Jurnal Teknologi

Full paper

Influence of Hydrophilic Polymer on Proteins Separation, Molecular Weight Cut-off (MWCO) and Average Pore Size of Polysulfone Blend Membrane

Asmadi Ali[a*], Rosli Mohd Yunus[b], Mohamad Awang[a], Mohd Azizi Che Yunus[c,d]

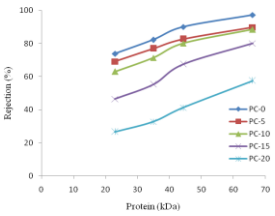
[a]*School of Ocean Engineering Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia*
[b]*Faculty of Chemical and Natural Resources, Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia*
[c]*Centre of Lipid Engineering and Applied Research (CLEAR), Ibnu Sina Insititute for Industrial and Scientific Research, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia*
[d]*Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor Malaysia*

*Corresponding author: asmadi@umt.edu.my

Article history

Received : 2 March 2015
Received in revised form : 24 April 2015
Accepted : 10 May 2015

Graphical abstract



Abstract

The aim of this study is to investigate the influence of different composition of cellulose acetate phtalate (CAP) on the membrane structural properties of polysulfone (PSf) membrane which in turn affect the separation performance of PSf/CAP blend membrane. The PSf/CAP blend membranes were prepared by using casting solutions contain 17 wt% of polymer via wet phase inversion process. The results showed that increasing the composition of CAP in PSf/CAP blend membranes increased molecular weight cut-off (MWCO), average pore size and pore density which then increased protein solution permeate fluxes but reduced proteins rejection of PSf/CAP blend membranes. Pure PSf membrane has the lowest membrane structural properties compared to blend membranes. This characteristic contributed to decrease in protein permeation flux and increase proteins rejection.

Keywords: CAP; blend membrane; proteins; MWCO; average pore size; pore density

1.0 INTRODUCTION

Nowadays fundamental research on membrane performance has been recognized as one of the most important elements in membrane fabrication process. The selection of polymer material as a polymer back-bone to prepare an ultrafiltration (UF) membrane via phase inversion process is very crucial due to the physical, chemical and mechanical properties of this membrane is strongly related to the selected polymer and this in turn affects the separation performance of the respective UF membrane.

Polysulfone (PSf) is one of the most popular polymer back-bone was used to fabricate and produce the commercial UF membrane. This membrane has been employed in various application of UF processes due to its poses an excellent mechanical property, a very good chemical and thermal stability as well as its high rigidity and creep resistance [1-4]. However, the main disadvantages of PSf membrane are due to its hydrophobic characteristics. The hydrophobic nature of PSf will produce membrane with hydrophobic surface or skin layer properties. The hydrophobicity of PSf membrane has restricted the application of the commercial PSf membranes in various aqueous applications

Polymer blend is a simple and efficient method for designing new materials to improve performance of the hydrophobic membranes. In recent years, PSf has been blended as membrane-forming polymer with several auxiliary polymers for improving the membrane properties in order to capitalize on the usefulness of PSf membranes in filtration operations. Several polymeric PSf blend membranes have been fabricated and investigated by few researchers such as polysulfone/polyimide (PSf/PI) [5], polysulfone/polyacrylic acid (PSf/PAA) [6], polysulfone/surfactant (Span-80) [7], polyacrylonitrilic/polysulfone (PAN/PS) [8] and polysulfone/polyurethane [9]. Their results showed that polymer blend is a promising method to improve performance of pure PSf membranes and it is a versatile method that produced high performance PSf membranes in terms of pure water permeability, product rate and anti-fouling membrane as well as better thermal and mechanical properties [5-7].

Cellulose acetate phthalate (CAP) is one of the potential hydrophilic organic polymers that can be used and explored in PSf polymer blend technique. CAP has a superior characteristics compare to cellulose acetate due to the presence of numerous acidic and carbonyl functional groups on its structure [4] and it was added to PSf casting solution to improve its hydrophilicity

properties [10]. It is well known that in UF membrane separation process, the separation performance of UF membrane solely related to the structural properties (such as pore size) of thin skin layer (top layer) of the membrane.

