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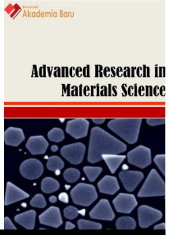

Fabrication and Performance of PSf/CA Blend Ultrafiltration Membrane on Effect of Different Polymer Ratio

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ABSTRACT

The study is focussed on the fabrication of various polysulfone/cellulose acetate (PSf/CA) polymer ratio with high polymer concentration of 20 wt. % via dry/wet phase inversion technique for membrane performances. These membranes were prepared by blending four different polysulfone/cellulose acetate ratios of 100/0, 90/10, 80/20 and 70/30 in a solvent, known as N-methyl-2-pyrrolidone (NMP). The effect of different polymer ratio on membrane characteristic are discussed in term of flux permeation, morphology, mechanical strength, fourier transform infrared spectroscopy (FTIR) analysis and flux recovery ratio (FRR). The increment of cellulose acetate composition resulted in different behaviours of membrane characteristic. The highest CA ratio (70/30) in PSf/CA composition obtained the highest flux permeation. Meanwhile, the flux recovery of 90/10 wt % membrane achieved the highest flux recovery, 59 % compared to 80/20 wt. % and 70/30 wt. % membranes with values of 12 % and 25 %, respectively. Interestingly, membrane with 80/20 wt. % observed an average improvement in flux permeation with a consistent increased. The formation of uniform finger-like voids in the sublayer of this membrane (80/20) encouraged a good mechanical strength for the membrane structure.

Keywords:
Blend membrane, polysulfone, cellulose acetate, polymer ratio

1. Introduction

Membrane technology has become an alternative and well-known separation technique due to fast process operation, energy efficient and no involvement in any phase change or chemical additives. This advance technology is used in various field such as food, chemical, and pharmaceutical industries [30, 31]. The polymeric membrane can be tailor-made in order to obtain the desired pore size distribution. The certain drawbacks of single polymer in the membrane matrix such as hydrophobic characteristic has gained importance and this is improved by fabricating a membrane with multiple components [13, 15]. The addition of blending multiple components not only alters the

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membrane properties but also enhances the flux permeation of the membranes [3, 30]. However, the membrane properties are still influenced by the compatibility of the individual polymers with each other and the mixing technique [30]. The compatibility of the hydrophobic-hydrophilic balance with the membrane properties can be significantly changed if the membrane is fabricated from multicomponent polymer blends [18]. The combination of cellulose acetate (CA) and polysulfone (PSf) is represented the use of polymer blend membrane that consists of hydrophilic and hydrophobic polymers. Hence, an investigation on the performance of PSf membrane with a hydrophilic polymer has been made to enhance the hydrophilicity of the membrane [31].

Polysulfone (PSf) is the most preferred polymer in the fabrication of ultrafiltration membrane. It has excellent mechanical property, a very good chemical and thermal stability as well as high rigidity and creep resistance [2, 6].

However, the hydrophobic characteristic of PSf polymer has led to the limitation in practical application. Therefore, hydrophilic polymer or additional component has become one of the most approachable materials for membrane modification as blending method is also identified as an attractive route to improve antifouling properties of the membrane [17]. The studies have proved the ability of the cellulose acetate polymer to impart high hydrophilicity to a membrane by reducing fouling properties of the membrane [28, 33]. Besides, CA has high biocompatibility, good toughness, high potential flux and relatively low cost [28]. Meanwhile, the limitations of CA which are low oxidation and chemical resistance, poor mechanical strength and not applicable in aggressive cleaning can be altered by blending with PSf polymer which facilitates the development of new material with the combination of polymers properties.

Hence, a study on membrane fabrication of polysulfone and cellulose acetate at high polymer concentration (20 wt. %) and the performance of fabricated membranes are reported. The effect of polymer ratios in the polymer matrix on flux permeation, morphology, mechanical strength and flux recovery are discussed and compared with the pure PSf membrane.

2. Experimental

2.1 Materials and Methods

Polysulfone (PSf, Ultrason E2010) was supplied by BASF (Ludwigshafen, Germany) in pellet form and used after drying at 60 ^{0}C for 24 hrs. Cellulose acetate (CA, M_w= 100,000 Da) in form of powder was purchased from Acros Organics. N-methyl-2-pyrrolidone (NMP) was obtained from Merck (Germany) and used as a solvent. Distilled water was provided as a non-solvent while ethanol and n-hexane from Merck (Germany) was used as the additional washing step after casting. Bovine serum albumin (BSA, Mw= ~66,000 Da) was received from Sigma Aldrich and used as a module solution for the flux recovery test. Disodium hydrogen phosphate dehydrates ($Na_2HPO_4.2H_2O$) and sodium dihydrogen phosphate monohydrates ($NaHPO_4.2H_2O$) were purchased from Merck (Darmstadt, Germany). Nitrogen gas was supplied by Stable Arm Sdn. Bhd. while other chemicals were commercially analytical grade and used without purification.

