

EFFECTS OF SPINNING PARAMETERS ON MORPHOLOGY OF POLY(VINYLIDENE FLUORIDE) HOLLOW FIBER

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Abstract

Poly(vinylidene fluoride) (PVDF) hollow fiber with asymmetric sponge-like structure was fabricated through immersion precipitation. The extrusion speed ratio and the type of dope solvent used in the spinning of hollow fiber were investigated. The extrusion speed ratios of 2:1, 4:1, and 8:1 were chosen for investigation, while two different solvents which were N-methyl-2-pyrrolidone (NMP) and N,N-dimethylacetamide (DMAc). These two solvents were used for polymer dope preparation. The highest extrusion speed ratio (8:1) showed the best feature required and hence it was chosen to investigate the effect of the different solvents. Investigations revealed higher extrusion speed ratio with the lowest extrusion speed successfully avoided die swell phenomenon, and produced asymmetric sponge-like membrane with high mechanical strength. With the application DMAc as solvent, macrovoids were significantly reduced and mechanical strength was increased. The results showed that the manipulation of the spinning conditions which were essential for hollow fiber fabrication to acquire distinctive characteristics for various industrial applications.

Key words: poly(vinylidene fluoride), hollow fiber membrane, morphology

1. INTRODUCTION

Membrane material development has dramatically increased the amount of industrial applications in separations, recovery, and purification. Application fields include blood purification (Yang et al. 2009, Yong et al. 2010, Hashino et al. 2011, Nishigochi et al. 2014), wastewater treatment (Wang et al. 2008, Wang et al. 2010, Cui et al. 2013, Zhu et al. 2015), pharmaceutical production (Diban and Stamatialis 2014), and a variety of industrial process separations such as food and beverages filtration (Chanachai et al. 2010) as well as gas separation (Li et al. 2002). The development of membrane has come up with several membrane structures for the above applications, such as membrane structure that is made into flat sheet, polymeric hollow fiber, and/or tubular membrane (Peng et al. 2012). At present, the most favorable membrane configuration used is polymeric hollow fiber. This is because the features of this hollow fiber provide larger surface area per unit volume which amplifies the results of the separation processes (Hou et al. 2012, Kajekar et al. 2015).

Poly(vinylidene fluoride) (PVDF) is a type of polymer widely explored and used in the field of membrane distillation due to its hydrophobic properties (Hou et al. 2012, Xiao et al. 2015) as well as its superior chemical and thermal stabilities as compared to other polymers such as polysulfone, polyethersulfone, and polyimide. Mackey et al. (2011) supplemented that the remarkable properties of PVDF are strongly associated with its semi-crystalline structure. Hence, the capability to manipulate the crystal phase and orientation can significantly enhance the property of PVDF polymer. This can be achieved by controlling the experimental parameters during fabrication. Experimental parameters include the solvent used for dissolving the polymer and the solvent used as the internal and external coagulants and spinning parameters, for instance, spinning flow rates. The solvent used in the fabrication of membrane strongly affects the morphology and mechanical strength of membrane (Yeow et al. 2005). In addition to membrane morphology, Lalia et al. (2013) stated that achieving an asymmetric membrane can exhibit higher water permeability rate which is crucial in separation processes. Yang et al. (2007) also mentioned that such an asymmetric membrane not only has a good permeability but also can provide a selective separation process. Moreover, an asymmetric membrane with a sponge-like structure may

have a better mechanical strength and prevent membranes from leakage, which finger-like macrovoids membranes are incompetent to achieve.

PVDF polymers are readily soluble in organic/polar solvents such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP) and tetrahydrofuran (THF) (Saxena and Gaur 2010, Ismail and Mansourizadeh 2010, Zhong et al. 2011, Hou et al. 2012). Among these solvents, DMAc and NMP are commonly used solvent for polymer dope solution preparation. In addition, due to the high solubility of PVDF polymers in these solvents at ambient temperature, PVDF hollow fiber membrane can also be fabricated using a simple method – phase inversion via immersion precipitation to produce microporous membrane. Phase inversion method is a straightforward procedure (Bonyadi and Chung 2009) as compared to other methods that have been reported (Du et al. 2007, Hassankiadeh et al. 2014). For example, non-solvent induced phase inversion separation that is frequently used in PVDF hollow fiber fabrication, which is an additional element added either in the polymer dope solution or the external coagulation bath (Yeow et al. 2005, Zhang et al. 2014).

