Improved Performance of PAN-based UF Membrane with PAN-g-PVA Amphiphilic Copolymer

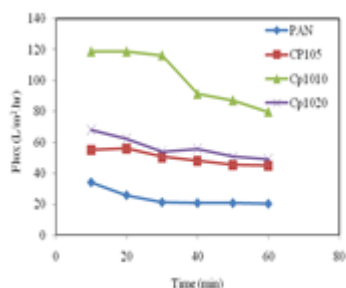N. A. M. Nazri[a], W. J. Lau[a], A. F. Ismail[a]*, M. A. R. Saidin[a]

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Abstract

The present study focuses on the effect of poly (acrylonitrile) (PAN)-g-poly (vinyl alcohol) (PVA) amphiphilic copolymer as an additive on fabrication of PAN-based UF hollow fiber membrane. The PAN-based hollow fiber membranes with different copolymer composition in dope solution were prepared via dry-wet phase inversion process. Compared to PAN-based membrane, membranes incorporated with PAN-g-PVA copolymer displayed good morphology and better hydrophilicity. It is found that pure water flux of the membrane incorporated with amphiphilic copolymer was 5 times higher than that of control membrane, recording 244.97 L/m^2.hr when tested at 1 bar. Results also showed that the UF membranes incorporated with amphiphilic copolymer were able to retain efficiently bovine serum albumin (BSA) (66 kDa) and possessed better anti-fouling performance.

Keywords: Amphiphilic copolymer; ultrafiltration; poly (acrylonitrile); protein rejection, poly (vinyl alcohol)

■1.0 INTRODUCTION

UF membrane has been widely used in a wide range of industrial applications such as water and wastewater treatment, reverse osmosis pretreatment, food manufacturing, protein separation/purification, etc. [1-3] Importantly, application of UF membrane has considered very important in the area involving proteinaceous solution such as in food and manufacturing, biomedical and wastewater treatment.[4]This type of membrane separation process is of great interest in industrial processes due to its promising advantages such as low operating cost, high permeability and ambient temperature operation. However, the application of UF membrane is still limited due to the fouling problem, which leads to flux decline, increase in maintenance cost as well as energy consumption.[5]Thus, it is utmost important to minimize the hydrophobic interaction between membrane surface and feed solution by increasing membrane surface hydrophilicity. Generally, intrinsic hydrophobic polymeric membrane surface is the main reason causing protein adsorption and other biomolecules onto membrane surface and internal pores.[5-7]

Among the available methods for UF membrane modification, surface modification using self-assembled amphiphilic copolymer have received noticeable interest in recent years as this method offers controllable structure, self-healing and desirable surface properties.[8]In view of this, the use of amphiphilic copolymer as an additive has become the focus of study among the community of membrane scientists. Ideal strategy of using amphiphilic copolymer in UF membrane fabrication includes high surface coverage with long-term stability, high permeability, internal pores modification, low cost and maintaining desirable bulk membrane properties.[9]

The use of amphiphilic copolymer additive is undoubtedly an attractive method as it involves surface segregation step during phase inversion process which can impart hydrophilicity of the membrane, leading to outstanding anti-fouling performance. Self-assembly exhibited by amphiphilic copolymers are in respect to interaction of the hydrophobic part with hydrophobic surface and hydrophilic part with water or hydrophilic surface. Importantly, in UF membrane application, the self-assembly properties have contributed to the formation of hydrophilic layer on surface by the stretch out of hydrophilic block to aqueous environment, hence resulting in protein fouling resistant.[10-12] Asatekin *et al*. performed experimental investigation on performance of PAN membrane with incorporation of PAN-g-PEO amphiphilic copolymer where highest flux of 1590 L/m^2.hr and complete flux recovery were reported. In addition, pure water permeability was observed to be mainly dependent on PEO content in copolymer and copolymer additive composition in dope solution. Higher PEO

