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Research Paper

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GRAPHICAL ABSTRACT

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PVP concentration

HIGHLIGHTS

- 7KH DLU JDS HuHFW RQ 39') KROORZ ¿EHU PHPEUDQHV LV PXFK PRUH HYLGHQW IRU WKH GRSH VROXW
- /DUJH PDFUR YRLGV FDYLWLHV LQ 39') KROORZ ¿EHU PHPEUDQHV DUH VXSSUHVVHG WR WKH ¿QJHU OL LQ GRSH VROXWLRQ
- 7KH K\GURSKLOLFLW\ DQG YLVFRVLW\ RI SRO\PHU VROXWLRQ VWURQJO\ DuHFW WKH PRUSKRORJLHV D

ABSTRACT

3RO\YLQ\OLGHQH ÀXRULGH SRO\YLQ\OS\UUROLGRQH 39') 393 KROORZ ¿EHU PHPEUDQHV ZHUH IDEULFD 393 FRQFHQWUDWLRQ WKH DLU JDS OHQJWK HuHFW DW WKH ORZ DQG KLJK 393 FRQFHQWUDWLRQ L OHQJWK RQ WKH FURVV VHFWLRQ VWUXFWXUH DQG PHPEUDQH SHUIRUPDQFH ZHUH LQYHVWLJDWHG 5H VROXWLRQ ZLWK WKH KLJK 393 FRQFHQWUDWLRQ WKDQ ORZ 393 FRQFHQWUDWLRQ ,Q RWKHU ZRUGV LQFUHDVHV DV WKH DLU JDS OHQJWK GHFUHDVHV :LWK LQFUHDVLQJ WKH 393 FRQFHQWUDWLRQ LQ GR JHU OLNH PDFUR YRLGV 0RUHRYHU WKH RXWHU VHSDUDWLRQ OD\HU LV WKLFNHQHG DQG WKH PHFKD

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1RQ VROYHQW LQGXFHG SKDVH VHSDUDWLRQ ,36 KDV EHHQ ZLGHO\ DSSOLHG IRU IDEULFDWLQJ PL LPPHUVLRQ SUHFLSLWDWLRQ ,3 DQG PHPEUDQH SUHSDUDWLRQ 8) DQG XOWUD¿OWUDWLRQ 8) PHPEUDQHV DV ZHOO DV KHDWHU PHPEUDQH PDWHULDOV ZKLFK FDQ EH DSSOLHG WR WKH 1,36 WHFKQLTXH LQFOXGH SRO\HWKHUVXOIRQH 36 SRO\HWKHUVXOIRQH 3(6 SRO\YLQ\OFKORULGH 39& SRO\YLQ\OLGHQH ÀXRULGH 39') DV DQ H[FHOOHQW PHPEUDQH PDWHULDO DSSOLFDWLRQV H J PHPEUDQH GLVWLOODWLRQ ZDVWHZDWHU WUHDWPHQW DQG VHDZDWHU

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concentration on PVDF hollow fibers. Authors concluded that the pure water permeability increased and the separation layer tended to be thinner with decrease of the air gap length from 15 to 5 cm. Moreover, decrease in PVP concentration from 5 to 2 % led to low permeability and high rejection values. However, no apparent effect observed on the membrane structure as PVP concentration increased from 2% to 5%. Khayet [4] reported that an increase in the air gap length from 1 to 80 cm resulted in the low permeability and high solute rejection values. Moreover, author reported that thinner and denser sponge-type structure (cross-section view) for PVDF hollow fiber membranes observed. Bonyadi et al. [12] studied the air gap length effect on the corrugation in the lumen contour of PVDF hollow fibers. In another work, Sukipaneenit and Chung [14] investigated the effect of non-solvent additives, including water/methanol/ethanol, on the morphology and mechanical properties of PVDF hollow fiber membranes.

