

Development and characterization of glycerol coating on the PAN/PVDF composite membranes

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Abstract. Studies on investigating the effects of glycerol coating on the intrinsic and permeation properties of polyacrylonitrile (PAN) - polyvinylidene fluoride (PVDF) membranes were carried out. The surface properties of the membranes were determined by using field-emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), fourier transform infrared spectroscopy (FTIR) and contact angle goniometer. The percentage of shrinkage, pore size, porosity and the water permeation of the membranes were also studied. The presence of new -OH and C-O bands in FTIR spectra showed that glycerol was successfully coated on the surface of the membranes. It was found that with increasing glycerol concentration from 0 to 30 vol%, the membranes exhibited higher water flux due to lower contact angle and larger pore size. However, the water flux was decreased when more than 20 vol% of glycerol was used as the coating material. It was due to the pores blocking on membrane surface and decreased surface roughness as shown by the FESEM and AFM images. Overall, glycerol coating can be a promising coating material to improve the surface properties of the membrane and its permeability performance.

1. Introduction

Polymeric membrane is widely used for water treatment due to its easy forming properties, higher flexibility, smaller space footprint and low operating cost [1]. Polyacrylonitrile (PAN) and polyvinylidene fluoride (PVDF) are widely studied due to their beneficial characteristics as host polymers. PVDF is well-known for its excellent thermal stability, chemical resistance and mechanical strength [2,3]. Meanwhile, PAN exhibits good chemical stability and good solubility in common organic solvents [4,5]. PAN also shows higher degree of hydrophilicity and better fouling resistance compared with other polymeric materials such as polyethersulfone (PES), polysulfone (PSf), and polyethylene (PE) [6]. The polymeric membrane prepared from the composites of PVDF and PAN may have the synergistic advantages of both PVDF and PAN. However, PVDF membrane would shrink after the drying process.^{7,8} Additionally, it is difficult to prepare a miscible blend of PVDF and PAN. Yin et al. [9] and Liu et al. [10] demonstrated that PAN/PVDF composites have rough surfaces, which are undesirable as it is prone to fouling. Hence, it is necessary to improve the surface properties of the PAN/PVDF membranes and minimises the shrinkage effect.

Surface modification on membrane affects its hydrophilicity, chemicals resistance and separation performance significantly [11]. An extra layer coated on the membrane surface can profoundly affect these characteristics and its propensity to foul. The modification can be done by using different coating or grafting methods in order to improve the hydrophilicity of the membrane and its anti-fouling property [12,13]. Compared to blending method, Mojtahedi et al. [14] reported that membranes surface modified via coating technique was more hydrophilic, which resulted in a higher water flux. Glycerol is known



as non-solvent additive for preparing porous membranes. Hess et al. [15] found that membranes prepared by increasing the glycerol concentration in the dope solution exhibited an increase in their mean pore size and porosity. Similar findings were also reported by other researchers [16,17]. However, the use of glycerol as the PAN/PVDF membrane surface coating material has not been studied extensively by the researchers.

In this study, an attempt was made to investigate the role of glycerol in improving its surface properties as well as reducing the effect of shrinkage on the PAN/PVDF membranes. The physical properties of the membranes were evaluated by using contact angle goniometer, Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM). Besides, the pore sizes, porosities and the water permeability of the membranes were also reported in this study.

2. Materials

Polyvinylidene fluoride (Shanghai ofluorine, PVDF T-1) and polyacrylonitrile (Sigma-Aldrich, 150kDa) were used as membrane forming materials. N-Methyl-2-pyrrolidone (Merck, 99.5%) was used as solvent to dissolve polymers. Glycerol (QReC, 99.5%) was used as the coating agent. All the chemicals were used without further purification.