2.2 Blend Membrane Preparation

The casting solution of 20 wt. % was prepared by blending different polymer ratios of polysulfone (PSf) and cellulose acetate (CA) in a solvent, known as N-methyl-2-pyrrolidone (NMP) (Table 1) under continuous stirring at 60 ^{0}C for 8 hrs. After the heating process of casting solution was completed, it was kept at rest until no air bubble presence. The casting solutions were then cast on a glass plate with the help of a casting knife by non-solvent induced phase separation (NIPS) technique [5]. The thickness of the spread casting solution was maintained to 200 µm (0.20 ± 0.05 mm) and immediately immersed into coagulation bath (water) at room temperature. The solidified membrane was kept in water for 24 hrs to remove the residual of solvent. Then, this was continued with the additional washing steps with ethanol and n-hexane. In ethanol, this membrane was immersed for another 24 hrs while in n-hexane for a continuous 2 hrs of the washing steps. The membranes were dried for 1 to 3 days at room temperature before undergoing the testing processes.

Table 1
Formulation of blend polymer ratio membrane

Membrane	Polymer (20 wt. %)		Solvent (wt. %)
	PSf	CA	NMP
PSf	100	0	80
PSf/CA-10	90	10	80
PSf/CA-20	80	20	80
PSf/CA-30	70	30	80

2.3 Characterization

The permeation studies were carried out using a dead-end stirred cell filtration system (Amicon stirred cell, 200 ml). The permeation studies involve compaction test and pure water permeation test. The compaction test of the blend membranes with an effective area of 28.7 cm^2 was initially pressurized with distilled water at 150 kPa for 2 hrs. The water flux was evaluated every 30 mins and continued with pure water permeation test at different transmembrane pressure within 100 to 300 kPa (Hamzah et al., 2014). The flux is calculated using equation (1) [18, 31].

$$J_{w1} = \frac{Q}{A \times t} \tag{1}$$

where, Q is the permeate volume (L); A is the membrane area (m^2); and t is the time (h).

The morphology analysis of the blend PSf/CA membranes were captured using Scanning Electron Microscopy of NOVA NANOSEM 230 with User-Friendly Windows xT Software. The membrane were cut and fractured in liquid nitrogen. The fractured membranes were then sputter-coated with gold for 1 to 2 min(s). The cross-section images of the blend membranes were obtained at different magnifications.

The functional groups and chemical structures of the blend membranes were identified using Fourier Transform Infrared Spectroscopy (FTIR) of Varian 3100 FTIR Excalibur Series. The dried membranes were cut into size of 1 cm x 4 cm. These membranes were held in the sample holder and the results were analysed in the transmittance mode. Each bands represent the functional groups of the components presence in the membrane. Different functional groups are represented at different range of infrared radiation wavelength.

The mechanical strength of these blend membranes were measured using TA-XT plus Texture Analyser by Texture Exponent Software Version 2.0.7.0 (Stable Microsystems, Godalming, UK) with stretching rate of 5 mm/min at room temperature. The samples were cut to the size of 63.5 mm x 12.7 mm according to the ASTM D256 standard.

2.4 Fouling Study

Fouling resistance was studied using stirred cell filtration system. The experiment was carried out with BSA solution to measure the flux recovery ratio (FRR) of the membranes. The BSA solution was prepared at concentration of 0.1 wt. % in phosphate buffer (0.5 M, pH 7.1). The water flux before (J_{w1}) and after (J_{w2}) filtration of BSA solution were calculated at 150 kPa for 30 mins of 5 mins interval. Meanwhile, the intermediate flux of BSA permeate was performed at the same pressure for 1 hr. The backwashing process with distilled water was performed at 200 kPa for 20 mins before continuing with the measurement of water flux of cleaned membrane. The FRR results were calculated to identify the fouling resistance of the membrane using equation (2) [5, 8].

$$\text{FRR }(\%)=\left(\frac{Jw2}{Jw1}\right)\times 100\% \tag{2}$$

where, J_{w1} is the water flux of neat membrane (Eq.1) and J_{w2} is the water flux of cleaned membrane.

3. Results and Discussion

The results of the blend membranes analysis were explained and discussed. The main focus of this paper is to present the effect of the cellulose acetate composition ratios in the base PSf polymer matrix toward the fouling resistance and the performance behaviour.

3.1 Effect of Compaction Time

The blend membranes of several compositions ratios were compacted with distilled water at 150 kPa for 2 hrs. The water flux of the blend membranes from PSf/CA composition of 100/0 to 70/30 wt. % at different compaction times is presented in Figure 1.

Figure 1 proved that the water flux of blend membranes decrease with increasing compaction time for all polymer ratios. The final 60 mins of compaction times shows an insignificant changes in water flux for PSf, PSf/CA-10 and PSf/CA-20 membranes. This indicates that the blend membranes have approached a complete compaction in the last 60 mins. The decline water flux at the early stages of compaction can be assigned to the reduction in the porosity volume as the arrangement of polymer segments and chains become closer during the compaction process [30]. However, membrane with polymer ratio of 70/30 wt. % has obtained a sharp reduction after 90 mins of compaction times which is from 89.9 $Lm^{-2}h^{-1}$ to 69.0 $Lm^{-2}h^{-1}$. This is suggested due to the high hydrophilic CA composition that requires extra compaction times for the rearrangement of polymer chains to reduce the porosity volume. High ratio of CA had caused the formation of larger size of pores in the membrane sublayers due to less miscibility of PSf and CA nature. Thus, a high water flux is observed for membrane with 70/30 wt. % composition. Similar relation has reported in a study on the addition of polysulfone in base cellulose acetate polymer blend membrane [29].

