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Polysulfone/Pluronic F127 Blend Ultrafiltration Membranes: Preparation and Characterizations

R. Raslan and A.W. Mohammad
Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment,
Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

Abstract: Membrane fouling phenomenon is a major problem for efficient use of ultrafiltration membranes and resulted in reduction of throughput and performance. Hence, an attempt has been made to develop a low-fouling membrane material by blending polymers. Blending of polysulfone (PSU) and Pluronic F127 was carried out to prepare membranes with hydrophilic and low-fouling property. PSU and Pluronic F127 were blended in 100/0, 90/10 and 80/20 compositions using N-methyl-2-pyrrolidinone (NMP) as solvent and membranes were prepared by the phase inversion technique. The membrane morphologies were characterized by Scanning Electron Microscopy (SEM). The results showed an asymmetric morphology of PSU/Pluronic F127 membranes. The static contact angles of blend membranes were measured using a contact angle goniometer. The decrease of static water contact angle with an increase in Pluronic F127 content indicated an increase of surface hydrophilicity. The stability of Pluronic F127 in blend membranes was evaluated by Attenuated Total Reflection Fourier transform infrared spectrometer (ATR-FTIR). The results analysis confirmed that Pluronic F127 could exist stably in blend membranes. The permeation flux of pure water under different pressures was investigated. It was found that blend membranes have higher permeability than that of PSU-control membrane.

Key words: Fouling, polysulfone, pluronic F127, ultrafiltration

INTRODUCTION

Ultrafiltration is becoming increasingly popular in many industries such as chemical, pharmaceutical, food, metal finishing and others for the purpose of separation, concentration, fractionation and purification of multicomponent molecular mixtures (Wang, 2001). This is due to its distinct advantage which include no phase change, low operating pressure, an ambient or relatively low operating temperature (Zhao *et al*., 2008).

However, one major problem that reduce its efficiency is fouling. Membrane fouling can occur in three ways which include adsorption of foulants, pore plugging and concentration polarization or gel layer formation (Dal-Cin *et al*., 1996). These may decrease the membrane permeability and shorten membrane's life leading to an increase in operating costs. Hence, minimization of membrane fouling is essential to achieve optimum applications.

A wide range of evidence shows that membranes with a greater degree of hydrophilicity have increased resistance to fouling (Richard *et al*., 2001). Polymers which are hydrophilic such as polyvinyl alcohol and polyvinylpyrrolidone are difficult or impossible to coagulate under practically feasible conditions because of their high affinity to water.

Therefore, it is generally inconvenient to make hydrophilic membranes out of highly hydrophilic polymers (Menaham *et al*., 1990). An alternative way to achieve hydrophilic-hydrophobic balance property is by polymer blends. This is a proven tool to develop new polymer membrane material with antifouling property (Richard *et al*., 2001; Sivakumar *et al*., 2006; Wang *et al*., 2006; Arthanareeswaran *et al*., 2007; Lv *et al*., 2007; Rahimpour and Madaeni, 2007; Zhao *et al*., 2008).

Polysulfone is a hydrophobic polymer that is commonly used as a membrane material, because of its high rigidity, strength, creep resistance, good thermal and stability (Sivakumar *et al*., 2006; Arthanareeswaran *et al*., 2007). Another choice of polymer that is compatible to polysulfone is pluronic F127. The hydrophilic poly (ethylene oxide) (PEO) segments in Pluronic F127 endowed the membranes surface with higher hydrophicility while the hydrophobic poly (propylene oxide) (PPO) segments in Pluronic F127 ensured the

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Corresponding Author: A.W. Mohammad, Department of Chemical and Process Engineering,
Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi,
Selangor, Malaysia

Pluronic copolymers to be firmly anchored in the polymer matrix. Previously, it has been blended with polyethersulfone and cellulose acetate and has proven to improve ultrafiltration performance as well as developing excellent antifouling property (Wang *et al*., 2006; Lv *et al*., 2007; Zhao *et al*., 2008).