3. Methodology

The polymer solution was prepared by dissolving 16 wt.% of polymer, with a ratio of PAN/PVDF: 80:20 in NMP at 65°C. The solution was allowed to stir at 400 rpm for four hours to achieve homogeneity. The solution was stored at room temperature for 24 hours to remove the bubbles. Membranes with approximate 200 μm were prepared by using the semi-automated casting machine at 7 cm/s. [18] The cast polymer solutions were immersed in reverse osmosis (RO) water to complete the phase inversion process. The membranes were then pre-treated in microwave at 100W for 30 minutes to remove excess NMP. The membranes were immersed in glycerol solution, ranged from 5, 10, 20 and 30 vol% for 1 hour followed by drying at room temperature. The membranes were labeled according to the volume percentage (vol %) of glycerol used; for instance, PAN/PVDF5 indicates 5 vol % of glycerol was coated on PAN/PVDF based composite membrane.

The shrinkage of the membrane was measured by comparing the length of the membranes before (L_i) and after (L_f) under different concentrations of glycerol. The equation to calculate the percentage of shrinkage is as below:-

$$\frac{L_i - L_f}{L_i} \times 100\% \quad (1)$$

The porosity (ϵ) of the membranes was measured using the gravimetric method and the porosity was calculated by using the following equation (2):

$$\epsilon = \frac{(w_a - w_b) / \rho_{\text{water}}}{(w_a - w_b) / \rho_{\text{water}} + w_b / \rho_{\text{membrane}}} \quad (2)$$

Where w_a = Weight of wet membrane (g), w_b = Weight of dry membrane (g), ρ_{water} = Density of water (g/cm^3), ρ_{membrane} = Density of membrane (g/cm^3).

The contact angle of the membrane was measured by using the contact angle goniometer (Attension/KSV Theta, Japan). Approximate 3 μL of RO water was dropped on the surface of the sample. The contact angle was measured from the water-membrane interface. At least 10 locations were arbitrarily chosen on the membrane surface in order to obtain an average value.

The water permeation of the membranes was determined by using the stirred ultrafiltration cell (Millipore, model 8050) at 2.5 bars. The flux(J) is calculated from the following equation:

$$J = \frac{Q}{AP} \quad (3)$$

Where Q the water flow rate in L/h is, A is the effective membrane surface area which is 13.4 cm² and P is the operating pressure (bar).

The surface and cross sectional images of the membranes were obtained using FESEM (Model: SU8020, Hitachi). The dry membrane samples were immersed in liquid nitrogen and fractured, followed by sputter-coating with platinum using a sputtering device. The effect of glycerol concentrations on the membrane surface roughness was studied by using non-contact AFM mode (Park SystemXE-100). FTIR spectra of the membranes were recorded in the mid IR region between 700cm⁻¹ and 4000 cm⁻¹ by using Perkin Elmer Spectrum One FTIR Spectrophotometer.

The pore radius (r_p) of the membranes were determined by using the Guerout-Elford-Ferry equation.¹⁹

$$r_p = \sqrt{\frac{(2.90 - 1.75\varepsilon)8V\mu\delta}{\varepsilon PA}} \quad (4)$$

Where V is the water flow rate in m³/s, μ is the dynamic viscosity of water at 25°C (0.891 mPa.s), and δ is the thickness of the membrane.