Although the effect of air gap length on performance and cross-section morphology of PVDF hollow fibers has been investigated, in order to better understanding the PVDF hollow fiber fabrication process, more studies should be done on this parameter. To the best of my knowledge, few efforts are contributed in the open literature on the effect of air gap length correlated for the PVP concentration in dope solution, mostly on the cross-sectional structure and membrane's performance.

Thus, the objective of this work is to investigate the effect of air gap length on the structure and PVDF membrane's performance spun by the dope solution containing low and high PVP concentration, respectively. Moreover, the effect of PVP concentration on the structure, specifically the separation layer, and mechanical properties of PVDF hollow fiber membranes is investigated.

2. Experimental and methods

2.1. Materials

Polyvinylidene fluoride granules (PVDF; Solef 6020, Solvay Advanced Polymers L.L.C., and Kynar 761A, Arkema Pte Ltd.) were used for preparing the dope solution. Polyvinylpyrrolidone (PVP, K17) and *N*-Methyl-2-Pyrrolidone (NMP) were purchased from ISP chemicals (M) Sdn Bhd.

2.2. Dope preparation

A known amount of PVDF and different amounts of PVP K17 were dissolved in NMP (solvent) to form the dope solution at 70 °C, as is shown in Table 1. Having mixed for 3 days, dope solution was then transferred to the dope tank for 5 h for degassing, before hollow fiber spinning.

Table 1
Dope solutions for hollow fiber spinning.

Dope No.	Composition		
	PVDF, %	PVP K17, %	NMP, %
1	(Kynar 761A) 15	15	70
2	(Kynar 761A) 15	5	80
3	(Solef 6020) 15	10	75
4	(Solef 6020) 15	5	80

2.3. Fiber spinning and post-treatment

Asymmetric PVDF hollow fiber membranes were fabricated by non-solvent induced phase separation (NIPS) technique and spun by dry-jet wet spinning process. The dope solution was extruded through a spinneret at a pre-designed flow rate by a gear pump and then passed through a certain distance of air gap before entering the coagulation batch. The tap water and mixture (8:2) of NMP and Milli-Q water were used as external coagulant and lumen coagulant (bore liquid), respectively. The spun hollow fibers were collected by a roller at the free falling velocity. The as-spun fibers were soaked in water for 2.5 day for solvent extraction into the water bath. Before drying the fibers, the post-treatment by immersing fibers in 40% of glycerol solution for 24 hrs was applied. All PVDF hollow fibers in this study were spun using the same spinning conditions except for air gap length. The room temperature was 28±1 ºC, and relative humidity was 82±2 %.

2.4. Hollow fiber membrane characterization

2.4.1. Morphology observation by SEM

Hollow fiber membrane cross section was observed by a scanning electron microscope (SEM). Hollow fibers were frozen and fractured in liquid nitrogen to prepare cross section samples.

2.4.2. Pure water permeability (PWP) measurement

PWP of hollow fiber membranes was measured by cross-flow mode testing setup in-house. 4 to 5 pieces of fibers with 15-cm effective length were potted into an acrylic tubing to form the lab-scale cross flow module. Milli-Q water was circulated in shell side of hollow fiber modules at 1 bar by entering module from the feed side and coming out from the rejection side. Then filtrated water was collected from the permeate side for permeability calculation (*LMH/bar*) by the following equation:

$$PWP = F_p / (n\pi DL) \quad (1)$$

where F_p is the permeate flow rate, *L/hr*; *n* is the number of fibers; *D* is the outer diameter of hollow fibers, *m*; *L* is the effective fiber length, *m*.

2.4.3. Mechanical strength measurement

Mechanical strength was tested by Instron 5965 tensile test machine at room temperature. Both ends of hollow fibers were clamped and pulled at 50 mm/min of elongation velocity starting with 100 mm of gauge length. Tensile stress and elongation at break were measured to show the mechanical properties of hollow fibers.