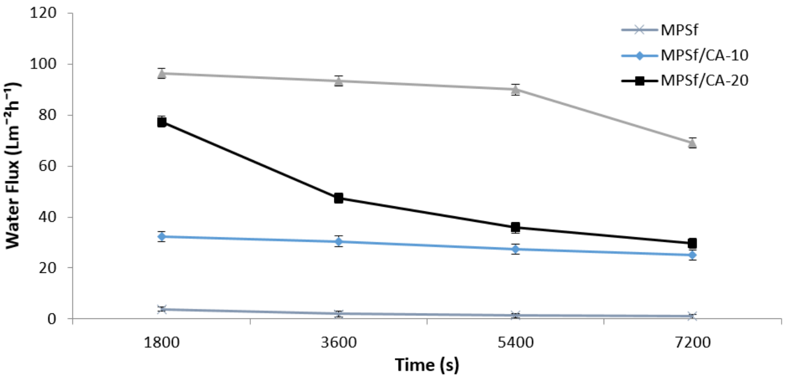

Fig.1. Effect of compaction on water flux of polymer ratios blend membranes

Furthermore, an increase in CA in the casting solution of blend membranes from 10 to 30 wt. % of total polymer has increased the water flux from 3.9 $Lm^{-2}h^{-1}$ to 96.2 $Lm^{-2}h^{-1}$. The relatively higher water flux of the blend membrane with higher CA ratios may occur from a small change of amorphous nature. The higher free energy of the blends had caused a low interaction between PSf and CA chains (partial compatibility) which led to a larger segmental gaps between both polymers [30]. Likewise, the increase in CA ratios has increased the glass transition temperature, T_g of the blends as PSf has lower T_g than CA which caused the alteration of polymer matrix properties from hard to soft segments [16]. Hence, a higher water flux has been observed for blend membranes with higher CA ratios.

3.2 Effect on Pure Water Permeation

The water flux of compacted membranes was measured by the time required for a selected volume of water permeation. Therefore, the effect of cellulose acetate ratios in the casting solution of PSf/CA composition on the pure water permeation (PWP) of the blend membranes are represented in Figure 2.

The blend membrane with 100/0 ratio of PSf/CA composition obtained the lowest flux within the transmembrane pressure (TMP) of 100 to 300 kPa. Further, the water flux of this PSf membrane increases from 6.4 $Lm^{-2}h^{-1}$ to 47.0 $Lm^{-2}h^{-1}$ with increasing TMP. From Figure 2, the increment of CA ratios in the PSf base matrix starts to significantly increase at 150 kPa and above. The addition of CA ratios from 10 to 30 wt. % of total polymer have increased from 47.0 $Lm^{-2}h^{-1}$ to 406.8 $Lm^{-2}h^{-1}$ at 300 kPa of the highest TMP. The influence of CA composition in the casting solution has two main changes on the properties of the blend membrane: (a) improves hydrophilicity and (b) modifies membrane behaviour/morphology. This is acknowledged by the study on the effect of polyethersulfone (PES) in cellulose acetate phthalate blend membrane (CAP) [24]. Moreover, the addition of CA improved the hydrophilicity of the membrane and also induced the formation of macrophase in the membrane sublayer which leads to increase the size of membrane pores. The low molecular attractive forces between CA and PSf composition has caused low miscibility between both components which also relates to the formation of larger pore size [30]. The low viscosity of the membrane solution speeds up the diffusional exchange rate of the solvent and the non-solvent [25]. Hence, this enhances the flux of the blend membranes with the addition of higher ratios of cellulose acetate.

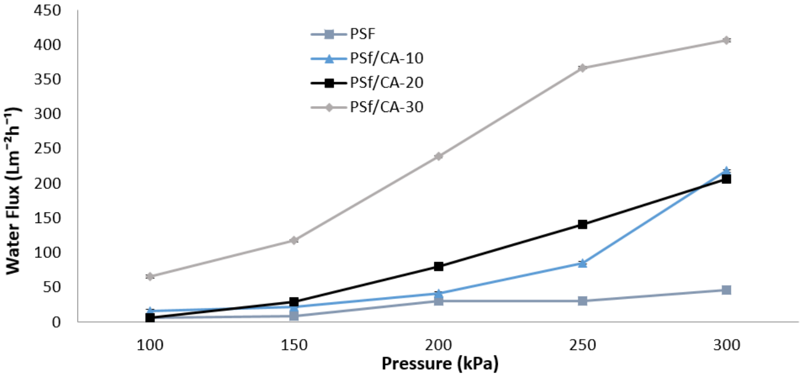

Fig.2. Effect of the polymer ratios on pure water permeation

However, the membrane with 90/10 ratio of 20 wt. % has slightly increased the flux to 218.2 $Lm^{-2}h^{-1}$ compared to 80/20 ratio with value of 206.2 $Lm^{-2}h^{-1}$ at 300 kPa. This happened due to the unstable polymer molecules reaction toward high pressure which reduced compatibility of two different polymers in the casting solution. The less compatible polymers matrix in the casting solution at high pressure would lead to high affinity of blends separation and increased the size of voids in rich polymer regions [25]. Interestingly, the high concentration (20 wt.%) of polymer matrix of PSf/CA polymer ratio obtained a better flux permeation than the previous study of PSf/CA membrane with 85/15 of 15 wt.% with value of 9.8 $Lm^{-2}h^{-1}$ at 345 kPa [31].. Besides, the reverse composition of CA/PSf at 80/20 ratio of 17.5 wt. % also obtained a lower flux with value of ~39.0 $Lm^{-2}h^{-1}$at 300 kPa [30]. This study explored the possibility of increasing PSf polymer had also increased the hydrophobicity of the membrane and resulted in lower flux permeation. Thus, this concludes that CA polymer has the ability to enhance the hydrophilicity of the blend membranes at high polymer concentration depending on the use of molecular weight of supplied CA polymer.