MATERIALS AND METHODS

Materials: Polysulfone (Udel P-1700) supplied by Solvay Advanced Polymers, L.L.C was used as the base polymer in the casting solution. 1-Methyl-2-Pyrrolidinone (NMP) supplied by J.T. Baker was used as a solvent without further purification. PEO-PPO-PEO triblock copolymer Pluronic F127 with a molecular weight of 12600 and a PEO content of 70 wt.% supplied by Sigma-Aldrich Co. (Shanghai) Limited USA was used as additive in the casting solution. Water purified from Heal Force® Ultra- pure Water System NW UF Series by Nison Instrument with resistivity of 18 MΩ cm was used for all the experiments. All chemicals used in this study were of analytical grade.

Preparation of Polysulfone/Pluronic F127 membrane: Polysulfone/Pluronic F127 membranes were prepared by phase inversion method. The formulations of casting solution were given in Table 1. Polysulfone was a membrane matrix whereas Pluronic F127 was a membrane modifier as well as a pore-forming agent. Polysulfone and various amount of Pluronic F127 were dissolved in NMP and stirred at 80°C for about 4 h to obtain homogeneous mixing and then left for overnight to allow complete release of bubbles. The solutions were then cast on glass plates with a filmographe doctor blade (Braive Instrument) and then immersed in a coagulation bath of deionized water. Subsequently, the membranes formed were peeled off and washed thoroughly with deionized water to remove any residual solvent. The prepared membranes were kept in deionized water before testing.

Characterization of Polysulfone/Pluronic F127 membrane: The cross-section morphologies of Polysulfone/Pluronic F127 membranes were observed using Scanning Electron Microscope (SEM) (SUPRA 55VP, Zeiss). The static contact angles of Polysulfone/Pluronic F127 membranes were measured at room temperature using a contact angle goniometer (CA-DT.A, Face Contact Angle Meter, Kyowa Kaimenkagaku Co. Ltd., Japan). A water drop with volume of 5 μL was dropped onto the membranes with a microsyringe in an atmosphere of air. At least 3 contact angles at different locations on one surface were averaged to get a reliable value.

Table 1: The formation of casting solutions for preparation of the Polysulfone/Pluronic F127 membranes

Membrane	PSU (g)	Pluronic F127 (g)	NMP (g)	$W_{F127}/W_{total\ polymer}$ (%)
P-0	14.16	-	51.40	0
P-10	12.74	1.42	51.40	10
P-20	11.33	2.83	51.40	20

The chemical composition of Polysulfone/Pluronic F127 membranes surfaces were analyzed by attenuated total internal reflection (ATR) fourier transform infrared spectrometer (FTIR) (Nicolet 6700, Nicolet Co., USA). The wet membrane samples with thickness of 250 μm were dried at room temperature.

Filtration experiments: The Milipore Stirred Ultrafiltration Cell (Model 8200) connected with a nitrogen gas cylinder and solution reservoir was used to measure permeability of the membrane. The maximum volume capacity of the cell is 200 mL. It accommodates 63.5 mm diameter membrane disk. The cell is designed for safe operation to 75 psi.

Permeability experiment was carried out using ultra pure water at a pressure up to 4.5 bar. Initially, each membrane was pressurized at 3 bar for 30 min. For each different applied pressure, fluxes are based on measurement of the first 5 mL of permeate. Then, flux was calculated using the following equation:

$$J_w = \frac{\Delta V}{A \Delta t} \tag{1}$$

where, A was the effective membrane area, ΔV was the volume of permeated water and Δt was the permeation time.

RESULTS AND DISCUSSION

Morphological studies: Scanning Electron Microscopy (SEM) is an important tool for the determination of morphology of the membranes. The SEM photographs of cross section of all the blend membranes were shown in Fig. 1a-c. All the PSU/Pluronic F127 membranes exhibited morphology of asymmetric structure consisting of a dense skin layer and a porous sublayer. Similar results were also observed by Zhao *et al*. (2008). Furthermore, all of the membranes show a straight finger like pores. At high Pluronic F127 content, bigger finger like pores could be observed obviously.