An extensive literature survey revealed that there is no published document discussed about the effect of CAP on structural properties and performance of PSf/CAP blend UF membrane. Hence, the aim of this study is to investigate the influence of different composition of CAP on the membrane structural properties which in turn affect the separation performance of PSf/CAP blend membrane. The structural properties of UF blend membranes were characterized in terms of MWCO, average pore size and pore density by investigating permeation and separation performance of proteins solution in the UF separation process.

■2.0 EXPERIMENTAL

2.1 Experimental Procedure

First, two types of asymmetric casting solutions membranes (PSf and PSf/CAP) were prepared and these casting solutions were cast on the steel plate by using a casting machine and then, immersed in the coagulation bath to produce flat sheet membranes. Next, the performance of these membranes was determined via proteins separation performance tests of different molecular weight of proteins. The permeation and rejection data of proteins from different membrane were investigated. Finally, the MWCO, average pore size and pore density of each PSf/CAP blend UF membranes were determined and calculated from the permeation and rejection data of proteins.

2.2 Materials

All materials used were of analytical grade. The PSf/CAP blend membranes were fabricated from casting solutions which consist of PSf (supplied by Amoco Chemical (USA) S. A.) as membrane back-bone polymer, CAP (purchased from Sigma-Adrich Co.) as hydrophilic polymer, *N*-Methyl-2-Pyrrolidone (NMP) from MERCK Schuchard OHG (Germany) was used as solvent. Distilled water was used as coagulation bath medium.

2.3 Membrane Preparation

Asymmetric PSf membrane and PSf/CAP blend membranes were prepared using casting solution formulations with 17 wt. % polymer concentration. Pure PSf membrane is marked as PC-0 membrane, while PSf/CAP blend membranes which contained 5, 10, 15 and 20 wt.% of CAP in 17 wt.% of polymer concentration in the casting solutions were marked as PC-5, PC-10, PC-15 and PC-20 membranes, respectively. Membranes were fabricated via simple wet phase inversion technique using a casting machine and then immersed directly into a coagulation bath for 24 h to remove excess solvent in the fabricated membranes. The prepared membranes were stored in distilled water prior usage.

2.4 Protein Separation Performance Test

Different molecular weight of proteins was used to study membrane separation performance of each membrane. Four different molecular weight of proteins were used in this separation such as trypsin (23 kDa), pepsin (35 kDa), egg albumin, EA (44.3 kDa) and bovine serum albumin, BSA (66 kDa). Trypsin, pepsin and EA were supplied by Sigma-Aldrich, and BSA was procured from Fluka, USA. All the proteins were used as received.

For protein permeation, a single solution of protein was prepared at concentration of 500 ppm by dissolving a pre-weighed protein powder in phosphate buffer. Protein solution was filled in the dead-end cell and it was pressurized at a constant pressure of 3 bar. The volume of permeate solution of the corresponding membranes was measured and collected in a graduated glass cylinder. The protein solutions were stirred homogenously at 100 rpm to avoid concentration polarization and fouling of proteins. The absorbance of feed and permeate of proteins were analyzed by UV-Vis spectrophotometer (Hitachi U-2000) at wavelength of 280 nm. From the feed and permeate concentrations, the percentage rejection of protein was calculated.

2.5 Molecular Weight Cut-off (MWCO), Average Pore Size and Pore Density

Molecular weight cut-off (MWCO) of the PSf/CAP blend membranes were determined by the rejection studies of different molecular weights of proteins. In this study, MWCO of the blend membranes were obtained based on the lowest molecular weight of protein that was rejected at 80% in the figure of proteins rejection versus molecular weight of proteins. As MWCO of the blend membranes were determined, the average pore size and pore density of blend membranes can be obtained as explained by Sarbolouki [11].

■3.0 RESULTS AND DISCUSSION

3.1 Protein Separation Performance

In protein separation studies, different molecular weight of proteins such as trypsin, pepsin, egg albumin (EA) and bovine serum albumin (BSA) were used to investigate protein solution fluxes and the rejection of the proteins. Figure 1 shows the permeate fluxes of protein solutions for PC-0, PC-5, PC10, PC-15 and PC-20 blend membranes respectively. This figure clearly displays that PC-0 membrane has the lowest permeate flux for each molecular weight of proteins meanwhile, PC-20 membrane which contains 20 wt% of CAP in blend casting solution shows the highest permeate flux of protein solutions.