3.3 Effect on Membrane Morphology

The cross-section images were captured by scanning electron microscopy (SEM) on PSf/CA polymer ratios membranes of 100/0, 90/10, 80/20 and 70/30 wt. %. The qualitative results are illustrated in Figure 3 which describes the morphology of each blend membranes on the effect of CA ratios composition. The blend membranes show an asymmetric structure with selective and supporting layers [9].

The neat PSf membrane (Figure 3 (A)) exhibits a dense skin layer with a small area of sponge-like structure. The image shows micropores finger-like structures in the top layer while a few and large size of finger-like structures in the bottom layer. The neat PSf seems to have less porosity volume compared to other blend membranes with CA compositions. The hydrophobic characteristic of this polymer leads to the less porosity volume of the PSf membrane. This occurred when high polymer concentration increased the viscosity of the casting solution which inhibited the diffusional exchange rate of NMP (solvent) and water (non-solvent) in sublayer [9]. Thus, it reduced the rate of precipitate exchange and decreased membrane porosity.

The addition of CA ratios in casting solution (Figure 3 (B), (C), and (D)) have obviously altered the morphology of blend membranes. The images displayed macrovoid and porous finger-like structures. Both of PSf/CA-10 (Figure 3 (B)) and PSf/CA-30 (Figure 3 (D)) membranes show a quite similar morphological structure with a combination of finger-like voids and macrovoid for the top and bottom layers of the membranes. However, PSf/CA-10 membrane has a denser skin layer compared to PSf/CA-30 membrane due to the composition of CA polymer. The lower ratio of CA exhibits lower flux permeation. This could be related to the interaction of the polymer matrix and the solvent as well as the kinetic of phase inversion which influenced the morphology of the blend membranes [1]. This phenomenon was due to an instantaneous demixing during the immersion process of the top surface of the skin layer with the water (non-solvent) and after a while, a delayed demixing occurred due to low exchange rate between solvent and non-solvent [34]. Thus, the finger-like voids were formed in the top layer while the delayed demixing had caused the formation of small macrovoid with sponge-like structures in the bottom layer. A previous study reported that the formation of macrovoid might occur when the viscosity of the casting solution was high and it led to a sudden collapsed of finger-like structures formation [1]. This is suggested that the morphology of membrane with PSf/CA ratios of 90/10 and 70/30 have exposed to high composition of PSf and CA polymers which caused inconsistency in flux permeation.

Interestingly, the morphology of membrane with 80/20 wt. % was significantly different. The morphology of this membrane was observed to form a uniform finger-like structures with fine tune arrangement. The voids of top and bottom layer are connected to each other. The uniform finger-like voids have seemed to assist the gradual trends of the water flux permeation in the previous sections. Hence, the appropriate selection of 80/20 of PSf/CA ratio has facilitated a good interaction between polymer matrixes during demixing process that formed a well-formed morphology of PSf/CA-20 blend membrane.