Contact angle: An efficient way to overcome membrane fouling is to increase hydrophilicity of membrane surface, which can be evaluated by water contact angle. Figure 2

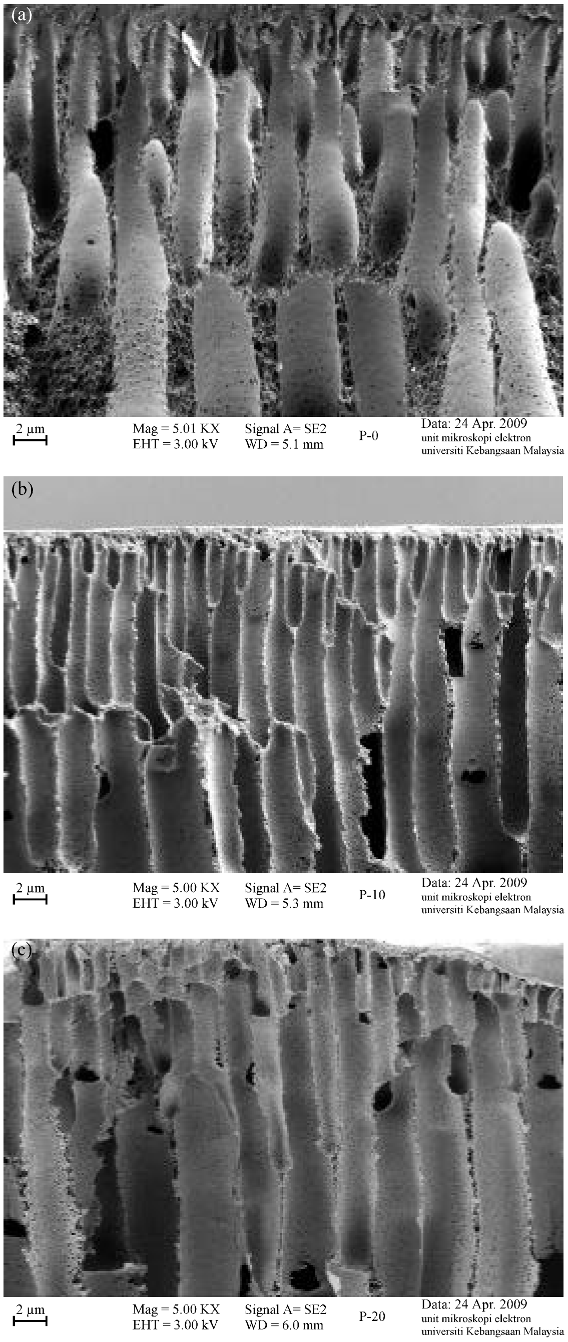

Fig. 1: Cross- sectional SEM morphology of (a) P-0, (b) P-10 and (c) P-20

shows the water contact angles of the PSU control membrane and the PSU/Pluronic F127 membranes. The PSU control membrane had the highest water contact angle 61° and the PSU/Pluronic F127 membranes had smaller water contact angles. These results revealed that there was a substantial increase of surface hydrophilicity for PSU/Pluronic F127 membrane due to surface modification. This result was also supported by Zhao *et al.* (2008).

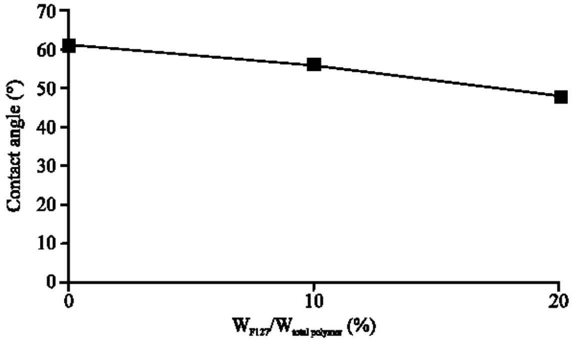

Fig. 2: Water contact angles of PSU/Pluronic F127 membranes as a function of pluronic F127 content