4. Results & Discussion

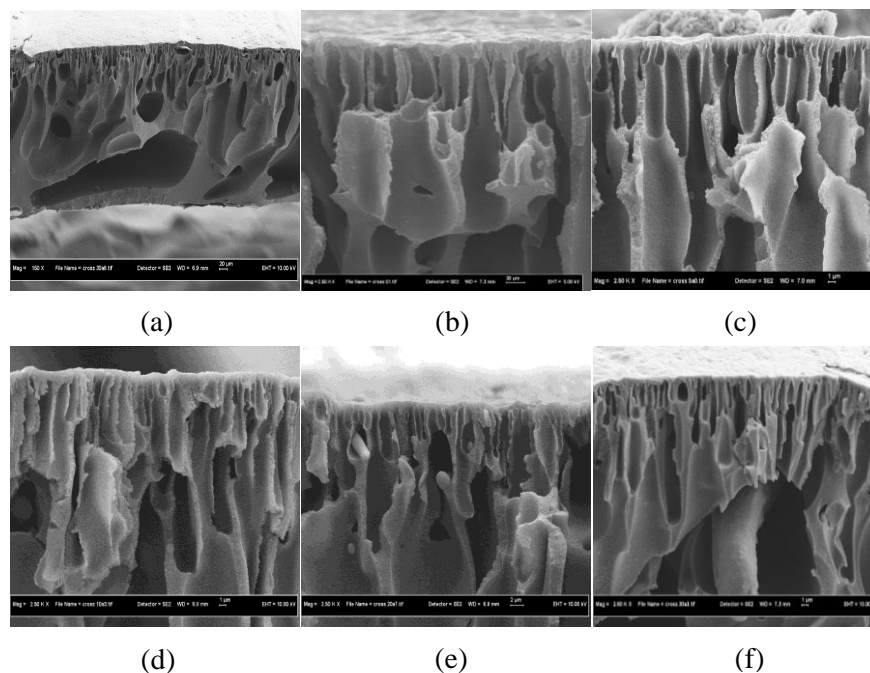


Figure 1. FESEM cross-sectional image of (a) PAN/PVDF (150x) (b) PAN/PVDF0 (2.5Kx) (c) PAN/PVDF5 (2.5Kx) (d) PAN/PVDF10 (2.5Kx) (e) PAN/PVDF20 (2.5Kx) and (f) PAN/PVDF30 (2.5Kx).

The overall cross-sectional image of the asymmetric PAN/PVDF is shown in Figure 1(a). A finger-like structure was observed under the skin layer and a porous macro voids structure was found in the support layer of the membrane. The formation of this structure was due to fast exchange of solvent and non-solvent during the phase inversion process [17,20]. This FESEM image was similar to the blended

PAN/PVDF membranes fabricated by Yang et al [20]. Figures 1 (b) to (f) showed the structure of the membranes after glycerol coating. Although different concentrations of glycerol were coated on the PAN/PVDF membranes, the cross sectional images were similar, where the finger like structures were found under the skin layer. This showed that the coating technique did not affect the intrinsic structure of the membrane, which was formed during the phase inversion process.

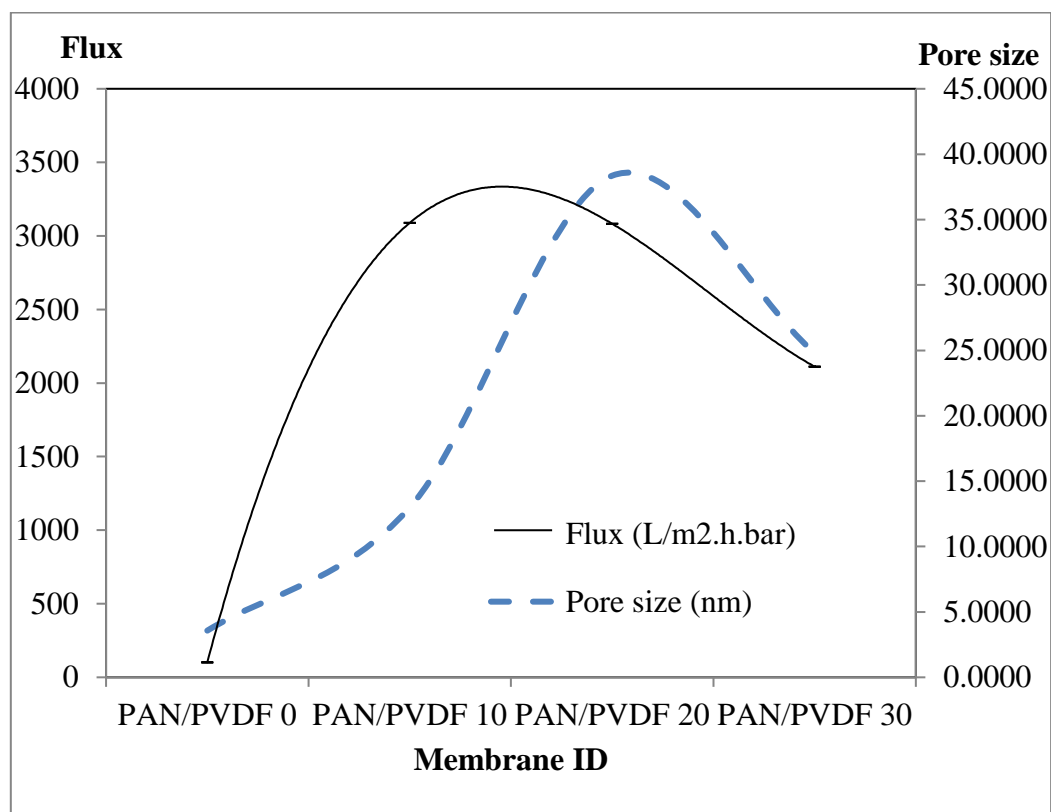
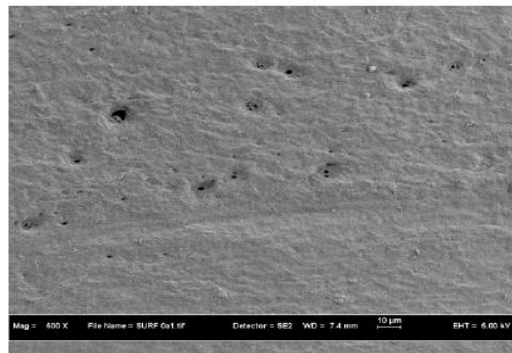