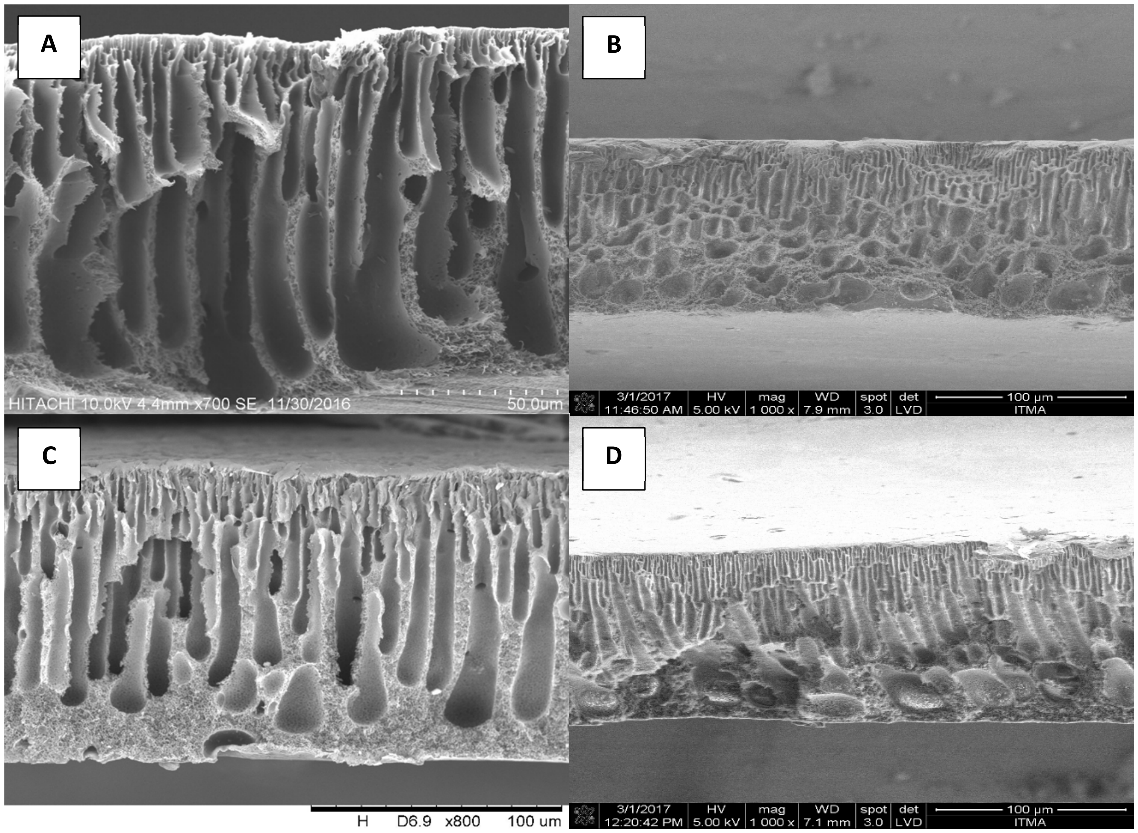

Fig. 3. SEM images of blend membranes. Cross-section (700 to 1000x); (A) 100/0; (B) 90/20; (C) 80/20; (D) 70/30 of PSf/CA polymer ratios

3.4 Effect on FTIR Analysis

Fourier transform infrared (FTIR) was used to analyse specific functional groups and chemical bonds that presence in casting solutions [12, 18]. The FTIR spectrum of neat PSf, CA and PSf/CA are presented in Figure 4 (a) to (c). The existence of PSf in the PSf/CA composition was assigned by the two small transmittance bands at wavenumbers 1294.92 cm^{-1} and 1323.42 cm^{-1}. These bands represent the asymmetric and symmetric stretching mode of sulfonate group. The asymmetric band has slightly stretched to 1294.95 cm^{-1} while symmetric band has slightly bent to 1323.37 cm^{-1} as observes in Figure 4 (c). This changes was claimed due to the existence of multicomponent in casting solution that encouraged the interaction with sulfonate chain. The previous studies had reported the same reason for the modification of PSf membrane [18, 19]. Furthermore, the presence of PSf polymer can be determined by the wavenumbers of aliphatic stretching CH_3 and a strong aromatic ether between 3000 to 2800 cm^{-1} and ~1240 cm^{-1}, respectively [14]. Besides, the CO bond of PSf chain bands (~1106 cm^{-1}) do not significantly change after adding CA composition in the polymer matrix. Meanwhile, the intensity of the strong aromatic ether is slightly bent when adding CA composition ratio in the casting solution. This is suggested that the interaction of OH bonds (3452.84 to 3366.94

cm^{-1}) in CA chain with the strong aromatic ether in PSf chain has influenced the intensity of the bands form. The phenomenon is proved by the wavenumber of OH bond in pure CA membrane has bent to 3366.94 cm^{-1} after blending PSf and CA together which shows the remaining of OH bonds have decreased in the polymer matrix.