Stability of PSU-F127 blend membranes: The stability of fouling-resistant ability of blend membranes was an important issue for practical concern (Wang *et al.*, 2006). ATR-FTIR was used to obtain the quantitative information of the existence and stability of Pluronic F127.The ATR-FTIR spectra of Pluronic F127, PSU control membrane and PSU-F127 blend membranes were shown in Fig. 3a and b. PSU control membrane was characterized by the peak at 1586 cm^{-1} corresponding to the C-H bond in aromatic system (Belfer *et al.*, 2000) while Pluronic F127 was characterized by C-O bond appearing at 1107 cm^{-1}. The characteristic peaks of Pluronic F127 in blend membranes were totally overlapped by PSU peaks due to the low content of Pluronic F127. However, the relative intensity of the C-O bond appearing at 1107 cm^{-1} increased with increasing Pluronic F127 content. This has also been described by Wang *et al.* (2006).

The height ratio between the peak of C-O bond at 1107 cm^{-1} and C-H bond in aromatic at 1586 cm^{-1} was shown in Fig. 3b. In particular the peak height ratio of PSU-F127 blend membranes was higher than PSU control membrane. This is the evident that Pluronic F127 exists stably in blend membranes.

Effect of operation pressure on pure water flux: The pure water fluxes of PSU-F127 blend membranes at different operation pressures between 0.5 to 4.5 bar were shown in Fig. 4. At the same operating pressure, pure water flux increased with the increasing Pluronic F127 content in blend membranes. The pure water flux of PSU control membrane and PSU-F127 blend membranes both increased

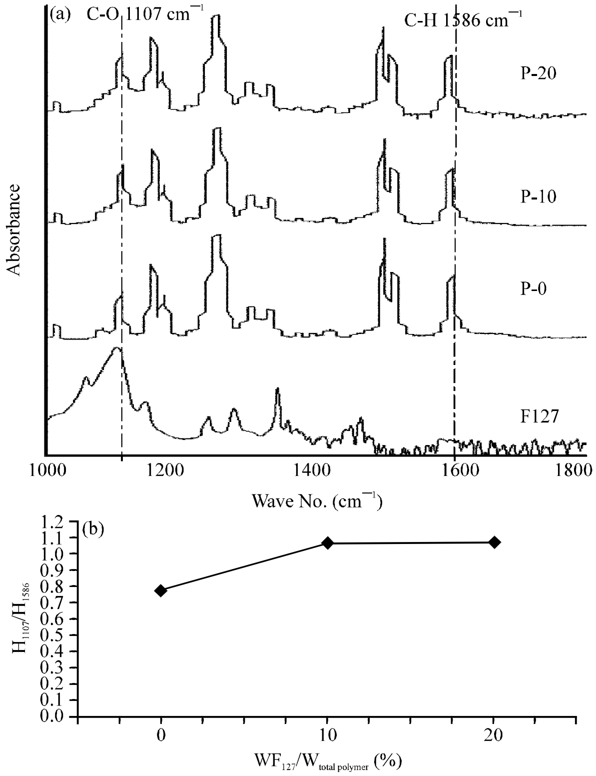

Fig. 3: ATR-FTIR spectra of Pluronic F127 and PSU-F127 Blend Membranes with different concentration of Pluronic F127 (a) and the peak intensity ratio between at 1107 and (b) 1586 cm^{-1} for PSU with different Pluronic F127 content in the mixture