Figure 2. The flux and the pore size data for PAN/PVDF membranes.

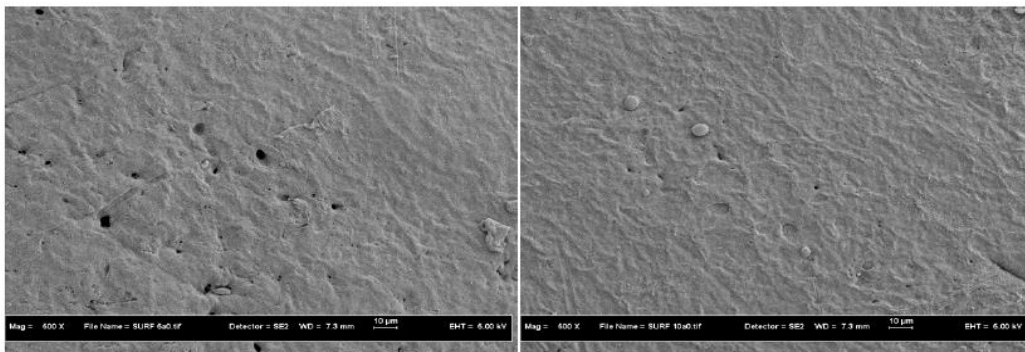
Figure 2 showed that the mean pore size of the membrane was the smallest for PAN/PVDF0 membrane, which was 3.58 nm and the biggest mean pore size was 38.37 nm for PAN/PVDF20 membrane. This was due to the minimum shrinkage in the latter membrane, as shown in Table 1. Without the glycerol coating, the shrinkage of PAN/PVDF0 membrane was ~20%. When the concentration of glycerol increased from 5 vol% to 20 vol%, the effect of shrinkage reduced from ~20% to ~3%. This showed that shrinkage might lead to pore collapse and hence reduced the membrane pore size. Further increase of glycerol beyond this concentration did not improve the shrinkage of the membrane but it blocked the pores on the membrane. This explains the smaller pore size for PAN/PVDF30 membrane compared to PAN/PVDF20 membrane. It is worth to mention that an increase of 0.07 μm membrane thickness was measured from PAN/PVDF0 to PAN/PVDF30 membranes, revealing that glycerol coating does to some extent governs membrane performance in this study. Experimental work conducted by Bilad et al. [21] showed that no pore size larger than 0.05 μm was found for the membrane which experienced severe shrinkage effect. Comparatively, for the modified membrane which possesses a high degree of resistance to shrinkage, maximum pore size with ~0.2 micron was reported.

