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INFLUENCE OF ACETONE ON THE PERFORMANCE OF POLYETHERSULFONE MEMBRANES

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ABSTRACT

In this study polyethersulfone (PES) ultrafiltration (UF) membrane were prepared from mixtures of two solvents containing N,N-dimethylformamide (DMF) as core solvent, acetone (AC) as co-solvent and tape water were used as coagulant bath. Throughout the study, the concentration of PES is kept fixed at 20 wt % and the AC is varied in the range of 20-25wt. %. The dope solutions were prepared under closed heating system and PES asymmetric membrane was cast by dry/wet phase inversion process. The solution viscosity was measured using a standard Brookfield viscometer. Membrane performance was characterized in terms of pure water permeation (PWP), permeation rate (PR) and solute separation of polyethylene glycol (PEG) solution of various molecular weights ranging from 600-35000 Dalton. Results revealed that the 22 wt% AC exhibits the best performance with MWCO at 90% rejection in the range of 9.13 kDa and low flux range of 6.70 (L.m^{-2}. hr^{-1}).

Keywords: Asymmetric, Polyethersulfone, Mixtures, Solvents.

1. INTRODUCTION

The introduction of additive or non solvent into casting solutions plays a significant role in the formation process of macrovoids. The important effects of this non solvent are suppression of macrovoids, improved interconnectivity of the pores and higher porosities in the top-layer and sub-layer [1-4]. The presence of the non solvents in the dope not only changes the thermodynamic state of the dope but also influences the conformation and dynamics of the polymer, which affects the kinetics of phase separation in turn. Several authors [5-10] have studied the performance and microstructures of polysulfone membranes with polyvinyl pyrrolidone (PVP) as additive. Hwang et al [11] prepared PES asymmetric membranes with a co-solvent system of dichloromethane and NMP as volatile and nonvolatile solvent, respectively, and the effect of PVP additive was examined in terms of pure water flux and solute rejection of the membrane. Kim and Lee [12] investigated the effect of PEG additive as a pore-former on the structure formation of PES membranes and their performances of thermodynamic and kinetic properties in phase inversion process. The effects of the water/PVP or water/PEG mixed non solvent were also studied. Chaturvedi et al. [13] focused on the effects of nature of non solvent, solvent, ambient humidity on membrane performance behavior of PES UF membranes. Xu et al [14] studied the effect of ethanol concentration on characterization and performance of PES hollow fiber UF membranes fabricated using dry/wet spinning process. Besides ethanol, the effect of methanol, n-propanol and water as non-solvent additives were also investigated. In another paper [15, 16] PVP and PEG were used as additives and NMP as solvent. Extensive research has been carried out to study the influence of additive such as PEG and PVP, on morphology and performance of polysulfone-NMP and PES-NMP membranes. However, very little is known regarding the usage of halogenated-based additives [17-21].

So far, study on acetone has been extensively performed. Ohya et al 1996. has reported that the addition of acetone in polymer solution has decreased the permeability but incredibly enhanced the solute rejection [22]. While Barth et al. investigated the physical properties of PSf-DMF-acetone polymer solution [23]. However, there are no reports yet on the effect of maximum concentration of acetone as co-solvent on the performance of polyether sulfone membranes. Thus, in this research, the effect of maximum concentration acetone as co-solvent on the performance of PES membranes is investigated.

2. EXPERIMENTAL DETAILS

2.1 Materials

PES (Ultrasont E 6020P); weight-average molecular weight (*Mw*) 58,000, weight-average molecular weight/number-average molecular weight (M_w/M_n) 3.6 procured from BASF was the base polymer used in the membrane casting solution. Analytical grade N, N-dimethylformamide DMF [HCON $(CH_3)_2$, M=73.10 g/mol] purchased from Merck (Germany) was used as the solvent. Commercial grade acetone was used as co-solvent in this study. Water was used as the coagulation bath. For the ultrafiltration experiments, PEG with various molecular weights (from PEG 600 to PEG 40000), were obtained from Fluka and used as the testing solution.

2.2. Preparation of Dope Solution

The dope solutions prepared consist of 20% PES and various compositions of DMF and acetone as tabulated in Table 1. The polymer dissolution process was carried out in a 1 liter 4 necked round bottomed flask with stainless steel stirrer and reflux condenser as described elsewhere [24]. Barnstead electro thermal heater with a rating of 230V~50/60 H_Z, 300 Watts was used. The dope temperature was kept constant at 90-95 ^oC for single solvent and 55-58 57 ^oC for double solvent by stirring at the rate of 1200 rpm. Dissolution of the polymer and additive took 7 hrs.

