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ULTRAFILTRATION AS PRETREATMENT OF REVERSE OSMOSIS: LOW FOULING ULTRAFILTRATION MEMBRANE PREPARED FROM POLYETHERSULFONE–AMPHIPHILIC BLOCK COPOLYMER BLEND

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Abstract

This paper demonstrates the preparation of polyethersulfone (PES) ultrafiltration (UF) membranes via wet phase inversion method using either poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) (Pluronic®, Plu) or polyethylene glycol (PEG) as hydrophilic modifier. Their effects on membrane structure as well as the resulting membrane performance and their stability in membrane polymer matrix were systematically investigated. The investigated membrane characteristics include surface hydrophilicity (by contact angle), surface chemistry (by FTIR spectroscopy) and water flux measurement. Visualization of membrane surface and cross section morphology was also done by scanning electron microscopy. The membrane performance was examined by investigation of adsorptive fouling and ultrafiltration using solution of bovine serum albumin as the model system. The stability of additive was examined by incubating the membrane in water (40^{o}C) for up to 10 days. The results show that modification effects on membrane characteristic and low fouling behavior were clearly observed. Further, amphiphilic Pluronic generally showed better performance than PEG.

Keywords: *membrane preparation, Pluronic®, polyethersulfone, poly(ethylene glycol)-b-poly(propylene glycol)-b- poly(ethylene glycol), ultrafiltration membrane*

Abstrak

Makalah ini melaporkan pembuatan membran ultrafiltrasi (UF) polyethersulfone (PES) dengan metode inversi fasa menggunakan poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) (Pluronic®, Plu) atau polyethylene glycol (PEG) untuk meningkatkan hidrofilisitas membran. Pengaruh penambahan Pluronic dan PEG terhadap struktur membran, kinerja membran dan kestabilannya dalam matrik polimer membran telah diamati. Karakterisasi membran yang dilakukan meliputi hifrofilisitas permukaan (dengan sudut kontak), sifat kimia permukaan membran (dengan spektroskop FTIR) dan pengukuran fluks air murni. Visualisasi morfologi membran baik permukaan dan penampang melintang dilakukan dengan menggunakan scanning electron microscopy. Kinerja membran diinvestigasi melalui pengamatan terhadap perilaku fouling adsorptif dan fouling ultrafiltrasi dengan menggunakan larutan protein bovine serum albumin sebagai umpan. Stabilitas Pluronic dan PEG dalam membran diuji dengan direndam dalam air bertemperatur 40^{o}C selama 10 hari. Hasil penelitian menujukkan bahwa pengaruh modifikasi dengan menggunakan Pluronic dan PEG terhadap karakteristik dan perilaku fouling jelas terlihat. Lebih lanjut, membran yang dibuat dengan menggunakan Pluronic menunjukkan kinerja yang lebih baik daripada membran yang dibuat dengan menggunakan PEG.

Kata kunci: *pembuatan membran, Pluronic®, polyethersulfone, poly(ethylene glycol)-b-poly(propylene glycol)-b- poly(ethylene glycol), membran ultrafiltrasi, fouling*

INTRODUCTION

Nowadays, ultrafiltration (UF) is generally recognized as a promising separation tool in many technical processes. UF has replaced not only the conventional separation techniques but it has also successfully been utilized to solve mass separation problems. The applications of UF include fractionation or concentration step in the food, pharmaceutical and biotechnological industries, pure water production and water and wastewater treatments (Baker, 2004; Cheryan 1998; Girard and Fukumoto, 2000; Jönsson and Trägård, 1990; Van Reis and Zydney, 2007). Recently, UF has also been proposed as promising process as pretreatment of reverse osmosis membrane (Ma *et al.*, 2007; van Hoof *et al.*, 1999, Van Houttem *et al.*, 1998). As consequence of this increasing demand, efforts to improve UF process performance are gaining more and more importance. In general, those efforts include feed pretreatment, advanced membrane and module design, and process condition optimization. However, in many cases, the heart for the performance of UF process is the membrane itself. In this regard, three important characteristics for achieving high performance UF membrane are high flux as well as selectivity, low fouling and performance stability for long term operation.