In spite of the simple and straightforward method of immersion precipitation in fabricating PVDF hollow fiber, this method has also led the hollow fiber to suffer from a couple of drawbacks due to its semi-crystalline structure. The drawbacks of immersion precipitation are low surface porosity (Bonyadi and Chung 2009) and large pore size (Yang et al. 2011, Xiao et al. 2015), resulting in poor membrane performances. Hence, the manipulation of the spinning parameters for hollow fiber membrane fabrication comes into effect. It enables the fabricated fibers to achieve particular characteristics for specific applications. Spinning parameters include the speed of the hollow fiber extrusion, the temperature of the coagulation bath, and the air gap between the spinneret and the coagulation bath. Between these parameters, the extrusion speed can be varied considerably to create different morphologies. The speed of the hollow fiber extrusion is affected by the polymer dope solution and the bore solution flow rate. Different ratios of the polymer dope and bore solution flow rate were reported. Ratios that are frequently used are 1:1, 2:1 and/ or 1: 0.75 (Bonyadi and Chung 2009, Hou et al. 2009, Yang et al. 2009). The membrane morphology also is greatly affected by the viscosity of different polymer dope compositions and concentrations. Therefore, these studies cannot be used as a comparison because they studied different polymer dope compositions and concentrations, and used different length of air gaps.

In addition, Sukitpaneenit and Chung (2009) stated that during the hollow fiber spinning, the rheology behavior of the polymer dope solutions under shear and elongation flows is another important parameter. This parameter has an impact on the membrane morphology resulting from the instability during the hollow fiber fabrication. As mentioned by Widjojo et al. (2010), the instabilities of the fabrication are categorized in five sections and die swell is one of the parameters implicated in extrudate distortion. Also, they stated that the development of die swell is highly associated to shear stress which corresponds to the study of Sukitpaneenit and Chung (2009). Thus, the utter removal of the instabilities in the polymer extrusion is highly recommended. Due to the instabilities are closely related to the major parameters for hollow fiber spinning from a polymer solution, a couple of parameters were taken into account in this study.

In this study, PVDF hollow fiber membranes were prepared by using immersion precipitation, also known as dry-wet spinning technique. The polymer dope solution flow rate was one of the key parameters that were taken into investigation. Also, two regularly used solvents, NMP and DMAc, were employed to examine the properties differences on hollow fiber membranes. The aims of the study were to demonstrate the effect of different extrusion speeds ratio and flow rates and solvents on hollow fiber membrane morphology. The relationship between performances of the membrane, hydrophobic-hydrophilic properties of corresponding polymer modification and final membrane morphology were also discussed.

2. EXPERIMENTAL

2.1. Materials

Poly (vinylidene fluoride) powder (PVDF, Mw 534,000 by GPC) purchased from Sigma-Aldrich (SG). N-methyl-1-pyrrolidone (NMP, >95%) and N,N-dimethylacetamide (DMAc) used as an organic solvent in polymer preparation. Glycerol (AR grade, 92.1g/mol) was supplied from Merck. The chemicals and polymers were used as received. Distilled water and tap water were used as a bore liquid and coagulation bath medium respectively.

2.2. Preparation and fabrication of hollow fiber membrane

The PVDF hollow fibers were fabricated by the immersion precipitation which involved the extrusion of a polymer dope solution through a spinneret. The spinneret with the diameter of an inner diameter (ID) and outer diameter (OD) are 0.5 mm and 0.86 mm respectively was used. Similar methods have been reported elsewhere (Yang et al. 2009, Ismail and Mansourizadeh 2010, Wongchitphimon et al. 2011, Hou et al. 2012). The PVDF powder was dried at 110 °C for at least 12 hours to remove any possible moisture trapped during transfer or storage. The desired amount of PVDF powder and NMP solvent were weighed. The PVDF powder was stirred at 100 rpm before NMP solvent was added. Once the NMP solvent was added, the polymer dope mixture was subjected to continuous stirring at 300 rpm, 60 °C until it was homogeneous. The homogenized polymer dope solution was transferred to a stainless steel syringe to degas at 60 °C for approximately 12 hours then it was let to cool to ambient temperature before spinning process. The preparation of polymer dope solution with DMAc solvent was repeated with the above polymer dope preparation.