Table 1: Dope composition

Membr. No.	PES% Wt. %	DMF Wt. %	Acetone Wt. %
1	20	80	0
2	20	60	20
3	20	59	21
4	20	58	22
5	20	57	23
6	20	56	24
7	20	55	25

2.3. Viscosity Measurement of Dope Solutions

The average apparent viscosities of polymer dope solutions were measured using Brookfield Digital Rheometer (mode1 DV-III, USA) equipped with a suitable sample adaptor (SC4-31). At each dope solution concentration, spindle SC4-31 which is a high-viscosity adaptor was used at different shear rates (3.4-44.2 sec-1) as a function of time and at 25 ^oC.

2.4. Membrane Casting

The dope solution was poured onto a clean glass plate at room temperature and it was casted on a glass plate using a casting knife with a thickness of 200 μm. Immediately after casting, the glass plate with the casted film was dipped into ordinary tap water at room temperature. After few minutes, a thin polymeric film separated out from the glass plate due to the phase inversion process. The membrane was washed with distilled water and transferred to another container ready to be tested in the cross flow filtration cell. All flat sheet membranes were visually inspected for defects and good areas were chosen for membrane evaluation.

2.5. Membrane Evaluation

The performances of the various lithium halides flat sheet membranes were evaluated in terms of pure water permeation fluxes (PWP), solute permeation fluxes (PR) and solute rejection rates (SR) in a stainless steel cross flow test cell at 3.5 bars [24]. All experiment was conduct at room temperature 25-26 ^oC. Membrane sample with an area of 2.0×10^{-3} m^2 was placed in the cross flow filtration test cell with the active skin layer facing the incoming feed. A minimum of three flat sheet samples were prepared for each condition so as to ensure the reproducibility and the average value was tabulated. Pure water permeation experiments were performed using double distilled deionized water. Pure water permeation fluxes (PWP) and solute permeation fluxes (PR) of membranes were obtained as follows:

$$J=\frac{Q}{\Delta t\times A} \qquad (1)$$

where J is the permeation flux for PEG solution ($Lm^{-2}h^{-1}$) or pure water, Q is the volumetric flow rate of permeate solution and Δt is the permeation time (h).

Solute rejection of membranes were evaluated with various molecular weight PEG solutions ranging from 200 to 36,000 kDa at 3.5 bar. The concentration of PEG solution used was 1000-500 ppm. The concentration of the feed and permeate solution were determined by the method described by Sabde, [20]. The absorbance was measured using the spectrophotometer (Shidmadzu UV-160) at a wavelength of 535 nm against a reagent blank [20]. The membrane solute rejection (*SR*) is defined as

$$SR=\left(1-\frac{C_p}{C_f}\right)\times100\% \qquad (2)$$

where C_f and C_p are the polyethylene glycol concentration in the feed solution and permeate solution, respectively.

3. RESULTS AND DISCUSSION

3.1. Effect of AC on the Viscosity of Dope Solution

Viscosity is considered as one of the important parameters influencing the exchange rate between solvent and non-solvent during the phase inversion process [8]. Therefore, the viscosities of the various dope solutions at different shear rates are illustrated in Fig. 1. Results show that most of the dope solutions prepared by co-solvent have a lower viscosity compared to prepare by PES/DMF dope solution. Specifically, the dope solution prepared by 20-22 wt.% AC has a lower apparent viscosity (approximately 50% lower) than the one prepared using the PES/DMF (Fig. 1). Since DMF penetrates most engineered polymers and makes them swell, therefore higher viscosity might be attributed to the fact that dimethylformamide is as a solvent with low evaporation rate with lepophilic and swilling tendency over AC due to formamide group when this group are heated at around 90-95 ^oC, it will attempt to swell rapidly to the ether group, respectively.

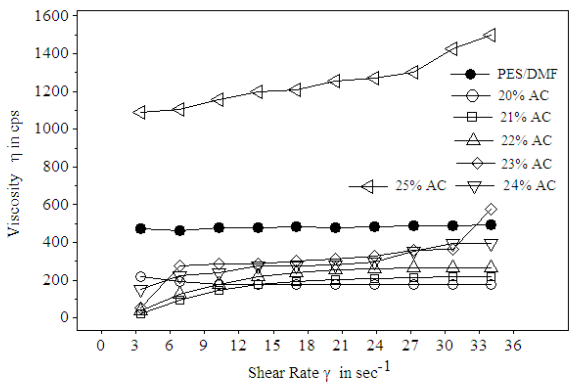

Fig 1. Viscosity versus shear rate of dope solution PES/DMF with various wt.% of AC.