Because of their mechanical strength, thermal and chemical stability as well as excellence film forming properties, sulfone polymers, e.g., polyethersulfone (PES), have been used very often for the fabrication of high performance commercial UF membranes. Nevertheless, the hydrophobicity of those materials can cause severe fouling problems; therefore, membrane modification is usually done to increase the membrane resistance towards fouling. Three different approaches including (i) membrane polymer modification (pre-modification), (ii) blending of the polymer membrane with a modifying agent (additive), and (iii) surface modification after membrane preparation (post-modification) have been proposed (Susanto and Ulbricht, 2009). Although stability of the modifying agent in the membrane matrix prepared by blending technique can be a problem, it is simple and the effect of hydrophilization of the polymer membrane can clearly be observed. Therefore, this technique seems to be of highest relevance from practical point of view. Polymeric additives (usually hydrophilic polymers) in a casting solution are also used in order to increase both pore size and porosity (pore-forming agent) and to suppress macrovoid formation. However, depending on the polymer membrane, solvent and phase inversion conditions, the opposite effect can also be observed.

Besides polyvinylpyrrolidone (PVP), polyethylene glycol (PEG) has been intensively used as additives during preparation of PES UF membranes by phase inversion methods. The mechanism of PES membrane formation with the presence of additive had well been explained in many previous publications (Boom *et al.*, 1992, 1994; Idris *et al.*, 2007; Lafreniere *et al.*, 1987; Liu *et al.*, 2003; Marchese *et al.*, 2003; Mosqueda-Jimenez, 2004; Wienk *et al.*, 1996; Yeo *et al.*, 2000). In sum, the performance of PES UF membrane could be increased with the addition of additive, however, the stability of PVP and PEG in matrix polymer membrane is a crucial problem. The objective of this work was to prepare low fouling PES UF membrane with stable hydrophilic character. Amphiphilic triblock copolymer of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*- poly(ethylene oxide) (Pluronic /Plu/) was used as additive. In this regard, the hydrophilic of the resulting membrane (from hydrophilic block PEO) was expected to be more stable due to hydrophobic–hydrophobic interaction between PPO and PES.

MATERIALS AND METHODS

Materials

Commercial PES (Ultrason E 6020 P) donated by BASF (Ludwigshafen, Germany) was used and dried at 120°C for at least 4 h before use. N-methyl-2-pyrrolidone (NMP) was purchased from Merck (Hohenbrunn, Germany). Polyethylene glycol (PEG) (MW ~ 10000 g/mol) was purchased from Fluka Chemie AG (Buchs, Germany) and Pluronic F127 (Plu) (MW ~ 12600 g/mol) was purchased from BASF (Mount Olive, NJ, US). The chemical structure of PES and Pluronic used is shown in Fig. 1. Bovine serum albumin (BSA) was purchased from ICN Biomedicals, Inc. (California, US). Potassium dihydrogen phosphate (KH_2PO_4) and disodium hydrogen phosphate dihydrate ($Na_2HPO_4.2H_2O$) were purchased from Fluka Chemie AG (Buchs, Germany). Nitrogen gas purchased from Messer Griesheim GmbH (Krefeld, Germany) was ultrahigh purity. Water purified with a Milli-Q system from Millipore was used for all experiments.

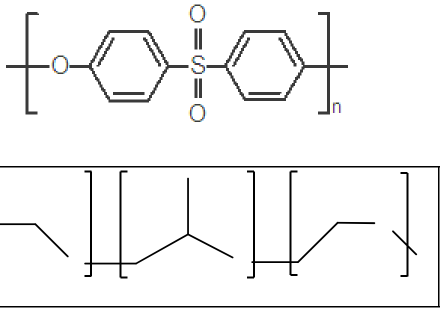

Fig. 1. Chemical structure of PES (top) and Pluronic (bottom) used

Methods

Membrane preparation

PES (15 wt%) was dissolved in NMP (75 wt%) with stirring, and either PEG or amphiphilic triblock copolymer (10 wt%) was added to the polymer solution. Slight heating (~45°C) was used during dissolution of PEG. This relative high concentration of additive was aimed to see significant effects on the resulting membrane. Polymer solution without an additive was also prepared for control experiments. The homogenous polymer solution was left without stirring until no bubbles were observed. The membranes were prepared by using Coatmaster 509 MC, Erichsen Testing Equipment. The polymer solution was cast with a thickness of 200 μm using a steel casting knife on a glass substrate (casting speed 25 mm/s) and subjected to humid air (RH = 50-60%) for 1 min. Thereafter, the proto-membrane was solidified in a coagulation bath containing water (20^{o}C $\underline{+}$ 1) for 1 hour. The resulting membranes were washed and soaked in the water for 24 h before drying. Drying was sequentially done by immersing in water, water/ethanol, ethanol, and hexane.