3. Results and discussion

3.1. The effect of air gap length on hollow fibers at low and high PVP concentration in dope solution

Figure 1 shows the cross section morphologies of hollow fibers spun with dope1 containing high concentration of PVP, 15%, at air gap length: 80, 40, 20, and 10 mm, respectively. As could be observed, hollow fibers spun at the air gap higher than 40 mm have an array of trim finger-like macro-voids which start to grow inwards with decrease of the air gap to 20 mm, and finger-like macro-voids grow to big voids as the air gap decreases to 10 mm.

The hollow fiber performance data are summarized in Table 2. As could be observed, the mechanical properties of hollow fibers start to substantially decrease with the decrease of the air gap from 40 mm. When the air gap decreases from 40 mm to 10 mm, the tensile stress and elongation decline by 30% and 63%, respectively. However, the pure water permeability increases by 166%. One possible reason is due to the higher orientation of polymer chain at high air gap length than that at the low air gap length [9]. The second possible reason can be the growth of finger-like macro-voids with the decrease of air gap; specifically at 10 mm of air gap, the macro-voids are almost across the membrane wall. The results may be caused from dry-jet wet-spinning process. During dry-jet wet-spinning process, the nascent fiber experienced a convective internal coagulation in the lumen and a non-convective external coagulation in the air gap region. Then, rapid solvent exchange at external surface in non-solvent coagulation batch; in the air gap region, the moisture-induced phase separation much slower than in coagulation batch slowed the speed of polymer chain contracting and provided a needed time to contracting polymer chains for conformation rearrangement [8]. As a result, when the air gap length decreases, the contracting polymer chains did not have enough time to rearrange conformation before quick phase separation in coagulation bath. This may result in the growth of finger-like macro-voids (see Figure 1). Furthermore, the as-spun fiber immersing in non-solvent coagulation bath was more rapid at low air gap length than high air gap. This leads to much more non-solvent and solvent trapped in the contracted polymer chains [4]. Consequently, more macro-voids are formed in membranes at the low air gap. The phenomenon is similar to the result reported by Chung and Hu [8] on PES hollow fiber membranes.

With the decrease of air gap, another factor, i.e. the effect of die swell, would become apparent [15], specifically for 10 mm air gap, leading to the decrease of mechanical properties and the increase of permeability due to the formation of more macro-voids.

On the other hand, when PVP concentration in the dope solution decreases to 5% (dope 2), the effect of the air gap length on hollow fiber membrane shows significant difference from the higher PVP concentration. Figure 2 shows the cross section morphologies of hollow fibers spun with dope2 containing low concentration of PVP (5%, at air gap: 40, 20, and 10 mm, respectively). As could be observed, there is no significant difference in

cross section structure, macro-voids shape and size, and the outer separation layer when decreasing air gap from 40 to 10 mm. Moreover, it can be observed that the thickness of outer separation layer is thinner compared to morphologies in Figure 1. This difference will be discussed in section 3.2.