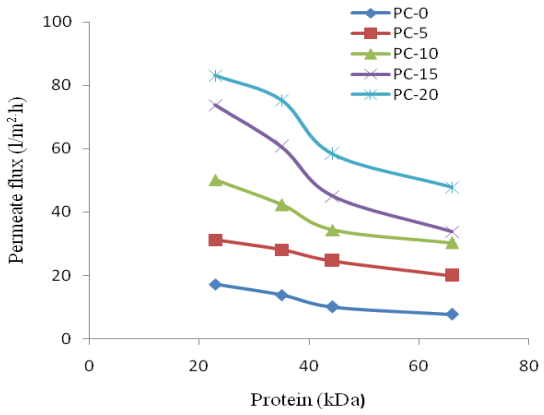


Figure 1 Permeate fluxes of different molecular weight of proteins for PSf and PSf/CAP blend membranes at operating pressure of 3 bar

Increased the CAP content in blend compositions gradually increased permeate fluxes of protein solution of each blend membranes. It was reported that an increase of hydrophilic polymer, CAP in polysulfone membranes increased hydrophilicity and porosity of the membranes and hence increase their permeate fluxes [10]. Hence, according to the experimental results, the sequence of the permeate flux for each membrane in the increasing permeate fluxes trend can be arranged based on the following sequence; PC-0<PC-5<PC-10<PC-15<PC-20.

Figure 2 shows rejection of proteins by PSf membrane and PSf/CAP blend membranes as a function of different molecular weight of proteins. PC-0 membrane shows the highest rejection of proteins and the percentage of proteins rejection decreased with further additional CAP content in the PSf/CAP blend membranes. PC-20 membrane showed the lowest rejection of proteins compared to PC-5, PC-10 and PC-15 blend membranes. Arthanareeswaran and his co-workers [1] claimed that higher amount of hydrophilic polymer which was blended with hydrophobic polymer in the casting solutions changed the macroscopic structure of the blend membranes and led to produce less hydrodynamic resistance, porous and open pores size of membranes. Membranes with these characteristics had low rejection of proteins but high permeation of protein solutions.

Based on individual molecular weight of protein performance as illustrated in the Figure 1 and Figure 2, it is observed that the permeate flux decreased with increasing molecular weight of protein but the solute rejection of protein solutions was in an increase trend with increasing molecular weight of proteins. Trypsin showed the highest fluxes compare to all proteins in the separation performance test. The order of permeate flux was found to be trypsin > pepsin > EA >BSA. These trends were due to the order of molecular weights of trypsin, pepsin, EA, and BSA which were 20.0, 35.0, 44.3 and 66.0 kDa respectively. BSA rejection shows the highest rejection among all of the proteins used in this experiment was due to its highest molecular weight of protein, 66.0 kDa.

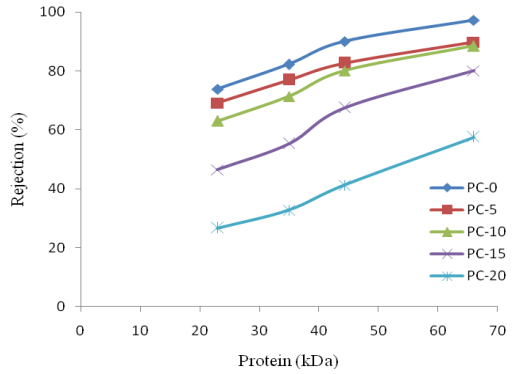


Figure 2 Rejection of different molecular weight of proteins for PSf and PSf/CAPblend membranes at operating pressure of 3 bar

3.2 Molecular Weight Cut-off (MWCO)

Molecular weight cut-off (MWCO) is a pore characteristics based on the rejection of a solute which has certain molecular weight. MWCO in this study was based on solute rejection in solute permeation test. Sarbolouki (1982) describes that MWCO of membrane can be determined through the lowest molecular weight of solute rejected more than 80% but less than 100%. MWCO for PSf membrane and PSf/CAP blend membranes was performed by separation performance test of different molecular weight of proteins at operating pressure of 3 bar. Based on 80% protein rejection, and referring to Figure 2, MWCO of PC-0 to PC-20 membranes is tabulated in Table 1.