The polymer dope solution and bore solution were dispensed through the spinneret at a controlled volume rate by syringe pumps, and the formation of the polymeric fiber membranes would first experience an air gap region before entering the external coagulation bath. The nascent hollow fiber was taken up by a roller at a free fall velocity and then it was transferred and stored in a distilled water bath. In this study, the air gap, temperature of the polymer dope solution and bore solutions, as well as the external coagulants, were kept constant during the spinning. The details of the spinning conditions were summarized in Table 1.

The remaining solvent in the hollow fiber membranes was thoroughly extracted using distilled water for at least three days where water was replenished daily. A post-treatment was performed to prevent the shrinkage and pores collapse of the porous structures of the hollow fiber membranes during drying process at ambient condition. The hollow fiber membrane was subjected to a 50 %v/v glycerol aqueous solution for two hours after solvent exchange. A desired length and amount of hollow fiber membranes were subsequently dried in air at ambient temperature before any further characterization and study. The remaining hollow fiber membranes were kept in distilled water until use.

Spinning conditions	Fiber-1	Fiber-6	Fiber-12
Speed ratio	*8:1	2:1	4:1
Dope solution flow rate (ml/min)	1.0	6.0	12.0
Bore solution/ Inner coagulant	Distilled water	Distilled water	Distilled water
Bore solution flow rate (ml/min)	0.15	3.0	3.0
External coagulant	Tap water	Tap water	Tap water
Air gap (mm)	50	50	50

Table 1. Standard experimental parameters for hollow fiber spinning. *Actual speed ratio was 7:1. The temperature of the polymer dope solution, bore solution, and external coagulant were maintained at ambient temperature: ± 25 °C.

2.3. Characterization

The morphology of the membranes was observed by field emission scanning electron microscope (FESEM) and atomic force microscopy (AFM). The prepared membranes were immersed in liquid nitrogen and fractured to obtain smooth cross-sections. Then, they were sputtered with platinum using a sputter coater (Quorum Q150RS). The cross-section, inner surface, and outer surface of the membrane were observed under the FESEM (Ultra-High-Resolution FE-SEM Hitachi SU 8000 series). Micrographs were taken at voltage of 5 and 10 kV.

The AFM analysis was performed using a digital Instruments Multimode 8 (Bruker, USA) to obtain morphology micrographs of the outer and inner surfaces of hollow fiber membrane sample. The membrane morphology was measured using ScanAsyst. At least three locations were randomly measured for each sample.

The mechanical properties of the hollow fiber membranes were measured using a texture analyzer (TA.XT plus) at ambient temperature. The membranes were pre-measured and air-dried before used. The purpose of this testing was to determine the tensile stress at break, tensile strain, and Young's modulus strength. They were measured to indicate the mechanical strength of the fibers and the degrees of deformation that could be expected under a given load. Each sample was clamped at the both ends with an initial gauge length of 25 mm. A testing speed was kept constant at 50mm/min. At least five fiber membranes were tested for each spinning condition.

3. RESULTS AND DISCUSSION

3.1. Effect of extrusion flow rate on hollow fiber membrane morphology

The determination of the morphology of a nascent hollow fiber membrane is important. In this study, the examination of the fiber membrane structure included the cross section of the fibers for each spinning condition, the surface roughness, and the wettability of the hollow fiber membrane.

As mentioned earlier in Section 1, the morphology of a membrane for separation purposes is greatly preferred with an asymmetric sponge-like structure. This typical structure provides better mechanical strength, at the same time increases the number of usages as leakage is prevented. In this study, not only the increase of speed ratios between the polymer dope solution and the bore solution were investigated but also the extrusion flow rate for each hollow fiber spinning was decreased by half. The expected ratios of extrusion speed for polymer dope solution to bore solution were 2:1, 4:1, and 8:1 as tabulated in Table 1. However, at the ratio of 8:1, an irregular inner structure was observed and a slight adjustment of the bore solution's flow rate was performed. This occurrence might be due to the weak stream of the bore solution which caused a non-circular structure to form (image not shown).