content and the additive composition have created strong resistance to fouling and improved of flux due to enhanced hydrophilicity by the migration of hydrophilic PEO. In another similar, PAN-r-DMMSA was incorporated to PAN membrane matrix, decrease of pure water flux from 497.0 L/m^2.hr to 276.61 L/m^2.hr and increase of flux recovery ratio from 47% to 95% were exhibited by the resulting membranes with increasing copolymer content. Upon the comparison of PAN membrane incorporated with PAN-g-PEO and PAN-r-DMMSA, it can be concluded that PAN-g-PEO copolymer additive offers better membrane performance as in comparison with PAN-r-DMMSA.[13] To the best of our knowledge, none of them have reported potential of PAN-g-PVA copolymer in UF membranes preparation.

Thus, this study aims to investigate potential of PAN as a backbone of graft copolymer and PVA as a hydrophilic side chain of the copolymer. PVA polymer is characterized as highly hydrophilic, good membrane forming property, biocompatibility as well as good physical and chemical stability.[14] Zhang *et al*. also highlighted the superior characteristics of PVA such as good mechanical strength, low fouling potential, thermal and pH stability as well as good resistant to most solvents.[15]However, limitation of PVA polymer is lied on susceptible to degradation, due to its solubility in water. As compared to PAN, application of PVA for UF technology is quite rare. Upon comparison, PVA is more employed in reverse osmosis and pervaporation areas. Several works have reported that PVA or PVA copolymer were utilized as a selective skin in reverse osmosis. Shang and Peng indicated that PVA composite has improved anti-fouling properties as well as water flux as compared to those composite without PVA.[16]

In order to gain a better understanding on the performance of PAN-based membrane incorporated with amphiphilic copolymer, therefore the main objective of this study to investigate the effect of PAN-g-PVA amphiphilic copolymer additive on PAN-based UF hollow fiber membrane. To the best of our knowledge, this is the first study conducting an experimental work associated with PAN-g-PVA amphiphilic copolymer additive. This study can contribute in development of UF membrane for application in purification/separation associated with proteinaceous component such as wastewater treatment, biomedical and food and manufacturing. To achieve the objectives of this study, different composition of PAN-g-PVA was added in dope solution containing DMSO and PAN. Filtration experiments using BSA as a modal foulants were conducted to investigate the anti-fouling properties of the resulted membranes.

■2.0 EXPERIMENTAL

2.1 Materials

PAN-based UF hollow fiber membranes were prepared using polyacrylonitrile (PAN, Mw 150 000) purchased from Sigma Aldrich. Dimethyl sulfoxide (DMSO) (ACS grade, assay 99.9%) that was purchased from Sigma Aldrich was used as solvent without purification. Polyvinyl alcohol (PVA) with degree of polymerization 1400 was purchased from Fluka (Mw 61 000 g/mol). Analytical reagent grade monomer, acrylonitrile (AN) was supplied by Merck (Mw 53.06 g/mol). Initiator for synthesis of PAN-g-PVA, ceric ammonium nitrate (0.1 M) was supplied from Sigma Aldrich. Bovine serum albumin (BSA) (66 kDa) was purchased from Sigma Aldrich.

2.2 Membrane Preparation

For dope solution preparation, certain amount of PAN and PAN-g-PVA were added into DMSO solvent that was weighted previously to achieve desired weight ratio of PAN: PVA in dope solution. Spinning dopes containing 12wt polymer were prepared through homogeneous stirring using IKA RW20 digital mechanical stirrer at 60 °C until it was completely dissolved as tabulated in Table 1. The homogeneous solution was then underwent dry-jet wet spinning process to fabricate hollow fiber membranes via phase inversion process

2.3 Characterizations

Scanning Electron Microscope (SEM) (Hitachi TM3000) was used to examine the spun membrane morphology. Hollow fiber membranes were immersed and fractured in liquid nitrogen before analysis. Sputtering gold used to coat the membranes before analysis by SEM taking place. SEM images of cross sectional area and surface were taken at different magnifications.