Hydraulic permeability measurement, adsorptive fouling and ultrafiltration procedures

All experiments were carried out by using a dead-end stirred cell filtration system (Amicon cell model 8010 for compaction, hydraulic permeability measurement and adsorptive fouling, model 8050 for UF experiments) connected to a reservoir (~ 450 mL) and pressurized by nitrogen from a gas tank. In all experiments, the membrane was firstly compacted for at least 1 h (this time was enough to achieve steady flux). Hydraulic membrane permeability was measured at different trans-membrane pressures within the range 100 to 400 kPa and at least 5 measurements from different membrane samples were averaged.

For static adsorption experiments (adsorptive fouling), a solution of BSA (1 g/L, pH 7 in phosphate buffer) was added to the cell and the outer membrane surface was exposed for 3 hours without any flux at a stirring rate of 300 rpm. Afterwards, the solution was removed, and the membrane surface was rinsed two times by filling the cell with pure water (5 mL) and shaking it for 30 seconds. Water fluxes before and after exposures were measured at the same pressure (300 kPa). The evaluation of membrane performance was expressed in terms of the relative flux reduction, RFR (Eq (1)).

$$\mathrm{RFR} = \frac{J_0 - J_a}{J_0} \mathrm{x}100\% \qquad (1)$$

Ultrafiltration experiments at a constant trans-membrane pressure (300 kPa) were conducted using a BSA solution (0.1 g/L, pH 7 in phosphate buffer) as the feed. The balance was connected to the PC, the weight of permeate was recorded online, and the flux was calculated. The permeate flux profile over filtration time was investigated. The compositions of BSA in the permeate ($C_{\mathrm{downstream}}$) and feed/retentate (C_{upstream}) sides of membrane were analyzed by measuring its UV absorbance at 280 nm. The apparent BSA rejection was calculated using equation (2).

$$R = 1 - \frac{C_{\mathrm{downstream}}}{C_{\mathrm{upstream}}} \qquad (2)$$

Membrane surface and cross-section morphology

The cross-section and top surface morphology of the membranes were observed by using a Quanta 400 FEG (FEI) environmental scanning electron microscope (ESEM) at standard high-vacuum conditions. A K 550 sputter coater (Emitech,U.K.) was used to coat the outer surface of the sample with gold/palladium. For cross section analysis, the membranes were broken in liquid nitrogen and sputtered for 1.5 min, while for analysis of outer membrane surface, sputtering was done for 0.5 min.

Surface hydrophilicity by contact angle (CA)

Sessile drops static CA was measured using an optical contact angle measurement system (OCA 15 Plus; Dataphysics GmbH, Filderstadt, Germany). Five μL of water was dropped on the membrane surface from a micro syringe with a stainless steel needle in room temperature (21$\underline{+}$1^{o}C). At least seven measurements of drops at different locations were averaged to obtain CA for one membrane sample.

Surface chemistry by ATR-FTIR spectroscopy

The membrane surface chemistry was analyzed by using the instrument Varian 3100 Fourier transform infrared spectroscopy (FTIR) Excalibur series. A total of 64 scans were performed at a resolution of 4 cm^{-1} and the temperature of 21+1°C. The Varian's Resolution Pro 4.0 was used to record the membrane spectra versus the corresponding background spectra.

Stability test

The stability of macromolecular additive in membrane polymer matrix was examined by incubating membrane samples in water (20 and 40^{o}C) for up to 10 days. Water is usually used for membrane washing before chemical cleaning will be done. In many of the cases, cleaning is done with help with slight heating. Surface hydrophilicity (by CA) was used to investigate change in membrane characteristic.

RESULTS AND DISCUSSIONS

Membrane Compaction and Hydraulic Permeability

In this part, pure water flux behavior during compaction was studied. The membranes were pressurized at high pressure (450 kPa) for 2 h. Fig. 2 shows an example of the water flux profile over time during compaction for all membranes. Indeed, gradual decrease in flux over the duration of compaction time was observed for all membranes, and flux reached a steady value after ~60 min of compaction. The steady fluxes were ~80%, ~40% and ~60% of the initial flux for PES (only), PES-PEG and PES-Plu, respectively. Interestingly, membrane prepared by using Pluronic as the additive had initially lower flux than membrane prepared using PEG as the additive, but beyond 30 min duration of compaction it showed higher flux. Because all membranes had asymmetric structure (cf.

SEM images), the compaction at high pressure would cause densification of the more porous support layer leading to a thickening of the skin layer (selective barrier). Consequently, thicker membrane would result in lower flux. Such phenomenon had been observed in the previously reported literature (Reinsch *et al.*, 2000; Brinkert *et al.*, 1993).