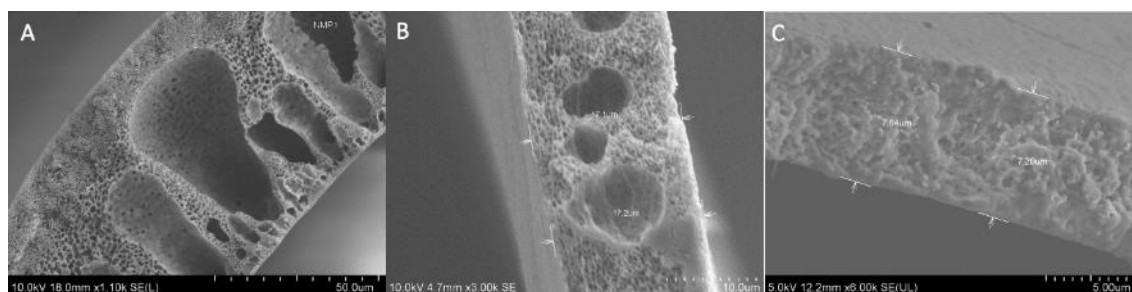


Figure 1. FESEM micrographs of cross-section PVDF hollow fiber membrane spun using different polymer dope and bore solution flow rates (A – C). All hollow fiber membranes were fabricated using NMP solvent. A= Dope: 1 ml/min; Bore: 0.15 ml/min, B= Dope: 6 ml/min; Bore: 3 ml/min; C= Dope: 12 ml/min; Bore: 3 ml/min.

Figure 1 showed that the flow rates of the polymer dope and bore solutions have significantly impacted on the morphology of the membrane as well as the wall thickness. The cross-sectional micrographs clearly showed the higher the polymer dope solution flow rate employed, the wall thickness of the fiber membrane was thinner and smaller or even macrovoid free was created. The wall thicknesses of the fiber membrane Fiber-1, Fiber-6, and Fiber-12 were 60 μm , 17 μm , and 8 μm respectively. Likewise, as the flow rate increased, the fiber membrane not only became denser and also the disappearance of the asymmetry structure, which could be seen clearly in Figure 1 (A). Two factors might have attributed to these unique phenomena: (1) the speed of flow rate was too high that it stretched the fiber during the extrusion, and (2) an immediate solvent exchange occurred once the fiber came in contact with the coagulation bath causing no delay during the phase inversion process. Hence, these phenomena suggested that in order to attain specific membrane properties, in this case, the wall thickness of the membrane, could be manipulated by the extrusion flow rate of the polymer dope and bore solutions. By examining the Fiber-6 and Fiber-12, although they possessed smaller or even macrovoid free, the wall thickness was too narrow and the circumference of the membrane was too large. Practicality, they inevitably collapsed once they were out of the water. There is a high probability that these fibers acquired a weak mechanical strength that is unfavorable especially in industrial application. The mechanical strength of the hollow fiber will be further discussed in the subsequent section.

In this preliminary investigation, the spinning condition for Fiber-1 presented the most satisfactory outcome. For example, the formation of asymmetric sponge-like structure and a more practical wall thickness, in spite of the formation of macrovoids. As the formation of macrovoids can be regulated by other factors such as the affinity of the solvents (Yeow et al. 2004) and the types of phase inversion method (Hassankiadeh et al. 2014). For this reason, the following investigation on the effect of different solvents on hollow fiber membrane morphology would be adopting Fiber-1's spinning conditions.

3.2. Effect of DMAc and NMP solvents on hollow fiber membrane morphology

As previously stated the development of the macrovoids could be manipulated by a couple of factors. In this study, two widely used solvents were chosen to undergo an examination comprehensively. They were DMAc and NMP. Figure 2 showed the FESEM micrographs of the hollow fiber fabricated using DMAc (Fiber-1A) and NMP (Fiber-1B). The affinity of the solvent has significantly influenced the morphology of the cross-section membranes. There were several distinctive features when DMAc was used. They were (1) the macrovoids formed on Fiber-1A was not only visually less obvious but also they did not wholly occupy the membrane as Fiber-1B; (2) the wall thickness of Fiber-1A was narrower than Fiber-1B; (3) the appearance of the hollow fiber membrane fabricated using DMAc was much more regular compared to NMP. The properties of the hollow fiber membranes fabricated using both solvents were tabulated in Table 2.

