger. Hollow fibers spun at a higher coagulant temperature can withstand a higher pressure.

(4) The surface pore size of the fibers becomes smaller at a higher take-up speed due to the stress-induced arrangement of PVDF macromolecules.

Acknowledgments

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