Besides that the drop of dope solution viscosity revealed that with the increase of the AC ratio, the average viscosity was decreased while this behavior is proportional to shear rate, which can be attributed to the higher polarity and boiling point of DMF over that of AC [23]. It can also be concluded that the decreased of solution viscosity with mixture of DMF/AC over DMF due to the nature of two solvents, since DMF is electrophilic solvent and AC is hydrophobic nature for PES therefore, up to particular ratio of AC over DMF were stable foe PES dope solution homogeneity and showed lower viscosity as compare to PES/DMF solution. However, beyond this ratio at 25 wt% of AC the viscosity dramatically increased due to the limited solubility of AC over DMF for PES and we can clearly observed in Fig. 1, this behavior attributed due to hydrophobic and hydrophilic moiety of both solvents for PES. Thus the concentration dependences of some properties exhibit extreme points in the $X = 0.1 - 0.3$ range (from here on, X is the mole fraction of the PES in the mixture). According to the character of AC interaction with DMF, hydrophilic and hydrophobic groups are conventionally distinguished in molecules of PES. It is also attributed that the solvation of PES in DMF/AC type of solvents mainly occurs through charge-dipole type of interaction, in the situation of higher amount of AC, the increment methyl groups of acetone with DMF are responsible for the solvation of the PES. However it is observed that in these solvent mixtures, if increasing the amount of AC for PES shall break these interactions. Iqbal [24] and Wang [25] has also reported similar behavior for PES and PVDF polymer solution.

3.2. Performance of the Membranes

3.2.1. Influence of Acetone on PWP and PR

The pure water permeation rates (PWP) and permeation rate of the membranes 1-7 produced from the various solutions are depicted in Figure 3 and 4. It is observed that the concentration of acetone is increased beyond 25 wt% the PWP rate begins to decreases. However when the concentration of acetone increases the PWP rates decreases up to ratio 20-21 wt.%. The highest PWP rate is obtained when acetone concentration is 23 wt. %. The reason for this behavior could be attributed substantial mixture ratio of DMF/AC for PES due to significant hydrophilic and hydrophobic moiety balance. In general, the single solvent prepared membrane 1 have almost closed PWP rates over AC ratio 20 wt% and this is clearly observed in Table 2. It is believed that the higher viscosity of the single solvent solution compared to DMF/AC mixture solution contributed to different rates of exchange between solvent and non solvent during the precipitation process. The high viscosity solution has the tendency to promote delayed demixing and this feature decreased the membrane resistance and increased the PWP.

The permeate rates (PR) of the single and mixture of DMF/AC solvents prepared membranes are shown in Fig. 2. The results showed that the ratio of AC 23 wt.% over DMF exhibits highest permeation rates when separating various PEG solutions. In general the single solvent membrane has closer PR rate with membrane 2 and 3.

Table 2: Pure water permeation of UF membrane prepared by different wt% of AC.

Membr No.	**P WP** ($L.m^{-2}.hr^{-1}$)
1	8.50
2	8.00
3	9.40
4	10.00
5	25.65
6	14.20
7	8.80

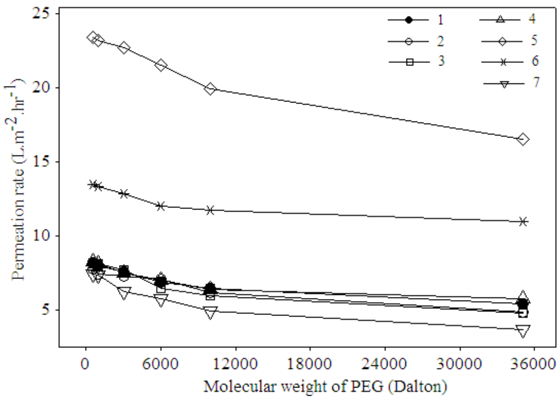

Fig 2. Permeation rate versus different molecular weight of PEG solution (Dalton)

However, when the AC ratio increases up to 23-25 % the PR rates of membrane 4-7 turns to increase but membrane 2-3 results clearly indicate that AC when used at that ratio as co-solvent has reduced the hydrophilic properties of the membrane and this is displayed by the lower PWP and PR rates. On the other hand, in the case of membrane 5 and 6, the PR increased almost 1.6-2.5 times higher as compare to membrane 1, 2, 3. There is the possibility that at this concentration between DMF/AC for PES shows significant balance of the hydrophilic and hydrophobic moieties has prevailed. Whereas the interaction can also be occurs due to hydrogen bonding in water besides the usual ion-dipole interaction between two solvents for PES during phase inversion process.