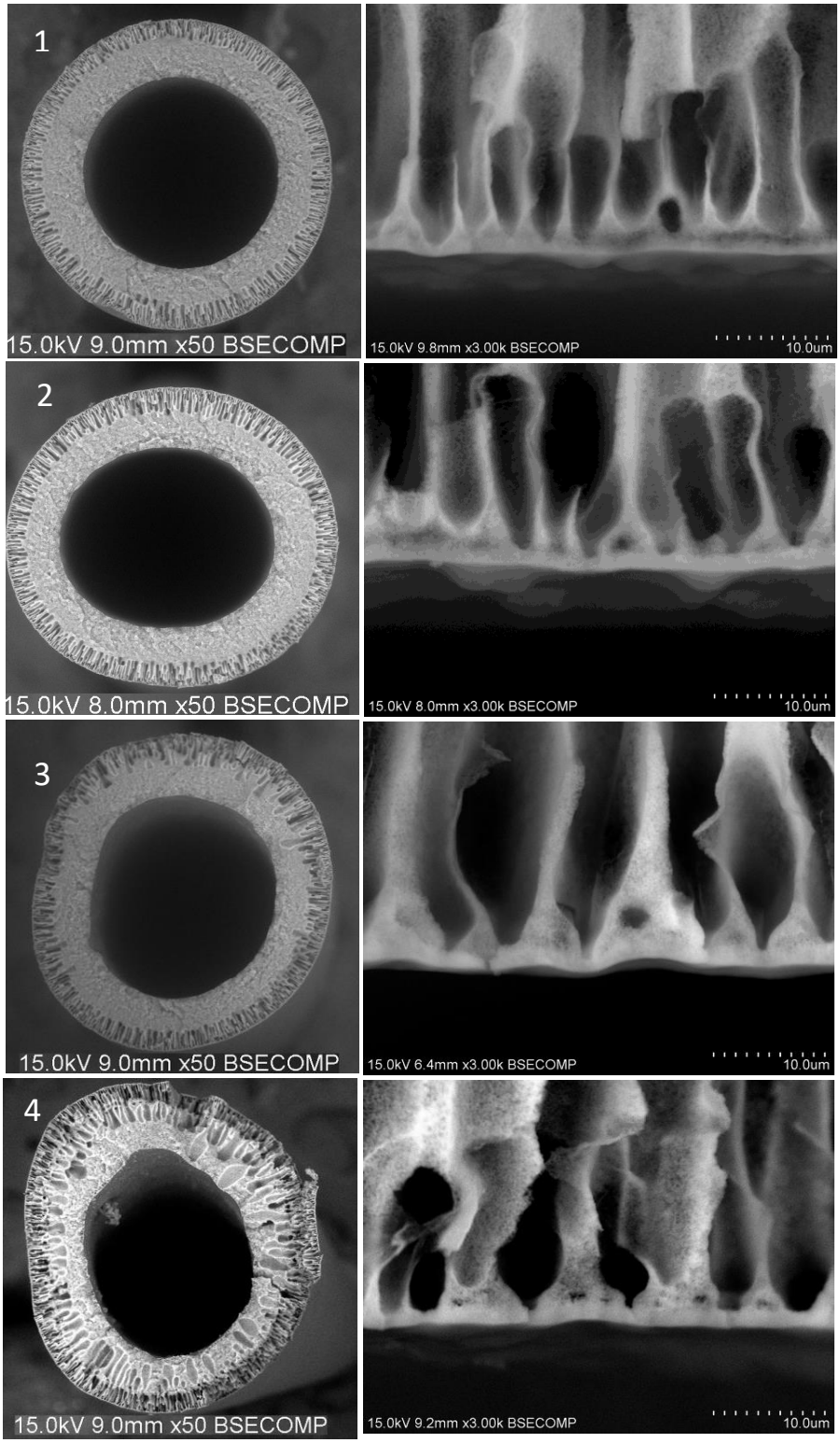

Fig. 1. SEM images of hollow fibers spun by dope 1 containing 15% of PVP at air gap (1) 80, (2) 40, (3) 20, and (4) 10 mm.

Table 2
Characterization data of PVDF hollow fibers (dope 1).

Air gap, mm	80	40	20	10
OD/ID, mm	1.00/0.62	1.00/0.62	0.98/0.54	1.12/0.62
Permeability, LMH/bar	87	80	107	213
Tensile stress, Mpa	4.06	3.85	3.19	2.67
Elongation at break, %	318	284	196	106

The performances of hollow fiber membranes were characterized and the results are summarized in Table 3. As can be seen, the PWP increases with decreasing air gap from 40 to 20 mm; however, with further decrease of the air gap to 10 mm, the PWP does not change, significantly. Whereas tensile stress and elongation do not show the same apparent change to those of fibers

spun by dope 1 with the decrease of air gap from 40 mm to 10 mm. The possible reason is due to the weak effect of die swell on as-spun fibers with low PVP concentration. The possible reason for lower PWP at higher air gap is that PVDF hollow fibers spun at the higher air gap length have the greater orientation and tighter molecular packing than that of lower air gap length [8]. A same observation was also reported by Chung and Hu [8] on PES hollow fibers, by Chung et al. [16] on polybezimidazole/polyetherimide hollow fibers and by Khayet [4] on PVDF hollow fibers.