Table 1. The properties of PAN/PVDF membranes.

Membrane ID	Shrinkages (%)	Contact angle (°)	Porosity (%)
PAN/PVDF0	19.9004 ± 2.5806	80.7042 ± 2.6456	35.0321 ± 3.0301
PAN/PVDF5	19.1525 ± 2.0781	70.8447 ± 2.8890	48.0192 ± 3.4825
PAN/PVDF10	19.4514 ± 2.0276	55.9529 ± 2.8548	53.8582 ± 2.9260
PAN/PVDF20	3.3323 ± 2.7832	59.2653 ± 2.6851	22.0000 ± 2.8284
PAN/PVDF30	3.9683 ± 2.3662	58.7473 ± 2.9418	20.0998 ± 4.9661

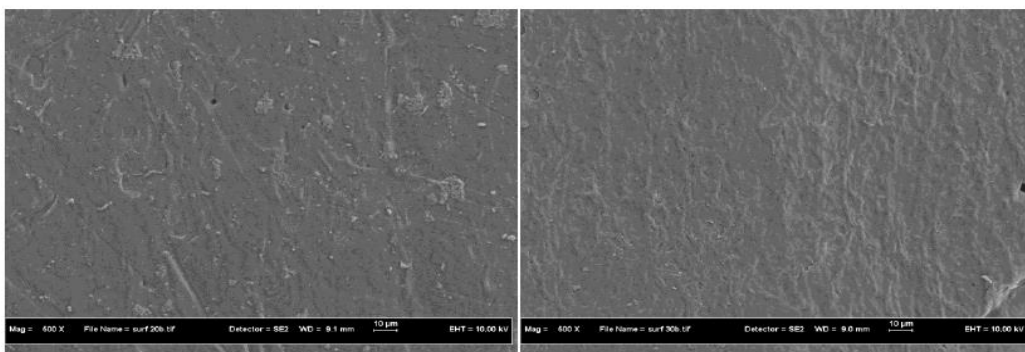


(a)



(b)

(c)



(d)

(e)

Figure 3. FESEM surface images of (a) PAN/PVDF0 (b) PAN/PVDF5 (c) PAN/PVDF10 (d) PAN/PVDF20 (e) and PAN/PVDF30.

Figure 2 also illustrated the influence of glycerol coating on the pure water permeation of the membranes. The lowest flux was observed in PAN/PVDF0 membrane due to its small mean pore size and hydrophobic surface as shown in Table 1. The contact angle of this PAN/PVDF0 membrane was 80.70° , which indicates the nature hydrophobicity of pristine PAN/PVDF membrane. When the concentration of glycerol in the coating solution was increased to 10 vol% and 20 vol%, the membranes pore size and the hydrophilicity were increased. Thus $\sim 3100 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$ of flux was found. Based on the data in Table 1, although PAN/PVDF20 membrane was slightly hydrophobic and less porous compared to PAN/PVDF10, the flux of the membrane was maintained at $\sim 3100 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$. It is due to the pore size of PAN/PVDF20, which is about 25 nm larger compared to PAN/PVDF10 membrane. When 30 vol% was coated on PAN/PVDF membrane surface, the flux of the PAN/PVDF30 membrane reduced to $\sim 2100 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$ due to its smaller pore size compared to PAN/PVDF20 membrane.