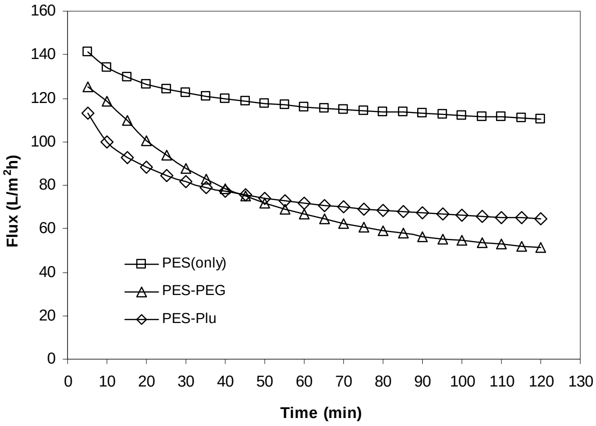

Fig. 2. Water flux profile over time during compaction at pressure of 450 kPa

Table 1 shows the hydraulic permeability of dried membrane measured after 1 h of compaction. It is important to mention that drying significantly decreased the hydraulic permeability of membrane (data not shown). In general, addition of a hydrophilic polymer can facilitate liquid demixing because the system will be closer to phase separation on the one hand, and slow down phase separation by hindering non solvent inflow to the polymer-solvent mixture (delayed demixing) due to higher viscosity on the other hand. By contrast, the polymer solution without an additive would facilitate faster solvent exchange due to much lower viscosity. It was reported that addition of 10% of PVP or PEG into 20% of PES in NMP solution increased the casting solution viscosity up to more 200% (from 0.70 Pa∗s to 2.75 Pa∗s) (Torrestiana-Sanchez *et al.*, 2001). In this work, the hydraulic permeability data of wet membranes (data not shown) showed that addition of a hydrophilic polymer increased the resulting water flux suggesting that the effect of delayed demixing was less significant compared to the effect of instantaneous liquid demixing.

Table 1. Hydraulic membrane permeability measured after 1 h compaction

No	Membrane	Lp (L/m^{2}hkPa)
1	PES	0.251 ± 0.16
2	PRS-PEG	0.101 ± 0.02
3	PES-Plu	0.131 ± 0.04

Membrane Morphology

As presented in Fig. 3, all membranes had asymmetric structure consisting of a thin fine porous structure selective barrier and a much thicker porous sub-structure. The phenomena behind the formation of this typical structure had been explained in many previous publications (Boom *et al.*, 1992; Wienk *et al.*, 1996). Visualization of surface morphology showed that the membrane surface had fine pore structure with dimensions in the nanometer range (< 10 nm). Comparing surface images of PES (only), PES-PEG and PES-Plu membranes, it appears that the PES-Plu membrane had the largest pore size. Nevertheless, it seems that the pore density of PES (only) membrane is higher than that of the PES-Plu membrane. Thus, smaller pore size but higher pore density for PES (only) compared to PES-Plu supports the previous discussion of hydraulic permeability.

Membrane surface hydrophilicity

It is seen in Fig. 4 that PES membrane without an additive had lower CA (~65°) than typically measured for non-porous PES film (~76°) (Susanto *et al.*, 2007). Porous structure in the outer membrane surface would be the reason for this difference. Therefore, care should be taken to interpret the CA results because the value is influenced not only by membrane material but also by surface porosity. Indeed, such effect is observed by comparing the CA data of PES (only), PES-PEG and PES-Plu membranes. The membrane prepared without an additive showed similar CA with membrane prepared with a hydrophilic additive. This could be explained because the PES (only) membrane had higher surface porosity as noticed by its higher permeability. Comparing the CA data of PES–PEG and PES-Plu membranes suggests that the contribution of hydrophobic part of block copolymer in Pluronic could be observed. It is interesting to note that PES-PEG membrane had significantly lower CA compared to other membranes indicating that it is the most hydrophilic membrane.

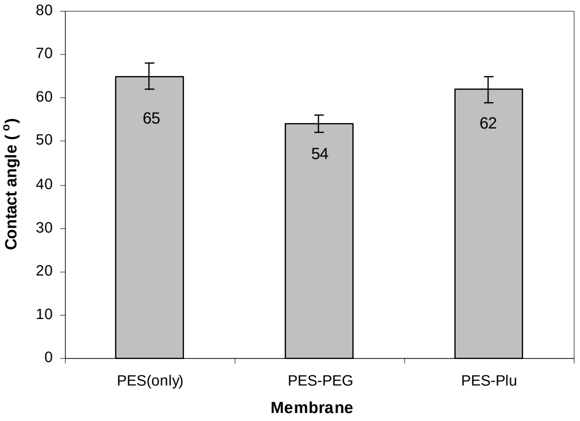

Fig. 4. Static contact angle (CA) measured by sessile drop method. The error bars represent standard deviation