The smallest MWCO for all membranes is observed for PC-0 membrane with 32.0 kDa. This is due to membrane formed from hydrophobic polymer such as polysulfone has tight polymer matrix structure and consequently small pores size was formed. The delayed demixing process in formation of polysulfone membrane would further promote aggregation of polymer molecules through chain entanglement attributed to produce small pore membrane and reduced flux [12].

Table 1 MWCO and pore properties of PSf and PSf/CAP blend membranes

Membrane	MWCO (kDa)	Average pore size (Å)	Pore density (pores/μm^2)
PC-0	32.0	35.5	1.77
PC-5	39.5	40.0	2.41
PC-10	44.0	42.0	4.10
PC-15	66.0	51.5	3.51
PC-20	> 66.0	> 51.5	ND

ND – not detectable.

The MWCO of PC-5, PC-10 and PC-15 membranes were estimated at about 39.5, 44.0 and 66.0 kDa respectively. PC-20 membrane has MWCO higher than 66 kDa. Higher CAP content in the PSf/CAP blend composition led to formation of high MWCO of membranes and these investigation results were in agreement with permeate fluxes which were increased with the increment of CAP content. The presence of hydrophilic CAP promotes the rapidness of precipitation in the membranes during wet phase separation and attributes to form membranes with bigger pore sizes and porous sub-layer structure.

3.3 Average Pore Size and Pore Density

The pure PSf membrane (PC-0) has the smallest average pore size of about 35.5 Å on the membrane surface as tabulated in Table 1. The estimated average pore size for PC-5, PC-10 and PC-15 were 40.0, 42.0 and 51.5 Å respectively. While for PC-20 which contains the highest CAP composition shows its average pore size greater than 51.5 Å. The increase average pore sizes of the resultant blend membranes were due to the increasing nature of immiscible phase behavior of blend, attributed to low molecular attractive forces between the blend components, and as a result produced membranes with open (bigger) pores size [13,14].

The pore density of PC-0 and PC-5 are about 1.77 and 2.41 pores/μm^2 respectively. By addition of 10 wt% of CAP, the pore density of PC-10 membrane surface increased to 4.10 pores/μm^2 but further increment of CAP content of 15 wt% decreased the pore density of PC-15 membrane to 3.51 pores/μm^2. It is evidenced that addition of CAP had significant effect on pore properties of the blend membranes. An increase in CAP composition increased the permeation rate through the membrane pores due to enhancement in pore size and pore density of the membrane.

From Table 1, the results revealed that an increase of CAP composition induced the formation of bigger average pore size and increased pore density as well as porosity of the blend membranes. The rapid driving force between solvent and non-solvent formed membrane with equally dispersed pores at the

skin membrane surface and the effect of extended segmental gap between polymer chains attributed to increment in pores size and porosity at the surface of skin blend membranes [15,16]. The membrane prepared without CAP content relatively had tight membrane surface with small average pores size and less porosity as well as pore density. As discussed earlier, PSf has hydrophobic property which contributes to the delayed phase inversion process during immersion precipitation which produced PC-0 membrane surface with the smallest average pore size, and the lowest porosity, pore density and hydrophilicity compared to the PSf/CAP blend membranes.

■4.0 CONCLUSION

In the protein separation performance study, the virgin PSf membrane showed the lowest permeate flux but the highest rejection of proteins compared to PSf/CAP blend membranes. PSf membrane also has the lowest MWCO, average pore size and pore density. It was due to the hydrophobic nature property of PSf polymer delayed the demixing process during phase inversion process which in turn produced membrane with tight surface structural properties. The addition of CAP from 5 to 20 wt% increased the permeate fluxes and decreased the proteins rejection. The experimental results also showed that the addition of CAP also increase the MWCO, average pore size and pore density of PSf/CAP blend membranes. The investigated results showed a hydrophilic CAP promotes the rapidness of demixing process and further promote the extension gap between polymer chains attributed to increment in MWCO, pore size and pores density of PSf/CAP blend membranes.