During the coating process, glycerol which carries three hydroxyl groups; is attached physically on the surface of the membrane. Thus, the hydrophilicity of the membrane is improved from 80.70° to 55.95° as the amount of glycerol is increased from 0 vol% to 10 vol% in the coating solution, as shown in Table 1. However, beyond this point, the PAN/PVDF20 and PAN/PVDF30 membranes became slightly hydrophobic compared to PAN/PVDF10. Similar trend is observed for the porosity of the membrane, where the PAN/PVDF 10 membrane was more porous compared to PAN/PVDF5 and PAN/PVDF0. Further increase in the concentration of glycerol in the coating solution reduces the porosity from $\sim 54\%$ for PAN/PVDF 10 membrane to $\sim 20\%$ for PAN/PVDF10 and PAN/PVDF20 membranes. Zhao et al. [22,23] reported that contact angle of a membrane is affected by its porosity. Hence, the low porosity in membranes PAN/PVDF20 and PAN/PVDF30 contributed to their high contact angle, compared to PAN/PVDF10 membrane.

FESEM images in Figure 3 shows that the use of glycerol coating improved the surface roughness of the membranes. In Figure 3 (a)-(c), defects due to the shrinkage effect was observed on the surface of the membranes. This is in agreement with the shrinkage data in Table 1, where approximately 20% of shrinkage was measured for these membranes. When the amount of glycerol in the coating solution is increased to 20 vol% and 30 vol%, defects free and smooth surface are seen in Figure 3 (d) and (e). The AFM images in Figure 4 also illustrated the similar finding where the roughness average (Ra) value of PAN/PVDF0 is 35.958 nm and this value is reduced to 23.822 nm for PAN/PVDF30 membrane.

Figure 5 shows the FTIR spectra of PAN/PVDF membranes. The characteristic peaks for the PAN/PVDF0 membrane are observed at 1451.61 cm^{-1} (stretching band of CH_2), 2919.58 cm^{-1} (C-H) and 1249.39 cm^{-1} (CN); which are consistent with the inherent characteristic of PVDF and PAN materials [24]. In addition to these, the peak at 1403.47 cm^{-1} could be attributed to β -phase of PVDF [25,26]. Compared to the control membrane, all the glycerol coated PAN/PVDF membranes showed broad peaks at 3424.43 cm^{-1} (stretching band of OH), 1179.17 cm^{-1} and 1097.64 cm^{-1} (stretching band of C-O) [20]. This is in agreement with the data presented in Table 1, where the hydrophilicity of the membranes increase along with the glycerol coating due to the attachment of $-\text{OH}$ group on the membranes surface.