Many studies have claimed that the solvent polarity has a strong effect on the solubility of PVDF (Yeow et al. 2004, Liu et al. 2011). In the review paper of Liu et al. (2011), a comparison of the solubility parameters of common solvents which included DMAc and NMP was tabulated. Four parameters were compared including the dispersion, polar, hydrogen bonding, and total solubility. The values for NMP were higher for most of the parameters compared to DMAc, except for the hydrogen bonding. The high solubility parameters of NMP was expected to create better outcome. However, based on the information provided by one of the major PVDF suppliers, Solvay (Solvay 2015), the effect of solvent on PVDF solubility at ambient temperature presented was contradictory to what have been reported by Liu et al. (2011). Graphs were plotted to compare the solubility of PVDF in DMAc and NMP. The graphs showed that the solubility of NMP was much lower compared to DMAc. This indicated that when the same weight percentage of PVDF was used for both solvents, the viscosity of a polymer solution in DMAc solvent would be lower than a polymer solution in NMP solvent. For this reason, the fabricated hollow fiber membrane showed in Figure 2 was corresponded to the later information provided by Solvay. Moreover, the solubility of both solvents also provides a better explanation on some of the features of the hollow fiber membrane. The distinctive features showed in this study by using DMAc and NMP solvents were the circumference and the wall thickness of the hollow fiber. Thus, a narrower and wider wall membrane and hollow fiber diameter were expected when DMAc was used.

Properties of membrane	DMAc Solvent (Fiber-1A)	NMP Solvent (Fiber-1B)
Outer diameter, μm	700	672
Inner diameter, μm	650	533
Wall thickness, μm	40-50	100-140
Macrovoid thickness, μm	15-20	20-40
Average pore radius, μm	1.0-0.3	0.5-1.4
Pore shape	Regular	Irregular

Table 2. The properties of hollow fiber membranes fabricated using DMAc and NMP solvents.

The spinning conditions of Fiber-1 were applied to study the effect of solvents for the hollow fiber fabrication. The main differences among the conditions were the speed ratio and speed of the flow rate. The foremost intention of having a higher ratio and a lower flow rate is to reduce the development of die swell during the spinning process. This die swell phenomenon is defined as a visco-elastic expansion (Pereira et al. 2000), and it is greatly dependent on the shear rate generated between the polymer dope and the spinneret. It not only has an influenced on the membrane morphology (Sukitpaneemit and Chung 2009) but also on the mechanical properties of the membrane.

During the hollow fiber spinning, a distinctive curve on the nascent fabricated hollow fiber at the end of the spinneret was noticeable when the polymer dope was at higher flow rate. This observation is fairly self-explanatory and clarified the formation of wafer-thin hollow fiber due to the die swell phenomenon as shown in Figure 1(C). It has demonstrated the formation of the thin membrane through expanding the internal fiber diameter thereby causing deformation of the hollow fiber membrane resulting in low reproducibility. Therefore, the elimination of this phenomenon is crucial to maximize the expediency and the repeatability of the hollow fiber production in the membrane industry. Otherwise, the fabricated end-products would encounter serious consequence including an increase in production cost due to the instability of the technical process and inconsistent fabrication which will lead to incompatible membrane properties.