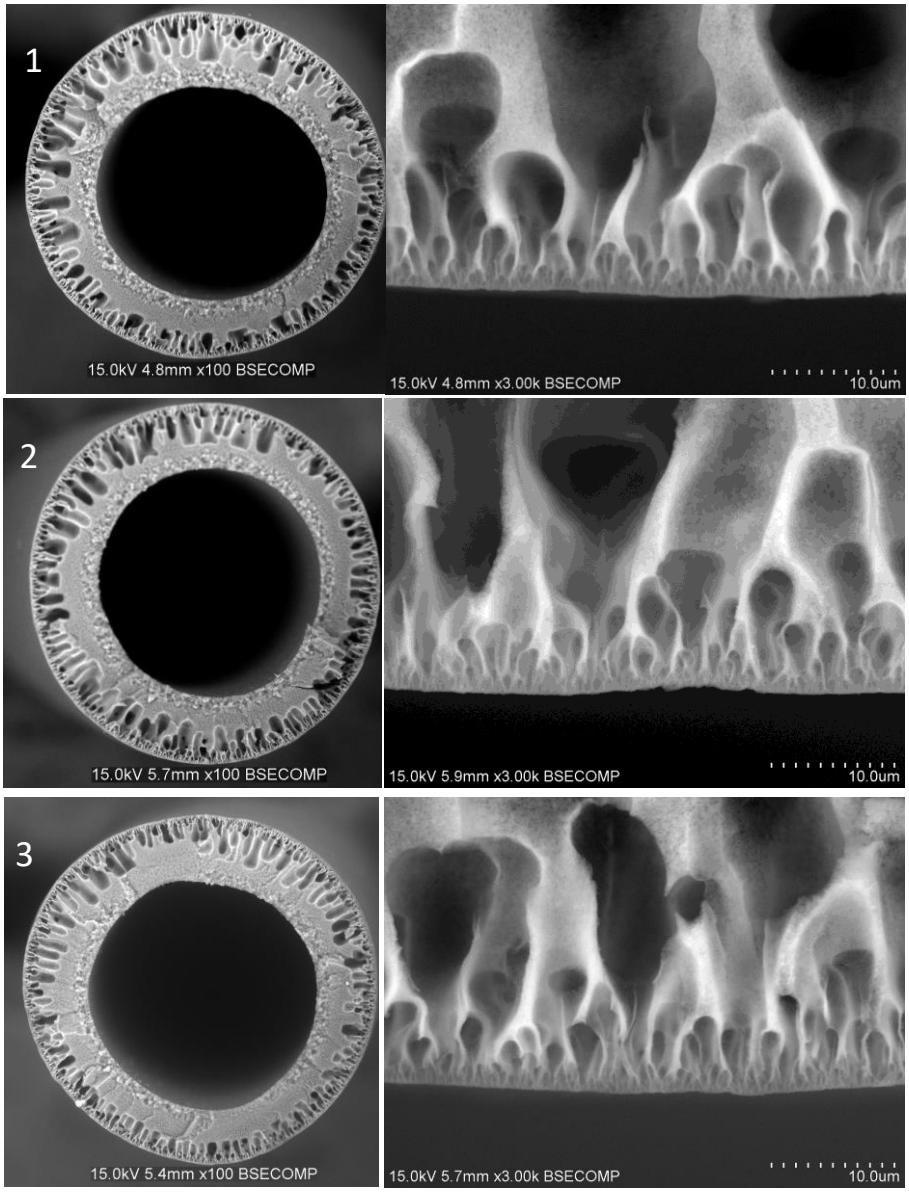

Fig. 2. SEM images of hollow fiber membranes spun by dope 2 containing 5% PVP at air gap (1) 40, (2) 20, and (3) 10 mm.