Acknowledgement

The authors wish to express their sincere gratitude to School of Ocean Engineerin, Universiti Malaysia Terengganu and Faculty of Chemical and Natural Resources, Universiti Malaysia Pahang for their cooperation and support.

References

[1] Arthanareeswaran, G., Thanikaivelan, P., Jaya, N., Mohan, D., Raajenthiren, M. 2007. Removal of Chromium from Aqueous Solution Using Cellulose Acetate and Sulfonated Poly(Ether Ether Ketone) Blend Ultrafiltration Membranes. *Journal of Hazardous Materials B.* 139: 44–49.

[2] Bowen, W. R., Doneva, T. A., Yin, H. B. 2001. Polysulfone-sulfonated Poly(Ether Ether) Ketone Blend Membranes: Systematic Synthesis and Characterization. *Journal of Membrane Science*. 181: 253–263.

[3] Mulder, M. 1996. Basic *Principles of Membrane Technology*. The Netherlands: Kluwer Academic Publishers.

[4] Rahimpour, A., Madaeni, S. S. 2007. Polyethersulfone (PES)/cellulose Acetate Phthalate (CAP) Blend Ultrafiltration Membranes: Preparation, Morphology, Performance and Antifouling Properties. *Journal of Membrane Science*. 305: 299–312.

[5] Ding, Y., Bikson, B. 2010. Macro and Meso Porous Polymeric Materials from Miscible Polysulfone/Polyimide Blens by Chemical Decomposition of Polyimides. *Polymer*. 51: 46–52.

[6] M'Bareck. C., Nguyen, Q. T., Alaoui, O. T., Barillier, D. 2009. Elaboration, Characterization and Application of Polysulfone and Polyacrylic Acid Blends as Ultrafiltration Membranes for Removal of Some Heavy Matals from Water. *Journal of Hazardous Materials*. 171: 93–101.

[7] Tsai, H. A., Huang, D. H., Fan, S. C., Wang, Y. C., Li, C. L., Lee, K. R., Lai, J. Y. 2002. Investigation of Surfactant Addition on the Vapor Permeation of Aqueous Ethanol Mixtures Through Polysulfone Hollow Fiber Membranes. *Journal of Membrane Science*. 198: 245–258.

[8] Ai-Lian, L., Qing, C. 1995. Polyacrylonitrilic/polysulfone (PAN/PS) Blend Ultrafiltration (UF) Membranes. *Desalination*. 101: 51–56.

[9] Nguyen, T. D., Solomon, B. A. 1993. New One-step Process for Preparation of Microporous Composite Polysulfone/Polyurethane Hollow-Fiber Membranes. *Desalination*. 90: 3–13.

[10] Ali A., Awang, M., Mat, R., Johari, A. Kamaruddin, M.J., Sulaiman, W.R.W. 2014. Influence of Hydrophilic Polymer on Pure Water Flux, Permeability Coefficient, and Porosity of Polysulfone Blend Membranes. *Advanced Materials Research*. 931–932: 168–172.

[11] Sarbolouki, M. N. 1982. A General Diagram for Estimating Pore Size of Ultrafiltration and Reverse Osmosis Membranes. *Separation Science Technology*. 17(2): 381–386.

[12] Kimmerle, K., Strathmann, H. 1990. Analysis of the Structure Determining Process of Phase Inversion Membranes. *Desalination*. 79: 283–302.

[13] Hwang, J. R., Koo, S. H, Kim, J. H., Higuchi, T. M. 1996. Effects of Casting Solution Composition Performance of Poly(Ether Sulfone) Membranes. *Journal of Applied Polymer Science*. 60: 1343–1348.

[14] Paul, D. R., Barlow, J. M., Keskkula, H. 1989. *Polymer Blends. Encyclopedia of Polymer Science and Engineering*. Vol. 12. New York: John Wiley and Sons.

[15] Rajesh, S., Maheswari, P., Senthikumar, S., Jayalakshmi, A., Mohan, D. 2011. Preparation and Characterization of Poly(Amide-Imide) Incorporated Cellulose Acetate Membranes for Polymer Enhanced Ultrafiltration of Metal Ions. *Chemical Engineering Journal*. 171: 33–44.

[16] Kesting, R. E. 1985. *Synthetic Polymeric Membranes, In: A Structural Perspective*. New York: Wiley.