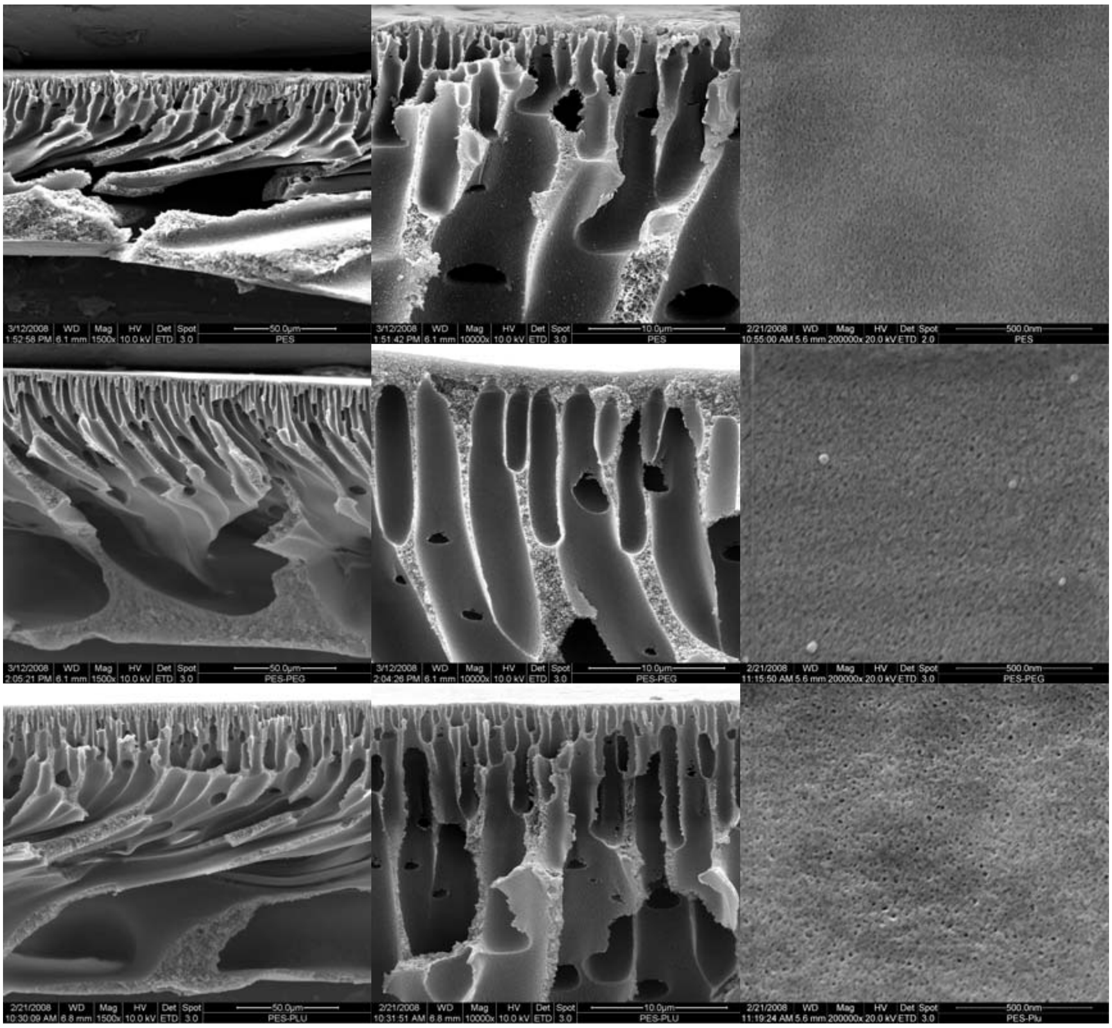

Fig. 3. SEM images of the cross section and membrane surface morphology: from the top to the bottom panel: PES (only), PES-PEG and PES-Plu, respectively.

Membranes surface chemistry

Fig. 5 shows the IR spectra of Pluronic additive used and of the membranes prepared with different polymer composition.