Degree of hydrophilicity of UF membranes was evaluated by tangent method using Contact angle system OCA 15pro (DataPhysics Instruments GmbH, Filderstadt). The hollow fibers were cut and deionized water was doped on the surface of the hollow fiber at 15-20 different points by using microsyringe. Contact angle values were then calculated from mean value of the different measurements.

Pure water flux, rejection and anti fouling experiments were carried out using a lab-scale cross flow UF membrane system. Hollow fiber bundle (10 fibers, 20 cm long) was placed in a pressure vessel. Feed solution was transferred from solution tank to pressure vessel by using low pressure booster pump. Before any experiment, the hollow fiber membranes were compacted at 1.5 bar pressure by using DI water until it reached steady state condition. Filtration experiment was operated at ambient temperature, 25 °C and 1 bar pressure. Initial pure water flux was then calculated by using Equation 1,

$$J_{WF} = \frac{V}{t \, x \, A} \tag{1}$$

Table 1 Hollow fiber PAN/PVA blend membranes with different PAN:PAN-g-PVA ratio

Sample code	^{a}PAN:PAN-g-PVA ratio
PAN	100:0
CP105	95:5
CP1010	90:10
CP1020	80:20

^{a}Total polymer weight in dope solution is 12 wt%

where V (L) is the volume of permeate, A (m^2) is the effective area of the hollow fiber membrane and t (hr) is the ultrafiltration time. The water permeation experiment was stopped after 30 min, and solution tank was emptied. For protein (BSA) rejection and anti-fouling analysis, the feed liquid was displaced with 1.0 g/L of BSA solution and the real-time fluxes were also recorded under 1 bar. Protein flux was measured until it reached constant flux (J_p). Then, protein rejection (R) was calculated using the following equation.

$$R(\%) = (1 - \frac{c_p}{c_f}) \, x \, 100 \tag{2}$$

where C_p is the permeate concentration (mg/L) and C_f is the feed concentration (mg/L). The concentration of protein solution in feed was determined by using UV-Vis spectrophotometer (DR5000, Hach). To investigate fouling analysis, the solution tank was refilled with DI water and the membrane was cleaned by using DI water for 30 min. Pure water flux (J_{w2}) was measured again after the cleaning process to measure flux recovery ratio (R_{FR}) by using following equation.

$$R_{FR}(\%) = \frac{J_{w2}}{J_{w1}} \times 100 \qquad (3)$$

■3.0 RESULTS AND DISCUSSION

3.1 Characterization of PAN/PAN-g-PVA Blend Membranes

Figure 1 shows the morphologies of PAN membrane and PAN/PAN-g-PVA blend membranes. As can be seen from the SEM images, all the membranes exhibited typical asymmetric UF membrane morphology with a dense top layer supported with finger-like porous sub layer. It could be noticed that the cross section of all the membranes composed of 3 layers, which are the top layer with thin finger-like structure extended from outer membrane surface, intermediate teardrop-like structure at the middle of the cross-section and bottom layer with small and thin finger-like layer extended from inner membrane lumen. Also, it can be observed that the size of finger-like near the outside membrane surface and teardrop-like layer at the middle of the membrane cross section increased, with the increase of PAN-g-PVA content in the membrane. Significant morphology change can be seen from CP1020 that was prepared from highest PAN-g-PVA copolymer content in dope solution, by which largest finger-like at the top layer and teardrop-like at the middle layer can be observed from membrane CP1020. It is found that the well-developed teardrop-like could suppress the formation of finger-like layer at the bottom layer at high composition of PAN-g-PVA in dope solution. With the addition of PAN-g-PVA copolymer to the PAN-based membrane, phase inversion process at the outer surface was faster than the phase inversion process at the inside surface, which may explain the increase of size for top and bottom layer. Membrane surface morphology of PAN-based membrane was also influenced by the composition of the PAN-g-PVA copolymer in the dope solution, as shown Figure 2 (right). As compared to PAN control membrane that possess smooth surface, the PAN/PAN-g-PVA blend membranes tended to have rougher surface and showed existence of pores on membrane surface at 10k magnification. Also, roughest surface and significant large pores could be observed from CP1020 membrane that was prepared from the highest PAN-g-PVA composition in the dope solution.