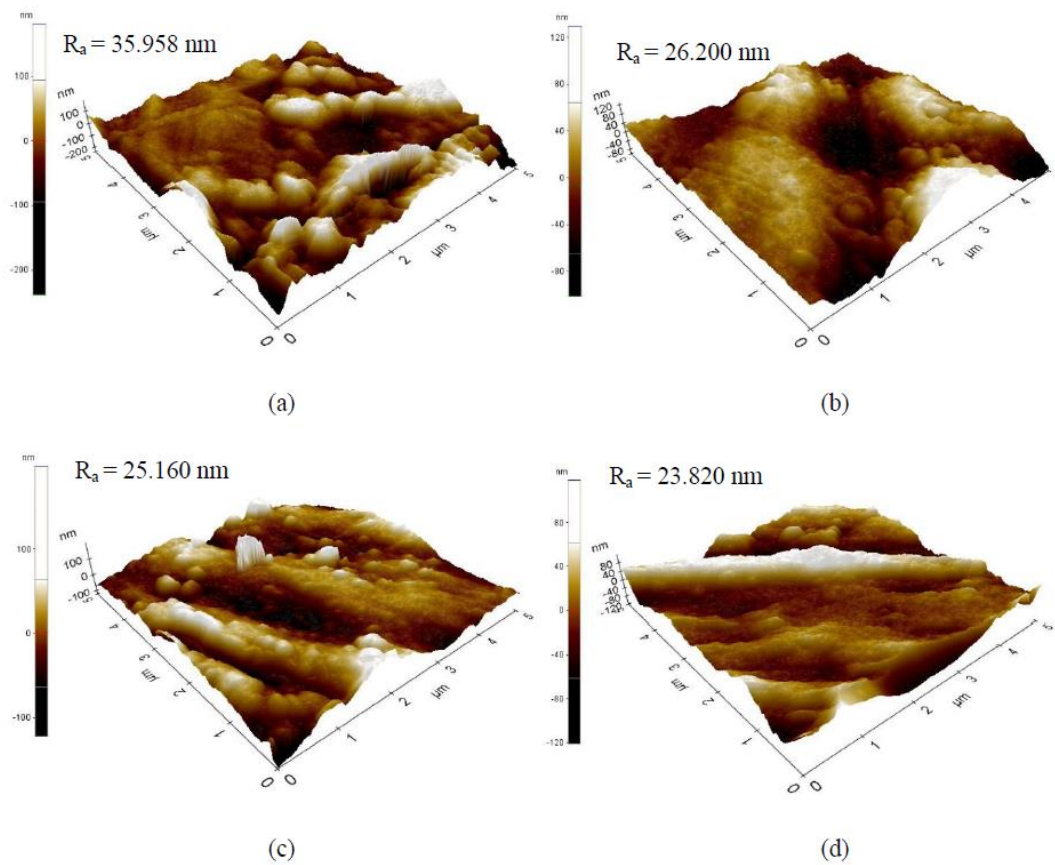


Figure 4. AFM surface images for (a) PAN/PVDF 0 (b) PAN/PVDF 10 (c) PAN/PVDF 20 and (d) PAN/PVDF 30 membranes.

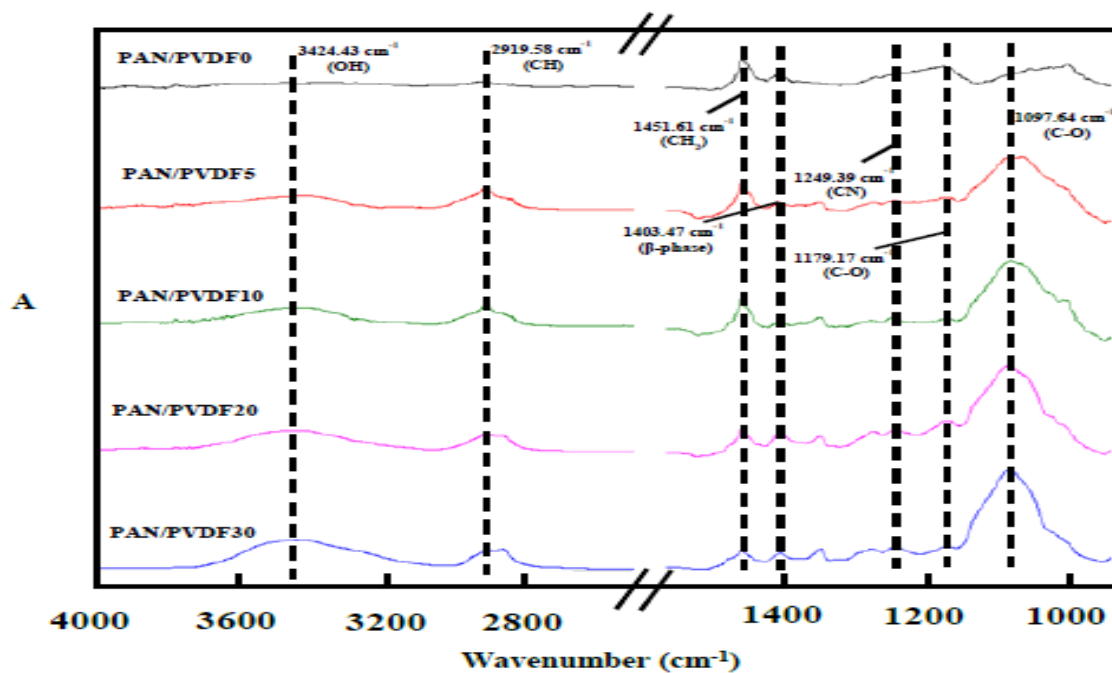


Figure 5. FTIR Spectra of PAN/PVDF membranes.