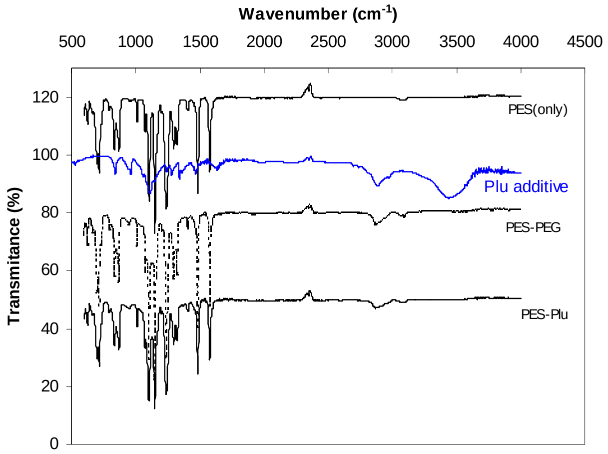

Fig. 5. FT-IR spectra of Pluronic additive and the membranes with different polymer composition

As expected, all membranes showed typical spectra of PES, i.e., aromatic bands at 1578 and 1485 cm^{-1} from the benzene ring and C = C bond stretch and aromatic ether band around 1240 cm^{-1}. No addition of peak was observed for the membranes prepared with addition of PEG or Plu. The reason for this result would be overlapping bands of the strongest bands for PEG and Plu (ether) with bands for PES. Indeed, a significant increase in transmittance at ~1105 cm^{-1}, due to additional intensity of C–O bond stretch (from PEG and Plu) was observed and this confirms the presence of the additives in the polymer membrane matrix. Overall, the IR spectra data indicate that changes in surface chemistry were detected after addition of Plu or PEG to the polymer membrane solution.

Adsorptive Fouling and Ultrafiltration Behavior

Adsorptive fouling and ultrafiltration were used to examine the influence of Pluronic additive on membrane performance. Adsorptive fouling was studied by exposing the outer membrane surface (selective barrier side) to protein (BSA) feed solution.

The relative water flux reduction (RFR) was used to identify the extent of adsorptive fouling. As clearly seen in Fig. 6, the membranes prepared with an addition of hydrophilic modifier show significantly higher resistance towards adsorptive fouling than the membrane prepared without an additive as noticed by their much lower RFR. It should be kept in mind that the effects of adsorptive fouling depend also on the barrier pore size, and the highest flux reductions were found for matching pores and solute sizes (Susanto *et al.*, 2007); but considering that the pore size distributions were different but still in the same range (cf. Fig. 3), the hydrophobicity of PES seemed to have an additional impact on RFR. This suggests that blending of hydrophilic macromolecular additive with polymer membrane could indeed significantly increase the hydrophilicity of the resulting membrane. PES-PEG membrane showed the lower RFR than the membranes prepared with addition of Pluronic. This result can be explained by the highest hydrophilicity of this membrane (cf. Fig. 4). It should be noted the protein in solution had negative charge and electrostatic interactions should not play a role.

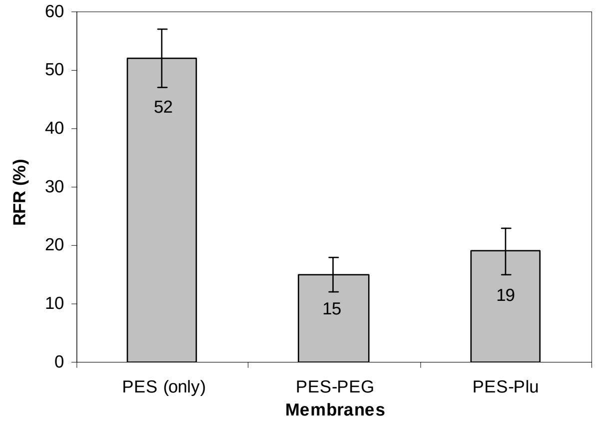

Fig. 6. Relative flux reduction after static adsorption using BSA (1 g/L in phosphate buffer 0.05 M, pH 7, 3 h exposure). The error bars represent standard deviation

Dead end stirred ultrafiltration with constant trans-membrane pressure (300 kPa) was performed to investigate the UF performance. The results are presented in terms of permeate flux relative to initial water flux (Fig. 7). It was observed that permeate flux dropped rapidly in the beginning of filtration for all membranes. On the one hand, this phenomenon indicates that concentration polarization has taken place. On the other hand, difference in flux profile for the membranes having similar rejection curve (PES-PEG and PES-Plu, data not shown) suggests that fouling also contributed to the permeate flux decline. Water flux measurements after external cleaning using water confirmed that both reversible and irreversible fouling have occurred. Furthermore, higher increase in water flux after external cleaning compared to permeate flux for membranes prepared with an additive implies that reversible fouling was more significant for those membranes than for the membrane prepared without an additive (data not shown). It is interesting to note that the PES (only) membrane had the highest permeability and a distinctly different pore size distribution. The higher observed BSA rejection could then be due to fouling (cf. below).