To evaluate the surface hydrophilicity of the prepared membrane with different composition of PAN-g-PVA copolymer, surface contact angles of the membranes were measured and the results were presemted in Table 2. The control PAN membrane showed water contact angle of 75.99°. The water contact angle decreased with increasing PAN-g-PVA copolymer content in dope solution, which indicates that the membrane surface became more hydrophilic after addition of the copolymer. The lowest contact angle of 56.76° was observed from CP1020 when the content of PAN-g-PVA in the total solid in dope solution amounted to 20 wt%. The contact angle results suggest that the presence of self-organized PAN-g-PVA

amphiphilic copolymer effectively enhanced membrane surface hydrophilicity.
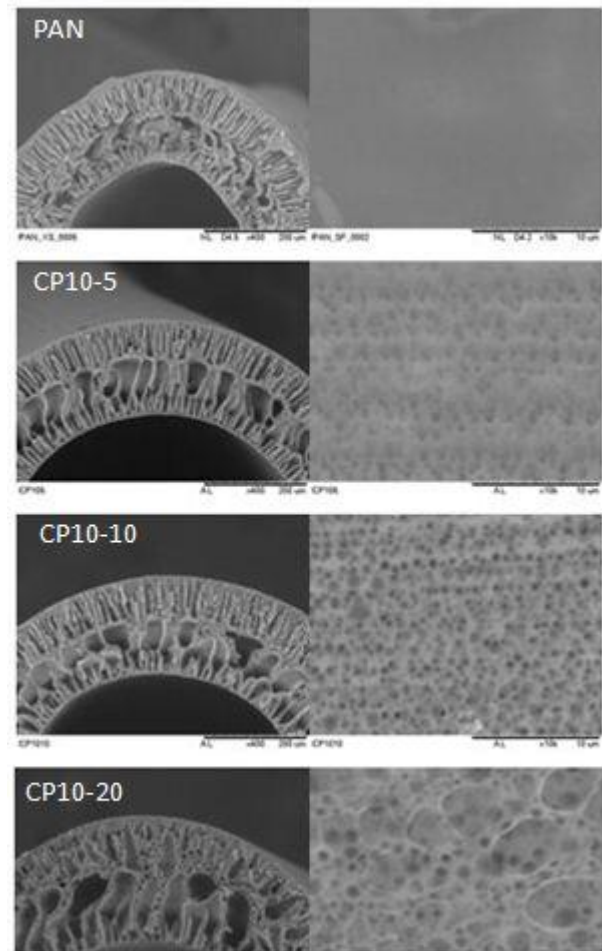
Figure 1 SEM images of cross section (left) and surface (right) morphology of the control PAN membrane and the PAN/PAN-g-PVA blend membranes, respectively

**Table 2** Membrane performance characteristics

Membrane	Contact angle (°)	PWF ((L/m².hr)	$R_{(\%)}$	(R_{FR}) (%)
PAN	75.99	43.06	92.69	73.12
CP105	64.44	102.14	99.94	79.14
CP1010	62.73	118.75	95.37	90.95
CP1020	56.76	244.97	98.50	47.12

3.2 Properties of PAN/PAN-g-PVA Blend Membranes

Ultrafiltration experiments were carried out to investigate the permeability and separation performance of the blend membranes. Table 2 presents the pure water flux data for PAN control membrane and the PAN/PAN-g-PVA blend membranes. Pure water flux for control membrane is 43.06 L/m².hr. However, pure water fluxed for blend membranes are remarkably higher than that of PAN membrane by which highest pure water flux was achieved by CP1020, prepared from highest copolymer composition. The increase of pure water flux with addition of PAN-g-PVA copolymer might be attributed to the increase of membrane surface hydrophilicity due to presence of hydrophilic PVA on membrane surface promoted by the

migration of the hydrophilic PVA chain toward aqueous water environment. The increase of hydrophilicity could lead to fast water transport through membrane during ultrafiltration experiment, hence leading to excellent pure water flux. Additionally, addition of PAN-g-PVA copolymer could facilitate formation of pore size which can be observed from SEM micropgraph. In term of BSA rejection performance, it could be deduced that all membranes demonstrated excellent BSA rejection of above 90%. Highest BSA rejection was achieved by CP105 which might be attributed to the smaller pore size as compared to other membrane.