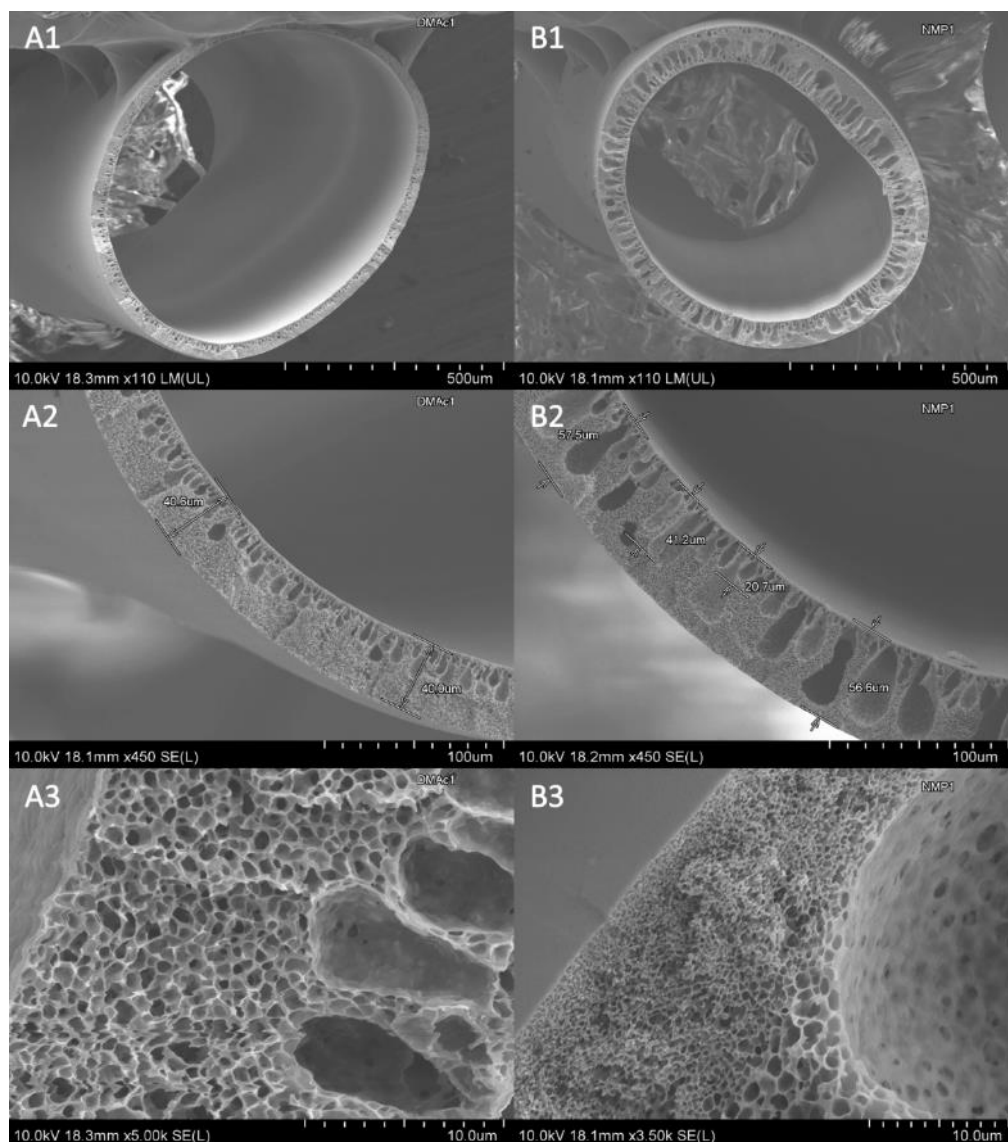


Figure 2. FESEM micrographs of cross-section PVDF hollow fiber membrane spun from 20 wt% polymer dope solution: A = fabricated by using DMAc solvent (Fiber-1A); B = fabricated by using NMP solvent (Fiber-1B).