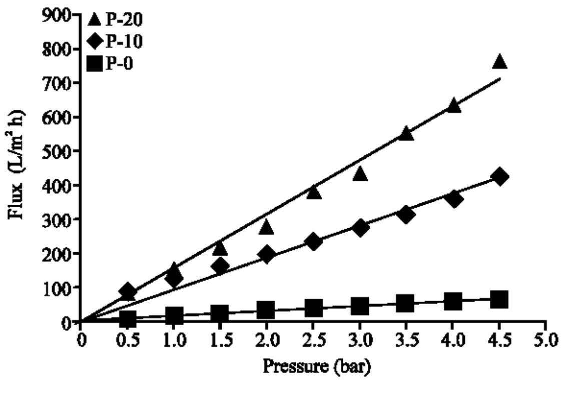

Fig. 4: The effect of operation pressure on pure water flux of different blends membranes

linearly with increasing operating pressure. Further, the slope of this linear proportionality of pure water flux to applied pressure was used to denote the hydraulic resistance during ultrafiltration. It is evident from these result that membranes prepared with Pluronic F127 had lower resistance compared to PSU control membrane. This may be explained by the fact that an increase in the composition of Pluronic F127 in the casting solution may enhance the hydrophilicity and the size of the pores.

CONCLUSION

The polymeric blend membranes based on PSU and the antifouling agent, Pluronic F127 has been developed by phase inversion technique. ATR-FTIR measurement indicates that Pluronic F127 can exist stably in blend membranes. The characterization of prepared membranes illustrates that the pure water flux was increased while the membrane hydraulic resistance was decreased, as the concentration of Pluronic F127 in the casting solution was increased. Evidently, SEM photographs showed that the pore size was also increased with increasing concentration of Pluronic F127. The decreasing of membrane hydraulic resistance may be due the increasing of hydrophilicity proven by the water contact angle data. The P-20 blend membrane shows highest pure water flux, hydrophilicity and porosity compared to other membranes.

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REFERENCES

Arthanareeswaran, G., D. Mohan and M. Raajenthiren, 2007. Preparation and performance of polysulfone-sulfonated poly(ether ether ketone) blend ultrafiltration membranes. Part I. Applied Surface Sci., 253: 8705-8712.

Belfer, S., R. Fainchtain, Y. Purinson and O. Kedem, 2000. Surface characterization by FTIR-ATR spectroscopy of polyethersulfone membranes-unmodified, modified and protein fouled. J. Membr. Sci., 172: 113-124.

Dal-Cin, M.M., F. McLellan, C.N. Striez, C.M. Tam, T.A. Tweddle and A. Kumar, 1996. Membrane performance with a pulp mill effluent: Relative contributions of fouling mechanisms. J. Membr. Sci., 12: 273-285.

Lv, C., Y. Su, Y. Wang, X. Ma, Q. Sun and Z.Y. Jiang, 2007. Enhanced permeation performance of cellulose acetate ultrafiltration membrane by incorporation of Pluronic F127. J. Membr. Sci., 294: 68-74.

Menaham, K., M. Heisler, I. Katsnelson and D. Velazques, 1990. Filtration Membranes and Method of Making the Same. Gelman Sciences Inc., University of Michigan, USA., pp: 964-990.

Rahimpour, A. and S.S. Madaeni, 2007. Polyethersulfon (PES)/cellulose acetate phthalate (CAP) blend ultrafiltration membranes: Preparation, morphology, performance and antifouling properties. J. Membr. Sci., 305: 299-312.

Richard, B.W., T.A. Doneva and H.B. Yin, 2001. Polysulfone-sulfonated poly(ether ether) ketone blend membranes: Systematic synthesis and characterisation. J. Membr. Sci., 181: 253-263.

Sivakumar, M., D.R. Mohan and R. Rangarajan, 2006. Studies on cellulose acetate-polysulfone ultrafiltration membranes: II. Effect of additive concentration. J. Membr. Sci., 268: 208-219.

Wang, W.K., 2001. Membrane Separations in Biotechnology. Marcel Dekker Inc., New York.

Wang, Y., Y. Su, Q. Sun, X. Ma and Z. Jiang, 2006. Improved permeation performance of Pluronic F127-polyethersulfone blend ultrafiltration membranes. J. Membr. Sci., 282: 44-51.

Zhao, W., Y. Su, C. Li, Q. Shi, X. Ning and Z. Jiang, 2008. Fabrication of antifouling polyethersulfone ultrafiltration membranes using Pluronic F127 as both surface modifier and pore-forming agent. J. Membr. Sci., 318: 405-412.