To investigate the effect of PAN:PAN-g-PVA ratio to the anti-fouling properties of the PAN/PAN-g-PVA blend membranes, BSA was used as a model foulants during ultrafiltration experiments and real-time fluxes were recorded, as shown in Figure 2. The flux data in Figure 2 revealed that all the PAN/PAN-g-PVA blend membranes had lower flux during protein filtration experiment. The low protein flux as compared to the initial pure water flux when replacing pure water with BSA solution could be due to the deposition of protein on the surface of membrane and/or adsorption of protein in the internal pores of membrane. However, highest protein flux was achieved by membrane CP1010 which indicates considerably high resistant to protein deposition and adsorption. To further characterize the anti-fouling properties of the prepared membrane, the membranes were cleaned and water flux after cleaning was measured. High flux recovery indicates the low potential of irreversible fouling. From Table 2, it can be observed that highest flux recovery of 90.95% was demonstrated by membrane CP1010, which described excellent anti-fouling performance of the membrane. Previous research reports pointed out that self-assembly properties of amphiphilic copolymer could facilitate formation of hydrophilic layer on surface by the stretch out of hydrophilic block to aqueous environment that could impart excellent anti-fouling properties of membrane.[11-12]Additionally, it should be noted that increasing the PAN-g-PVA content in total solid in dope solution of up to 10 wt% could enhance the flux recovery of the membrane, however further increase to 20 wt% in total solid during membrane preparation could lead to low flux recovery. This phenomenon might be caused by the migration of the amphiphilic copolymer to aqueous water environment at higher composition due to the strong affinity of hydrophilic PVA side chain with water environment.
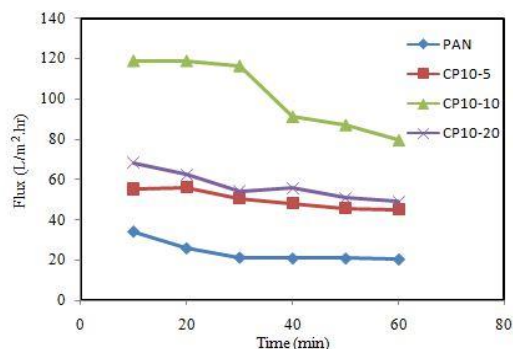
Figure 2 Effect of PAN:PAN-g-PVA ratio in dope solution on protein flux

■4.0 CONCLUSION

PAN/PAN-g-PVA hollow fiber blend membranes were prepared via dry/wet phase inversion process. The SEM results indicated that addition of PAN-g-PVA to PAN-based membrane could lead to the increase of size of finger-like near the outside membrane surface and teardrop-like layer at the middle of the membrane cross section. From contact angle analysis, it is found that contact angle decreased from 75.99° of control PAN membrane to 56.76° for the most hydrophilic membrane (CP1020) which indicates that the membrane surface became more hydrophilic after addition of the PAN-g-PVA copolymer. The enhanced hydrophilicity of the blend membrane was resulted from surface coverage of PVA chain on membrane surface due self-organized behaviour of the PAN-g-PVA amphiphilic copolymer during phase inversion process. Excellent pure water flux as high as 244.97 L/m^2.hr, which was about 5.69 times higher than the control PAN membrane. Blend membranes also demonstrated better protein filtration flux as compared to the PAN control membrane which indicated better fouling resistant. Moreover, high flux recovery of 90.95% for CP1010 membrane explained the enhancement of anti-fouling properties of membrane prepared with optimum composition of PAN-g-PVA in dope solution.

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