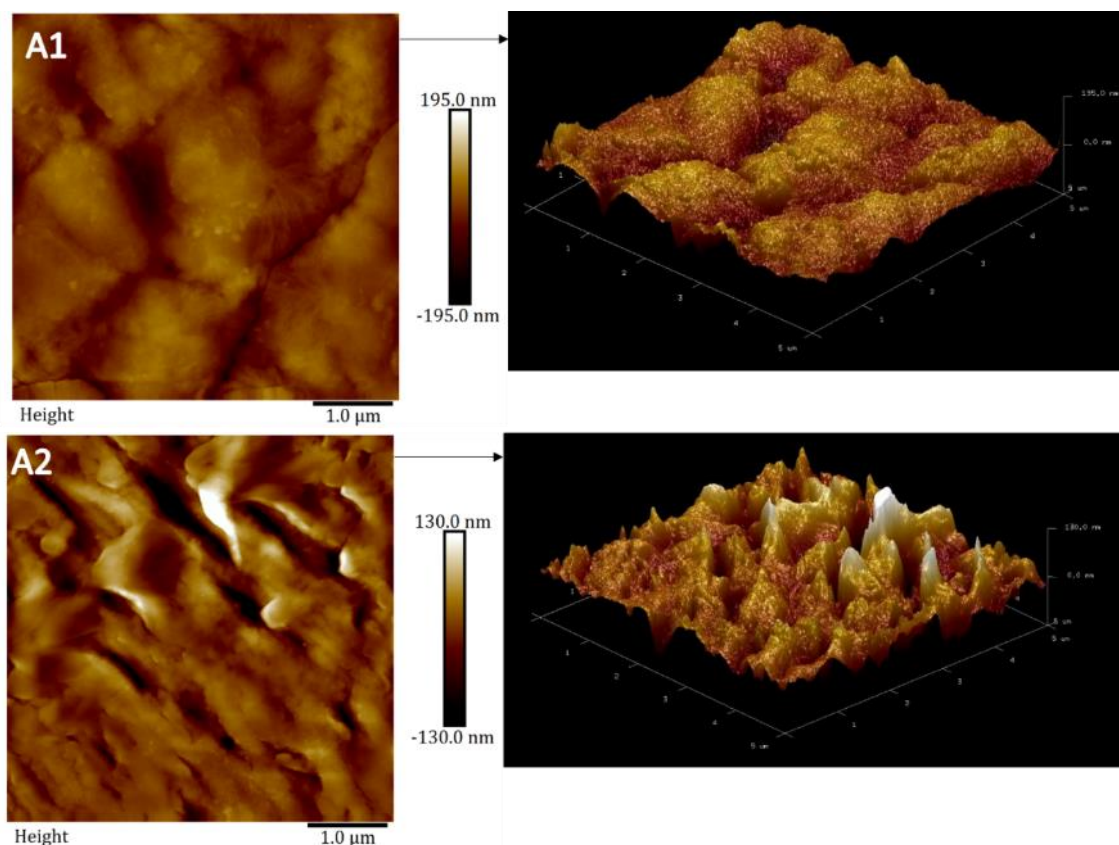
The mechanical properties of the hollow fibers for each condition were listed in Table 3. It can be seen that the tensile stress at break and Young's modulus of the hollow fiber using NMP (Fiber-1B, Fiber-6, and Fiber-12) increased from 0.37 to 0.58 MPa and 0.15 to 0.22 MPa respectively as the flow rate of the polymer dope solutions decreased from 12 to 1 ml/min. The tensile stress indicates that a slow and steady speed extrusion produces a hollow fiber with higher toughness. The increases of the tensile stress may also credit to the increase of the membrane wall thickness. Furthermore, Young's modulus measures the resistance of a material to elastic deformation under certain load. It defines a stiff material with high Young's modulus has barely any or only slight changes in shape under certain load, whereas a flexible material with a low Young's modulus will change its shape significantly. This suggested that the PVDF hollow fiber is a flexible material and when the higher polymer dope flow rate was used the flexibility increased. However for the tensile strain or the elongation at break of the hollow fiber did not demonstrate an obvious difference. The values for Fiber-1B, Fiber-6, and Fiber-12 were 268.9, 259.1, and 266.2 % respectively. Surprisingly, the strain of the membrane exhibited using DMAc was much higher at 369.2 %, but lower at Young's modulus with a value of 0.18 MPa. The strain difference between membrane using NMP and DMAc may be affected by the formation of macrovoids. Thus, the

result complemented with the studies done by various researchers made that the possession of large macrovoids reduced the mechanical strength of a hollow membrane.

	Young's modulus (MPa)	Tensile stress (MPa)	Tensile strain (%)
Fiber-1A	0.1764 ± 0.09	0.5910 ± 0.13	369.2 ± 91.5
Fiber-1B	0.2211 ± 0.04	0.5770 ± 0.05	268.9 ± 52.0
Fiber-6	0.2048 ± 0.06	0.4994 ± 0.10	259.1 ± 91.3
Fiber-12	0.1547 ± 0.05	0.3755 ± 0.06	266.2 ± 99.4

Table 3. Mechanical properties of PVDF hollow fibers fabricated with different flow rates and solvents.

Figure 3 showed the surface roughness of the hollow fiber membrane fabricated using DMAc and NMP. The surface roughness of the membrane is also associated with the wettability of the membrane surface. A hydrophilic material has good wettability while as hydrophobic material has poor wettability. In this study, the determination of the surface roughness is to study the hydrophobicity of the polymer membrane. It was expressed as the rougher the membrane surface, the higher hydrophobicity of the membrane. The surface roughness was calculated in term of roughness ratio. It is defined as the ratio between the actual and projected solid surface area. If the ratio is equal to one, it is a smooth surface and more than one for a rough surface. The roughness ratio for the inner and outer surface membrane using DMAc and NMP are 1.12 and 1.09, and 1.14 and 1.23 respectively. The values indicated that all surfaces were exhibiting hydrophobic properties, where the membrane using NMP has a higher hydrophobicity. For some specific industrial applications for example membrane distillation, a higher hydrophobicity membrane is more favorable to avoid wettability.