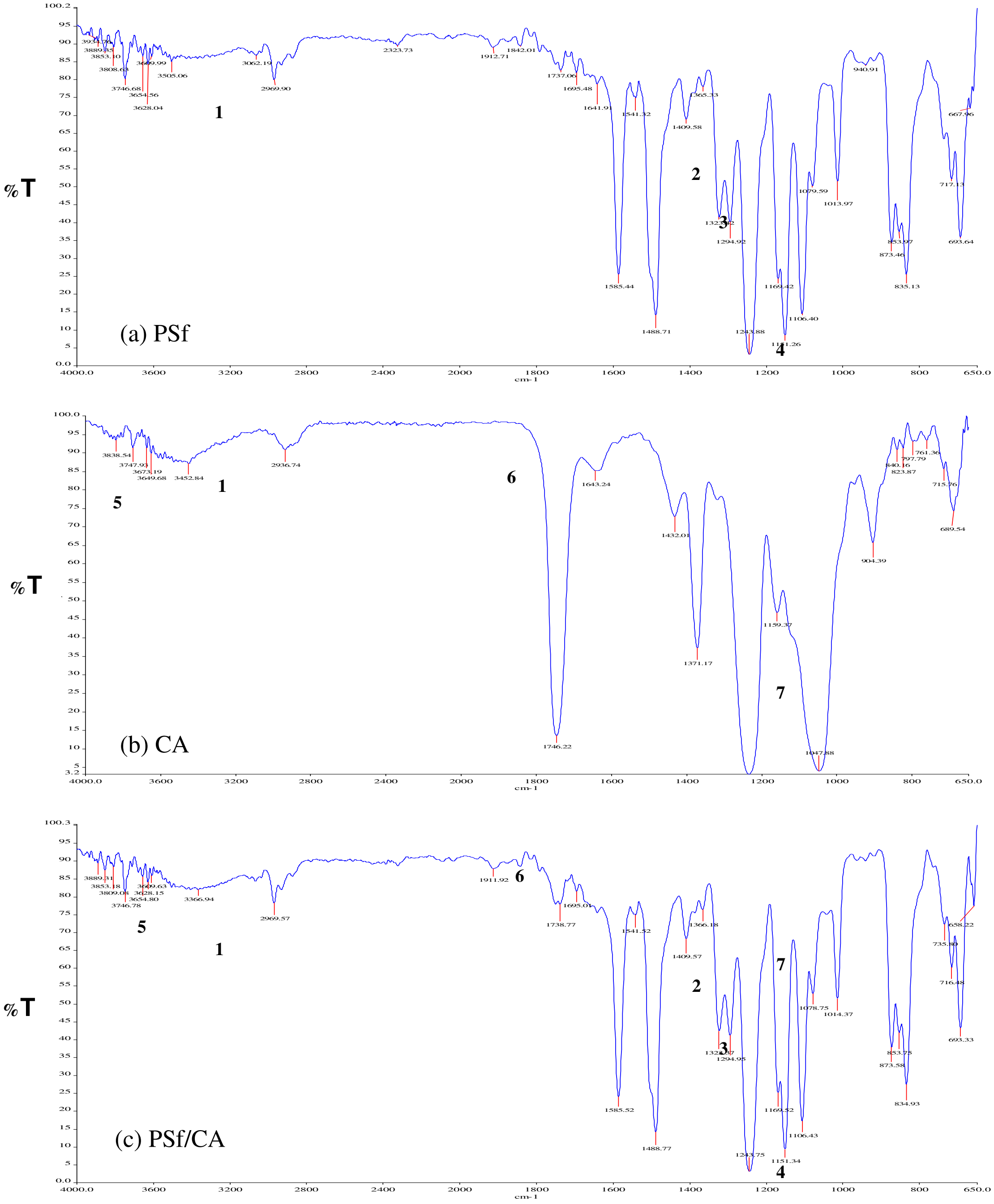

Fig. 4. (a) to (c) represent the FTIR spectra of membrane with absence and presence of PSf and CA polymers. (1) aliphatic CH_3 in PSf and CH_2 group in CA; (2) Sulfonate group in PSf; (3) aromatic ether in PSf; (4) CO bond in PSf; (5) OH bond in CA; (6) carbonyl groups (C=O) in CA; (7) ether chain (C-O-C) in CA

In addition, the presence of CA polymer has been identified by wavenumbers of a small band at approximately between 2700 to 2900 cm^{-1} for CH_2 group and OH bonds around 3500 cm^{-1} (explained in above paragraph) [18, 23]. However, the interaction between aliphatic CH_3 of PSf and CH_2 group of CA has shifted the band to 2969.57 cm^{-1} after blending the PSf/CA composition. The significant bands of pure CA membrane at 1065 to 1041 cm^{-1} and ~1746 cm^{-1} are assigned for C-O-C ether chain and carbonyl group (C=O) [12, 18]. The unstable double bound of carbonyl group has encourage PSf chain to bind with CA chain which shifts the C=O band to 1738.77 cm^{-1}. The attraction between the molecules inside casting solution had suggested to cause surface segregation which is due to the amphiphilic nature of membrane materials. The affinity of multicomponent materials toward the non-solvent (water) has facilitated the arrangement of hydrophilic segment of membrane materials chain on the membrane surface while the hydrophobic segment of them are intensely embedded in membrane matrix [25]. Hence, the amphiphilic PSf/CA membranes produce a higher water flux permeation compared to the neat hydrophobic PSf membrane.

3.5 Effect on Mechanical Properties

The addition of CA in the casting solutions has observed a slight reduction of the mechanical strength of the blend membranes compared to the neat PSf membrane. The lower mechanical strength of CA than PSf polymer has changed the mechanical properties of the blend membrane [25]. This reduction was due to the entrapment of CA in the polymer matrix which facilitated the formation of voids in the sublayer of blend membrane.

Figure 5 shows the tensile strength of blend membranes, specifically, neat PSf, PSf/CA-10, PSf/CA-20 and PSf/CA-30 which is slightly decreased from 5.1 MPa to 4.7 MPa, 4.7 MPa and 4.9 MPa, respectively. Interestingly, the trend shows that a higher CA ratio obtains a higher tensile strength. The results can relate with the morphology of blend membranes. The numerous finger-like voids in the top layer and small macrovoid in the bottom layer prompted different strength to the membrane structure of PSf/CA-30. The separated voids might help in improving the tensile strength due to the fine arrangement of finger-like voids in the top layer. However, the addition of CA in the casting solution still reduced the tensile strength of blend membranes due to the low mechanical stability of CA polymer which influenced the thickness of the blend membrane [11]. Thus, the blend membranes with CA ratios have lower tensile strength than the neat PSf membrane.

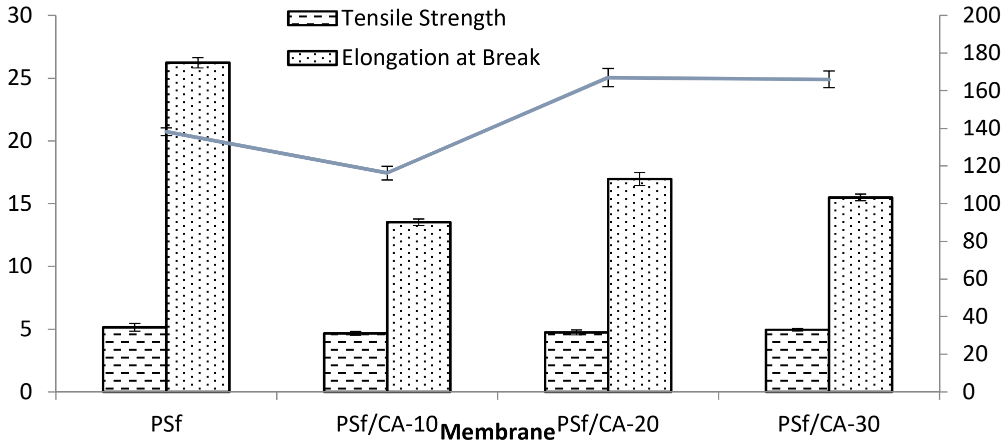

Fig. 5. Mechanical strength of the different polymer ratios membranes; tensile strength, Young’s modulus and elongation at break