Table 4 lists the maximum differences of hollow fiber performance as the air gap decreases from 40 to 10 mm for dope solution containing 15% (dope 1) and 5% of PVP (dope 2), respectively. It is observed that the maximum difference for high PVP concentration is more than 2 times higher than that of low PVP concentration. The results illustrate that the effects of the air gap length and die swell on PVDF hollow fiber performance are much stronger for high PVP concentration than that of low PVP concentration. It is hypothesized that the most likely reason is due to the hydrophilicity and viscosity of the polymer solution. For the hydrophobic PVDF solution, moisture-induced phase separation in air gap region is less; the change of air gap length has less effect on moisture-induced phase separation. The hydrophilicity of as-spun PVDF fibers is promoted after adding PVP in the dope solution, and subsequently enhances moisture-induced phase separation in air gap region. In addition, the viscosity of PVDF solution is increased with the increase of PVP in PVDF solution, which leads to the stronger effect of die swell on as-span fibers with high PVP concentration [15]. Therefore, the effects of air gap length and die swell on PVDF hollow fibers is more evident at high PVP concentration than that of low PVP concentration. Thus, it can be concluded that the effect extent of air gap length and die swell on PVDF hollow fiber performance is correlated to the PVP concentration or hydrophilicity and viscosity of polymer solution.

Table 3
Characterization data of PVDF hollow fiber membranes (dope 2).

Air gap, mm	40	20	10
OD/ID, mm	0.89/0.56	0.86/0.55	0.91/0.54
Permeability, LMH/bar	114	181	179
Tensile stress, Mpa	2.59	3.09	2.63
Elongation at break, %	175	195	199

Table 4
Maximum difference of hollow fiber performance with changing air gap from 40 to 10 mm.

Max. difference	5% PVP	15% PVP
Permeability, LMH/bar	67	133
Tensile stress, Mpa	0.5	1.18
Elongation at break, %	24	178

3.2. PVP concentration effect on PVDF hollow fiber membranes

Based on the discussions in section 3.1, it can be concluded that cross section morphologies for high PVP concentration are different from low PVP concentration. Hence, the cross section morphologies for low and high PVP concentration at the same air gap are compared in Figure 3. As could be observed, the large macro-voids/cavities are suppressed to finger-like macro-voids and the outer separation layer indicated by arrows becomes thicker as PVP concentration in the dope solution increases from 5% to 15%. The result of macro-void suppression by the high concentration PVP is in agreement with the literature [5, 11, 17]. The addition of PVP in the dope solution, on the one hand, accelerates the diffusion of solvent and non-solvent due to its hydrophilicity (thermodynamic effect) and, on the other hand, hinders the diffusion of solvent and non-solvent due to the increase of the dope viscosity (kinetic effect) during the phase separation [5, 11, 14]. Therefore, the large macro-voids/cavities form as the thermodynamic effect is predominated. Conversely, finger-like macro-voids form as the kinetic effect is predominated. The finding of thickening the outer separation layer as increasing PVP concentration, to the best of my knowledge, is the first time to be reported on PVDF hollow fibers. The possible reason is due to the moisture-induced phase separation in the air gap region, which is evident at high PVP concentration. The hollow fiber performance data are summarized in Table 5. As could be observed, the tensile stress and elongation increase by 49% and by 62%, respectively, as PVP concentration increases from 5% to 15%. However, the pure water permeability decreases by 30% for the same conditions. The increase of mechanical properties may be attributed to the suppression of macro-voids and thickening of the outer separation layer. Adding higher PVP concentration in the dope solution not only increases the total polymer concentration of attending membrane formation (which is due to more PVP trapped in polymer matrix during the phase separation), but also suppresses the macro-voids and declines the density of the macro-voids. This counterbalances or suppresses the hydrophilic effect of the PVP on PWP. This phenomenon was also observed on PES/PVP/NMP dope solution in the current work.