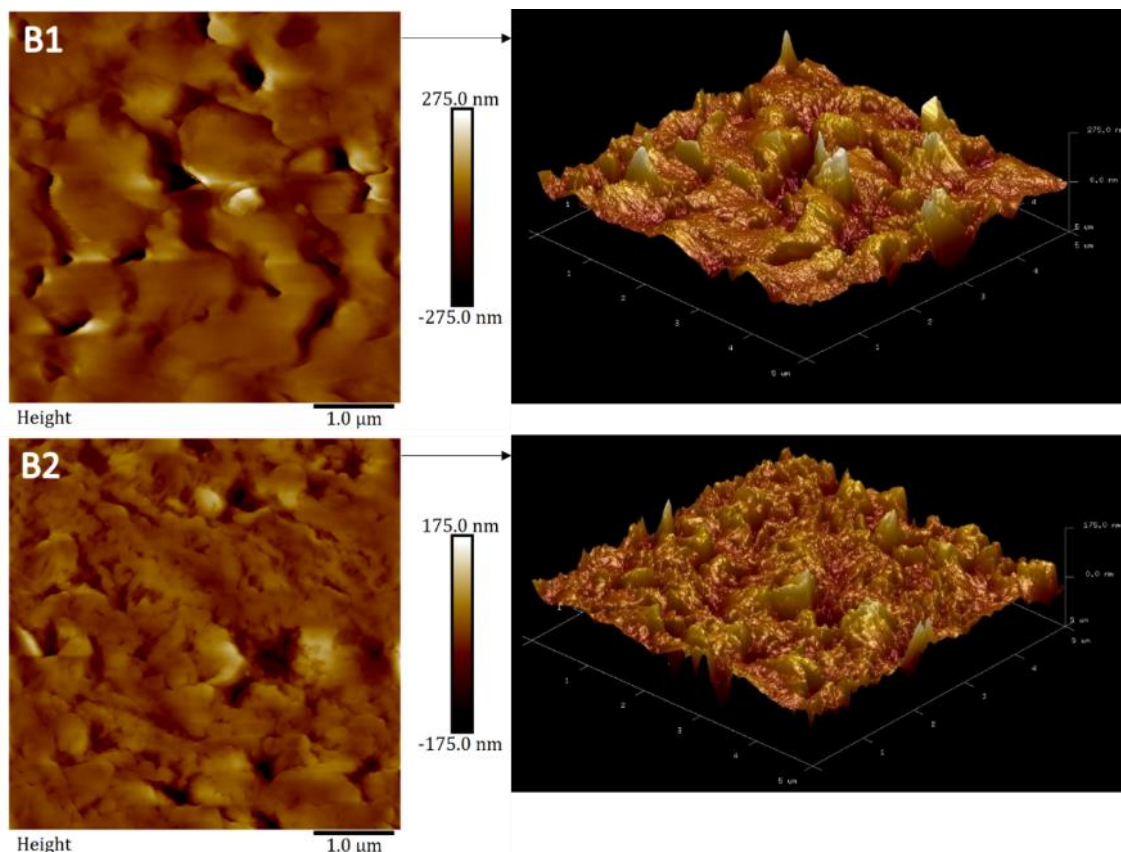


Figure 3. AFM micrographs of the effect of different solvents on surface roughness of the outer (A1 & B1) and inner (A2 & B2) surface of the membranes. Hollow fiber membrane fabricated using (A) DMAc solvent and (B) NMP solvent.

4. CONCLUSION

Two fabrication parameters of PVDF hollow fiber membranes were studied. They were the effects of the ratio and speed of the extrusion flow rate and solvents on polymer dope solution. In the study of extrusion flow rate, at higher speed ratio in conjunction with lower flow rate, the wall thickness of the membrane was thicker, smaller circumference, and more importantly its exhibited higher mechanical strength. Moreover, it also minimized the fabrication instability by avoiding the formation of die swell. Despite having macrovoid free at a higher flow rate, the asymmetric structure of membrane disappeared and collapsed during drying process due to large circumference. In the examination of different solvents applied in the fabrication process, the selection of solvents plays an important role. The fabrication of the hollow fiber membrane using NMP and DMAc showed considerable effects on the membrane morphology. Massive macrovoids were formed using NMP compared to DMAc. Due to the formation of macrovoids in membrane using NMP, weaker mechanical properties were observed. The results demonstrated the manipulation of the spinning conditions were essential for hollow fiber fabrication to acquire distinctive characteristics for specific applications.

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