A quite similar trend is observed for Young's modulus which shows a fluctuate trend due to the results of elongation at break of blend membranes. The addition of different ratios of CA polymer have reduced the elasticity of the blend membranes as shown in Figure 5. The elasticity of these membranes represent by the elongation at break that decrease from 26.2 % (100/0) to 13.5 % (90/10), 17.0 % (80/20) and 15.5 % (70/30) with increasing CA ratios. However, the addition of CA composition more than 10 % obtains higher elasticity. This explained that the formation of connected finger-like voids from top to bottom layers of PSf/CA-20 membrane has enhanced the elasticity of the membrane structure. Thus, it obtains the highest elasticity compared to 90/10 and 70/30 of CA composition ratios that have macrovoid in the sublayer. However, the highest mechanical strength for the neat PSf membrane is claimed due to the original characteristic of the PSf polymer which has high strength, rigidity, creep resistance and dimensional stability. This advantages come from the replicating phenelyne rings that presence in the PSf chain [21]. Therefore, the morphology of membrane structure has significantly played an important role for the improvement of mechanical strength of the blend membrane. This concludes that the ratio of 80/20 wt. % has a better mechanical strength compared to other blend membranes as it tends to have a greater stretching rate.

3.6 Effect on Fouling Resistance

Fouling study was investigated for further analysis on the different polymer ratios of blend membranes with bovine serum albumin (BSA). The fouling study focuses on the flux recovery ratio (FRR) which represents the surface modification of the blend membranes. In general, the higher the FRR values, the higher the hydrophilicity and antifouling properties of the blend membranes [36]. FRR values of the blend membranes is presented in Figure 6 (b). The intermediate process between BSA solution filtration and final flux permeation was carried out by backwashing process in order to evaluate a flux of cleaned blend membrane. Thus, the efficiency of the backwashing process can be determined by FRR % parameter for clarification of antifouling property of the blend membranes [22].

The initial flux shows an increasing trend with the addition of higher CA composition ratios while the final flux obtains a different behaviour as seen in Figure 6 (a). The final flux is observed to have higher flux for the blend membranes with higher CA ratios. This behaviour was claimed due to the unstable casting solution which altered the membrane morphology after experienced the backwashing process. The high pressure during backwashing process had disturbed the pore structures. The weak interaction between two polymers in the membrane matrix encouraged the formation of macrovoid [7, 35] in PSf/CA-10 and PSf/CA-30 which was suggested to occur due to the accumulation of CA molecules in the bottom layer of the blend membranes. Moreover, the presence of second polymer changed the condition of casting solution closed to liquid-liquid demixing boundary which reduced the degree of solubility between polymer matrix and solvent [4, 26]. Therefore, these show a possibility of the flux permeation to be affected after BSA permeation and backwashing process.

Furthermore, PSf/CA-30 has no permeates volume for flux calculation. This membrane is observed to be easily fouled. This can be explained by physicochemical properties of the membrane and the feed solution (BSA). The severe fouling might occur when pH of the protein solution was equal to the iso-electric point of the protein and reduced the flux permeation [27]. However, a higher and lower pH of the protein solution than the iso-electric point enhanced the flux permeation [10]. This clarified that the possibility of BSA solution to obtain an equal value with it iso-electric is high. Besides, the previous study had argued on the hydrophobic behaviour of the protein at the iso-electric point which led to high adsorption on the membrane due to the hydrophobic interaction [20, 27]. Therefore, it is clearly assumed that the physicochemical properties between membrane and BSA solution has disturbed the pH and experienced high adsorption in the voids layer of PSf/CA-30 blend membrane.

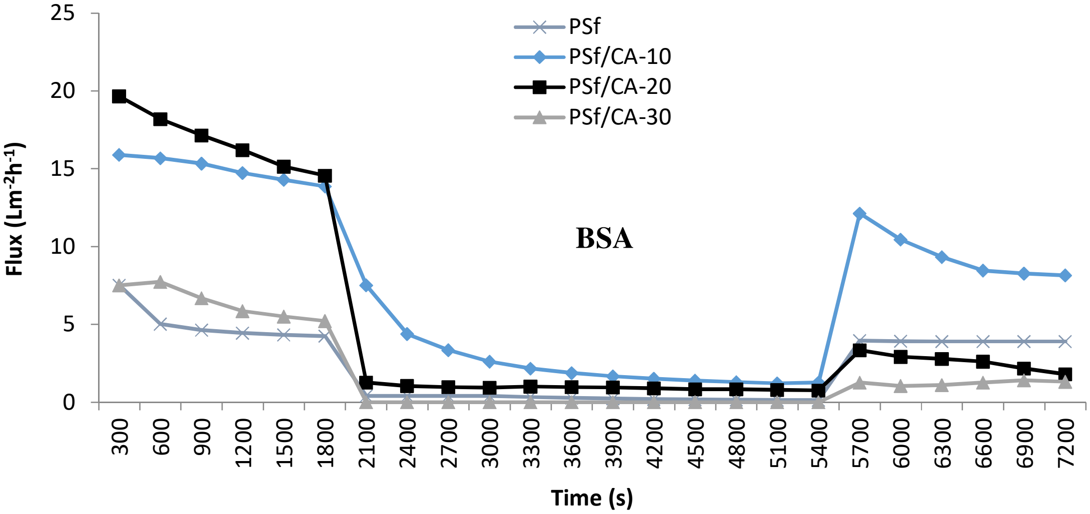

Fig. 6(a). Time-dependent flux for blend membrane composition with different polymer ratios. The ultrafiltration process includes permeation of initial water permeation, BSA solution permeation and final water permeation after backwashing process