5. Conclusion

The intrinsic and permeation properties of PAN/PVDF membranes coated with varied vol% of glycerol have been studied. Glycerol was successfully coated on the membranes as new -OH and C-O stretching bands are found in the FTIR spectra. Experimental results revealed that at least 20 vol% of glycerol is required to minimize the shrinkage effect on the membranes. It also minimized the collapse of pores and resulted in the largest membrane surface pore size. The glycerol coating increased the water flux of the membrane as the membrane became more hydrophilic and porous. FESEM and AFM images showed that glycerol coating improved the surface roughness of the membranes. Based on the results obtained from this study, it shows that glycerol can be a very promising coating material to improve the PAN/PVDF membrane flux performance and surface properties, which might extend membrane application in industrial water and wastewater treatment process.

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References

- [1] Ng L Y, Mohammad A W, Leo C P and Hilal N 2013 *Desalination* **308** 15–33
- [2] Ji J, Liu F, Hashim N A, Abed M R M and Li K 2015 *React. Funct. Polymers* **86** 134–153
- [3] Hong G, Xin L, Ziyi W, Bao'an L, Jixiao W and Shichang W 2018 *Chinese Journal Of Chemical Engineering* 1-6
- [4] Nazri N A M, Lau W J, Ismail A F and Veerasamy D 2015 *Desalination Water Treat* **55**, 1771-85
- [5] Jian C, Jian Z, Liling Z, Gregory S. O and Tai S C 2017 *J. Membr. Sci* **539** 295–304
- [6] Jung B 2004 *J. Membr. Sci* **229** 129–136
- [7] Jian K and Pintauro E N 1997 *J. Membr. Sci* **135** 41-53
- [8] Wang D, Li K and Teo W K 2000 *J. Membr. Sci* **178** 13–23
- [9] Yin X, Cheng H, Wang X and Yao Y 1998 *J. Memb. Sci* **146** 179-184
- [10] Liu T Y, Lin W C, Huang L Y, Chen S Y and Yang M C 2005 *Polym. Adv. Technol* **16** 413-9
- [11] Yin J and Deng B 2015 *J. Membr. Sci* **479** 256–75
- [12] Rana D and Matsuura T 2010 *Chem. Rev* **110** 2448-71
- [13] Sun J X, Gui E C and Zhen L X 2018 *Journal of Industrial and Engineering Chemistry* **58** 179–188
- [14] Mojtahedi Y M, Mehrnia M R and Homayoonfal M 2013 *Desalination and Water Treat* **51** 6736-42
- [15] Hess S C, Kohll A X, Raso R A, Schumacher C M, Grass R N and Stark W J 2015 *ACS Appl. Mater. Interfaces* **7** 611-7
- [16] Shim H C, Yeh Y S and Yasuda H 1990 *J. Membr. Sci* **50** 299-317
- [17] Lee J, Park B, Kim J and Park S B 2015 *Macromol. Res* **23** 291-9
- [18] Chan M K, Rao P, Eu Y K and Lim J M Y 2015 *Mater. Manuf. Processes* 1941-7
- [19] Ye L, Fan Z and Zhou J 1981 *Membrane Science and Technology* **2** 24-30
- [20] Yang M C and Liu T Y 2003 *J. Membr. Sci* **226** 119–130
- [21] Bilad M R, Burrieza E G, Mavukkandy M O, Al Marzooqi F A and Arafat H A 2015 *Desalination* **376** 62–72
- [22] Zhao Y H, Zhu B K, Ma X T and Xu Y Y 2007 *J. Membr. Sci* **290** 222
- [23] Chan M K, Ng S C, Noorkhaniza S and Choo C M 2016 *Innovation and Analytics Conference & Exhibition (IACE)* 1-5
- [24] Hashim N A, Liu Y and Li K 2011 *Chem. Eng. Sci* **66** 1565–75
- [25] Socrates G, 2001 Wiley, New York
- [26] Manjula D D, Anand P A and Kim J K 2018 *Vibrational Spectroscopy* **94** 74–82