In order to further investigate the effect of PVP concentration, Solef 6020 was used to prepare the dope solution, dope 3 and 4. The cross section morphologies of PVDF hollow fibers spun with the dope 3 and 4 at 40 mm of air gap length are shown in Figure 4. It can be observed that large macro-voids/cavities are suppressed and the outer separation layer is thickened as the PVP increases from 5% to 10%, consistent to the results of Kynar 761A PVDF. The hollow fiber performance data are listed in Table 6. It can be calculated that the tensile stress increases by 36%, which is in good agreement with results for Kynar 761A in the trend, while the elongation is the same. However, the PWP is promoted by 27% for this group of the dope solutions. One of the possible reasons is the lower PVP concentration in dope 3 than that of dope 1. For dope 3, the effect of PVP hydrophilicity exceeds the effect of macro-void suppression. More comprehensive studies should be carried out for investigating the PVP effect on PWP and pore size distribution of hollow fibers.

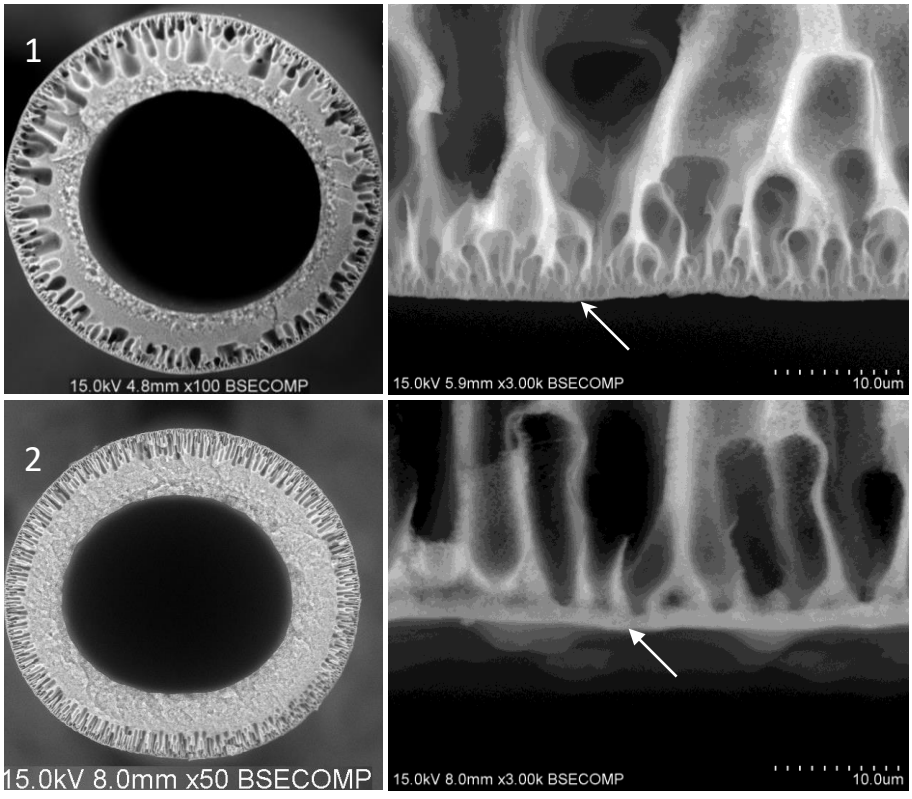

Fig. 3. SEM images of PVDF hollow fiber spun by the dope containing PVP concentration: (1) 5 %, (2) 15 %; PVDF resin: Kynar 761A; air gap: 40 mm.

Table 5
Effect of PVP concentration in the dope solution on the hollow fiber performance.

PVDF	PVP, %	Air gap, mm	Permeability, LMH/bar	Tensile stress, Mpa	Elongation at break, %
Kynar 761A	5	40	114	2.59	175
Kynar 761A	15	40	80	3.85	284

Table 6
Effect of PVP concentration in the dope on the hollow fiber performance.