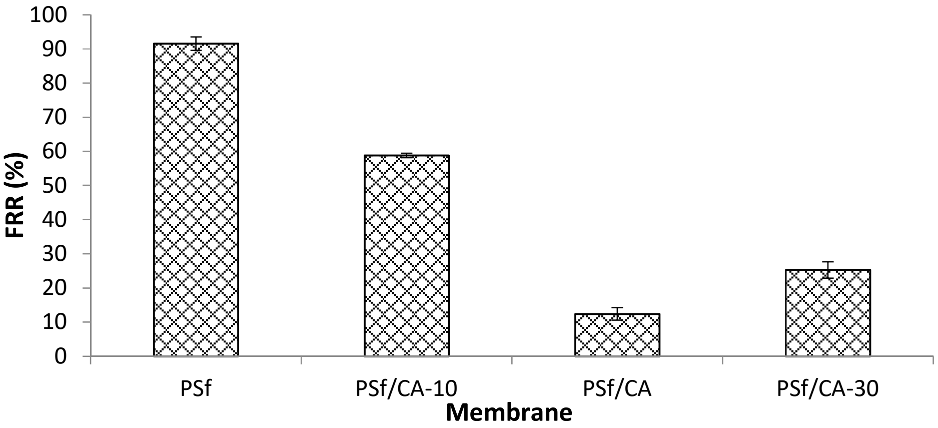

Fig. 6(b). Percentage of flux recovery ratio (FRR) of blend membranes with different polymer ratios after BSA solution permeation

From Figure 6 (b), PSf/CA-10 obtains the highest FRR value (59 %) among the blend membranes with CA ratios. The high pressure during backwashing process has assisted the flux recovery of final flux that observes to achieve merely close to the initial flux. The unstable pore structures of this membrane causes a low separation of BSA molecules as it reaches a higher permeate flux at the first 20 mins of BSA permeation. Thus, it is said that PSf/CA-10 membrane has exposed to reversible fouling which can be removed by physical cleaning [25]. However, PSf/CA-20 with 20 % of CA ratio has the lowest FRR value of 12 %. This significant reduction was due to the fine arrangement and connected sublayer of finger-like voids which caused a direct blockage of BSA molecules. This pores blockage might need several hours to be completely removed by physical cleaning due to the excessive of BSA molecules inside each finger-like voids which had resulted in a lower final flux permeation compared to the highest initial flux. Moreover, PSf/CA-30 has achieved approximately half of the FRR value of PSf/CA-10 membrane which is 25 %. The increase of CA ratio up to 30 % has increases the hydrophilicity of blend membrane. The increment of hydrophilic characteristic causes a larger size of pores. However, increase in pore size has increased the effect of fouling [25]. The increment in pore size was declared to induce an accumulation of BSA molecules in certain pores especially in macrovoid structures. Besides, the explanation on the severe absorption of solute molecules in previous paragraph had also proved the reason of flux reduction. Hence, a higher FRR % was obtained by PSf/CA-30 compared to PSf/CA-20. This concludes that the morphology of different types of voids in membrane sublayer facilitates the flux recovery of the blend membranes as observes in SEM images of PSf/CA-10 and PSf/CA-30 membranes.

4. Conclusion

The neat PSf membrane and PSf/CA composition membranes were prepared by phase inversion method. Several techniques were carried out for the characterization performances. The results have proved the addition of CA compositions in the polymer matrix influence the properties of blend membranes. The addition of CA composition has improved the hydrophilic characteristic of the blend membranes. In term of water flux permeation, the highest CA ratio (70/30 wt. %) obtained the highest PWP. Meanwhile, the membrane with 80/20 wt. % resulted in lower flux but with a consistent increased than other blend membranes. Further, the morphology analysis of these blend membranes has found that the ratio of 80/20 wt. % membrane forms a uniform arrangement of finger-like voids in the sublayer. This structure is more favourable compared to the membranes with 90/10 wt. % and 70/30 wt. % of PSf/CA composition. The connected finger-like voids of the top and bottom layer facilitates the consistency of flux permeation than the formation of finger-like voids and macrovoid of the separated layers (90/10 and 70/30 wt. %). Besides, the membrane with 80/20 wt. % has also approached a good mechanical strength compared to 90/10 wt. % and 70/30 wt. % which represented by Young’s modulus. In term of FRR results, the most recovered flux was obtained by the membrane with 90/10 wt. % with the value of 59 % while membrane with 80/20 wt. % only achieved up to 12 % which was the lowest. Overall, PSf/CA-20 (80/20 wt. %) is highly considered as an appropriate membrane in term of permeation and durable properties compared to other blend membranes as this membrane has shown a high tendency of a good multicomponent interaction inside the polymer matrix.

However, the addition of CA in casting solution has slightly reduced the flux recovery especially for the membrane with 80/20 wt. %. This problem has been considered as a disadvantage for this type of blend membrane. The blend membrane with 80/20 wt. % may improve the FRR % if it incorporates with various additives compositions.

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