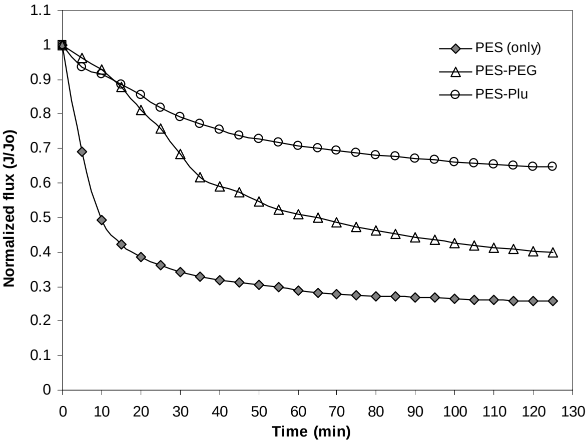

Fig. 7. Normalized flux during ultrafiltration of BSA solutions (0.1 g/L in phosphate buffer 0.05 M, pH 7) at a trans-membrane pressure of 300 kPa.

Indeed, the presence of PEG or Pluronic increased the normalized flux indicating higher resistance towards fouling has been obtained. The membrane prepared without an additive had permeate flux of only ~30% relative to the initial water flux, whereas the PES-Plu membrane had the highest permeate flux (more than 70%). Of course, the highest initial flux of the membrane without an additive also contributed to the lowest normalized flux but the effect of hydrophilic modifier was quite clear. Interestingly, at the beginning of filtration PES-PEG membrane had higher normalized flux than PES-Plu membrane but further decrease with filtration time was more significant. The possible reason for this phenomenon would be the stability of the additive in the matrix polymer membrane (cf. stability test part).

Rejection data presented in Table 2 show that the PES membrane prepared without an additive had the highest protein rejection while all membranes prepared with an additive showed similar protein rejection. This result is in good agreement with rejection curve if the molar mass of BSA is fitted. In general, performance test showed that the membrane prepared with addition of Pluronic as modifier agent showed the best performance, i.e., the lowest flux decline and similar rejection could be obtained.

Table 2. Apparent protein rejection

No	Membrane	Rejection (%)
1	PES(only)	87
2	PESS-PEG	75
3	PES-Plu	72

Stability Test Study

In this work, the stability of hydrophilic additive in water (20 and 40^{o}C) was investigated. Contact angle was used as indicator to evaluate the membrane stability.

Fig. 8 shows that no change in CA was observed for the PES (only) membrane after soaking in water (40^{o}C). For the membranes prepared with an additive, soaking in the water 40^{o}C did not change the CA of PES-Plu membranes. Indeed, significant increase in CA was observed for PES-PEG after incubating in water even only after 2 days of incubating. This indicates that the stability of PEG in the matrix membrane polymer was quite low. Consequently, hydrophilic character of the resulting membrane would easily be reduced even only water is used for cleaning. Similar results with respect to stability in water at 40^{o}C were found during stability test in water at 20^{o}C (data not shown).

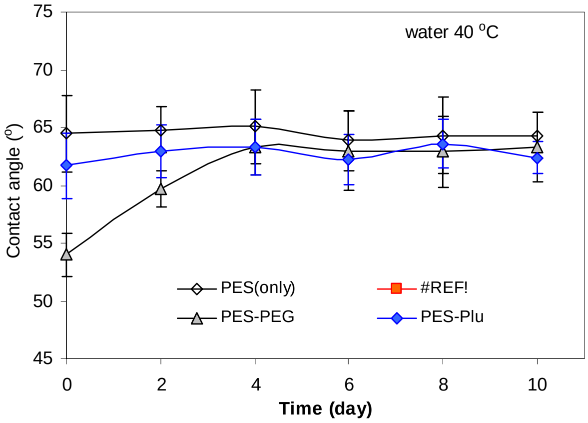

Fig. 8. Stability test in water (40^{o}C) investigated by measuring the contact angle as a function of incubating time.

CONCLUSIONS

The effects of Pluronic and PEG (for comparison) on the characteristics, performance and stability of PES membranes prepared by phase inversion have been investigated. Indeed, the presence of those macromolecular additives in polymer membrane matrix as noticed by FTIR data significantly determined the characteristic as well as performance of the resulting membranes. This observation was confirmed by investigation of PES membrane prepared without an additive as comparison. PES membrane prepared with addition of Pluronic (PES-Plu) showed the higher hydraulic permeability than PES-PEG. Surface hydrophilicity measured with CA indicates that the PES-PEG membrane was the most hydrophilic membrane; nevertheless, the stability of that macromolecular additive within the membrane polymer matrix was the most crucial problem. Performance evaluation via investigation of adsorptive fouling and ultrafiltration using BSA suggests that PES-PEG membrane showed the lowest RFR after static adsorption followed by PES-Plu. Ultrafiltration experiments demonstrated that the antifouling effects of PES-Plu were the most efficient at similar protein rejection: Permeate flux during ultrafiltration of PES-Plu was much higher than of PES-PEG membrane, and more than 70% of the initial water flux could be recovered after UF just by external cleaning with water. Overall, performance test and stability study suggest that amphiphilic Pluronic could increase performance of PES UF membrane and long term modification effect could be obtained.