PVDF	PVP, %	Air gap, mm	Permeability, LMH/bar	Tensile stress, Mpa	Elongation at break, %
Solef 6020	5	40	181	2.5	212
Solef 6020	10	40	230	3.4	216

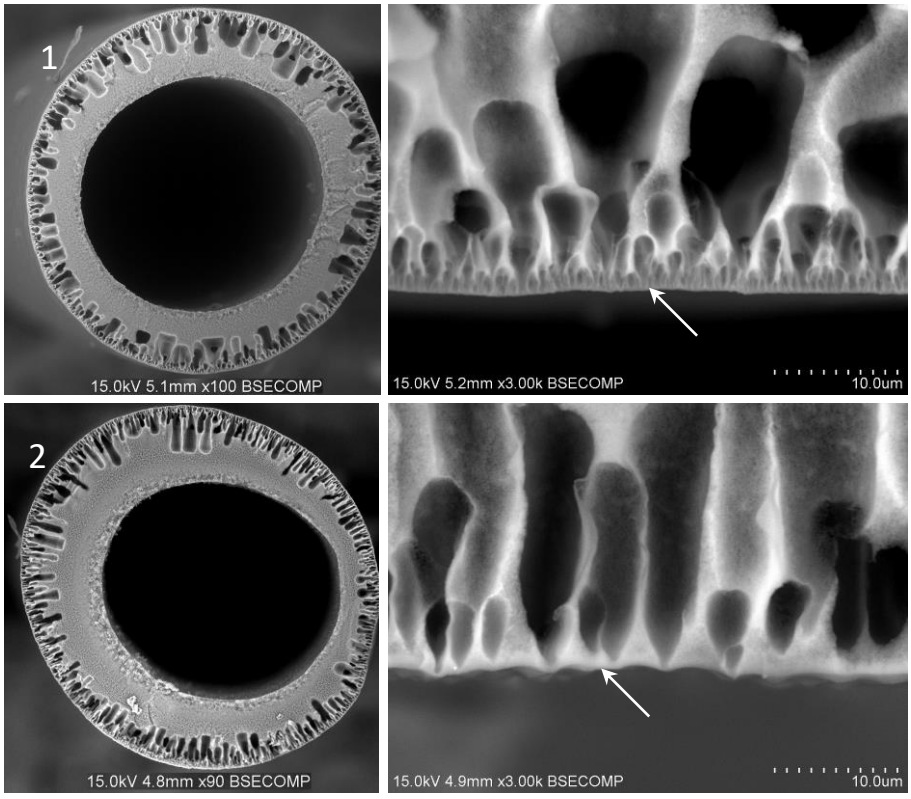

Fig. 4. SEM images of hollow fiber spun by the dope containing PVP concentration: (1) 5 %, (2) 10 %; PVDF resin: Solef 6020; air gap: 40 mm.

4. Conclusions

The correlated effects of the air gap length and PVP concentration on PVDF hollow fibers have been investigated in this work. Effects of the air gap length on the cross-section morphologies and performance of PVDF hollow fibers are much more evident for the high PVP concentration than that of the low PVP concentration. For the dope with high PVP concentration, finger-like macro-voids grow inwards and become large, the PWP increases and mechanical properties decrease with decreasing the air gap. However, there is no similar and apparent finding for the dope with low PVP concentration. It may be due to the moisture-induced phase separation, which is strongly affected by the hydrophilicity of as-spun hollow fibers, and die swell effect affected by the dope viscosity in air gap region during dry-jet wet-spinning process.

The effect of PVP concentration on the cross section morphologies and performance of PVDF hollow fibers has been also studies, simultaneously. With the increase of PVP concentration in the dope solution, the large macro-voids/cavities are suppressed to finger-like macro-voids. This is due to the predominated kinetic effect. Moreover, the thickness of the outer separation layer is enhanced due to the moisture-induced phase separation in the air gap region, leading to the increase of the tensile stress and elongation. The changes of PWP with PVP concentration should be due to the competition between thermodynamic effect and kinetic effect. Thus the details of PVP effect on PWP and pore size distribution of PVDF hollow fibers will be investigated in the future.

5. Acknowledgements

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