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REFERENCES

Baker, R.W., (2004), *Membrane Technology and Applications*, 2nd ed., John Wiley & Sons, Ltd., Chichester.

Boom, R.M., Reinders, H.W., Rolevink, H.H.W., van den Boomgaard, Th., and Smolders, C.A., (1994), Equilibrium thermodynamics of a quaternary membrane-forming system with two polymers. I. Experiments, *Macromolecules*, 27, 2041.

Boom, R.M., Wienk, I.M., Van den Boomgaard, Th., and Smolders, C.A. (1992), Microstructures in phase inversion membranes. Part 2. The role of a polymeric additive, *J. Membr. Sci.* 73, 277.

Cheryan, M., (1998), *Ultrafiltration and microfiltration handbook*, Technomic Publishing Company Inc., Pennsylvania.

Girard, B. and Fukumoto, L.R., (2000), Membrane processing of fruit juices and beverages: a review, *Critical Rev. Biotechnol.* 20 (2), 109.

Idris, A., Zain, N.M, and Noordin, M.Y., (2007), Synthesis, characterization and performance of asymmetric polyetehrsulfone (PES) ultrafiltration membranes with polyethylene glycol of different molecular weights as additives, *Desalination*, 207, 324.

Jönsson, A.S. and Trägårdh, G., (1990), Ultrafiltration applications, *Desalination* 77, 135.

Lafreniere, L.Y., Talbot, F.D.F, Matsuura, T., and Sourirajan, S., (1987), Effect of polyvinylpyrrolidone additive on the performance of polyethersulfone ultrafiltration membranes, *Ind. Eng. Chem. Res*, 26, 2385.

Liu, Y., Koops, G.H., and Strathmann, H., (2003), Characterization of morphology controlled polyethersulfone hollow fiber membrane by the addition of polyethylene glycol to the dope and bore liquid solution, *J. Membr. Sci.*, 223, 187.

Marchese, J., Ponce, M., Ochoa, N.A., Pradanos, P., Palacio, L., and Hernandez, A., (2003), Fouling behaviour of polyethersulfone UF membranes made with different PVP, *J. Membr. Sci.*, 211, 1.

Mosqueda-Jimenez, D.B., Narbaitz, R.M., Matsuura, T., Chowdhury, G., Pleizier, G., and Santerre, J.P., (2004), Influence of processing conditions on the properties of ultrafiltration membranes, *J. Membr. Sci.*, 231, 209.

Reinsch, V.E., Greenberg, A.R., Kelley, S.S., Peterson, R., and Bond, L.J., (2000), A new technique for the simultaneous, real-time measurement of membrane compaction and performance during exposure to high-pressure gas, *J. Membr. Sci.*, 171, 217.

Susanto, H., Franzka, S., and Ulbricht, M., (2007), Dextran fouling of polyethersulfone ultrafiltration membranes–Causes, extent and consequences, *J. Membr. Sci.*, 296, 147.

Susanto, H. and Ulbricht, M., (2009), *Polymeric membranes for molecular separations*, in E. Drioli, L. Giorno (Eds), Membrane operations. Innovative Separations and Transformations, Wiley – VCH, Weinheim.

Torrestiana-Sanchez, B., Ortiz-Basurto, R.I, and Fuente, E.B., (1999), Effect of nonsolvents on properties of spinning solutions and polyethersulfone hollow fiber ultrafiltration membranes, *J. Membr. Sci.*, 152, 19.

Van Reis, R. and Zydney, A., (2007), Bioprocess membrane technology, *J. Membr. Sci.*, 297, 16.

Wienk, M., Boom, R.M., Beerlage, M.A.M., Bulte, A.M.W, and Smolders, C.A., (1996), Recent advances in the formation of phase inversion membranes made from amorphous or semi-crystalline polymers, *J. Membr. Sci.*, 113, 361.

Yeo, H.T, Lee, S.T., and Han, M.J., (2000), Role of polymer additive in casting solution in preparation of phase inversion polysulfone membranes, *J. Chem. Eng. Japan*, 33, 180.