The overall PWP and PR results indicate that the ratio of AC as a co-solvent has a strong effect on the structure of the casting solution which in turn affects the membrane performance. It appears that the AC nature of the hydrogen bond donating probably the process of attraction and association of two solvents polarities with molecules of PES. the PES polymer by hydrogen bonding with the carbonyl carbon as well as react with the amide solvent altering the solvent power [9]. This could lead to an optimum swelling of the polymer with desirable distribution of the size of the super molecular polymer aggregates and the degree of polymer network within the aggregates. It is significant to note that the casting solution viscosity is lower at control molar volume of AC which is attributed to the balance moieties for PES membrane.

Figure 3 show the rejection rates of the PES/DMF and PES/DMF/AC membranes for the various PEG solutions. Results revealed that the presence of control amount AC has not only improved the permeation rates but also the rejection rates as compared t. Increases in AC concentration to 22-23 wt.% has increased the membrane permeation and rejection rate. In membranes 1, 2 and 3 AC beyond 24-25wt% value does not result in increase rejection and permeation rates. The MWCO of the 4 & 5 membranes at 90% rejection rates is 9.7 kDa and 31.5 kDa with permeation rates of 7 and 17 L.m^{-2}.hr^{-1} for PEG 10,000 and 35000 Dalton solutions. It is observed that using 22-23 wt.% of AC as co-solvent in the casting solutions causes the development of a denser upper coating in the membrane. A further increase in AC beyond 24, 25 wt% of AC does not improve its rejection rates although its permeation rate also decreased. Maximum permeation rate can be obtained at 22 wt% AC with some reduction in rejection rates.

The PES/DMF membranes without AC exhibited MWCO of approximately 37 kDa. Meanwhile the PES/DMF/AC membranes have maximum MWCO around kDa and 39.5 kDa respectively, which is even lower than membrane 1. In general the AC prepared membranes has smaller pore sizes thus explaining for the higher rejection rates. It appears that the presence of control molar volume of AC as co-solvent with DMF has improved the hydrophilic and hydrophobic moieties properties of the membrane thus improving not only the permeation rate but also the rejection rates of the membranes. It seems that AC acts as a pore reducer observed by the reduction in the permeation rate.

MWCO of the membranes and smaller pore sizes, the swelling property is balanced by the introduction of AC thus producing membranes with excellent rejection rates and reasonably high flux. In addition the production cost of the membranes is lower because AC is a cheaper solvent compared to DMF.

Another observation is the good and improved rejection rates observed for all the membranes 1, 2 and 3 compared with the membrane 1. In the AC membranes high rejection rates are contributed to the smaller pore sizes membranes produced as observed in Fig. 3.

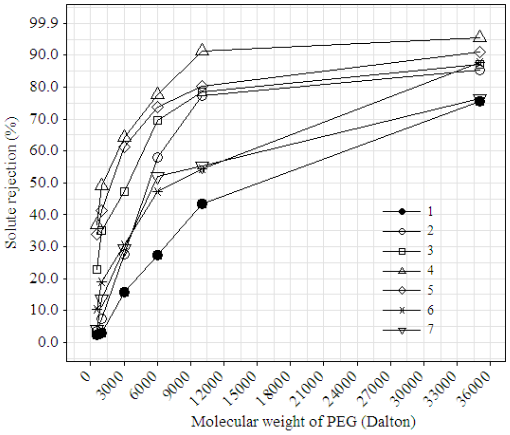

Fig 3. Rejection rate versus different molecular weight of PEG solution (Dalton).

The observation of lowered PR and higher rejection rates in the case of membranes prepared with the low volatile additive AC is confirmed by findings in the literature. Barth [12], who performed the phase inversion and membranes evaluation of PES and PSU with AC exhibiting similar properties, also obtained lower fluxes and higher retention after storing the membrane forming films in water for prolonged times.

4. CONCLUSION

In summary membranes produced from dope solutions containing co-solvent acetone are superior in terms of permeation flux rates, rejection rates and quality of membranes compared to those membranes prepared without AC. The addition of AC to PES-DMF casting solutions has a significant effect on both solution properties as observed from its viscosities. The results indicates that AC interact very strongly with DMF and under closed heating system leading to the formation of DMF-acetone complexes and, hence, retain in the solvation power of DMF for PES. With addition of AC in the casting solution, membranes porosity decreases, asymmetric skin layer becomes very thin, producing membranes with slightly lower permeation rates but excellent the rejection rate.

5. ACKNOWLEDGEMENT

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6. REFERENCES

1. Jung, B. Yoona, J. K., Kima, B. and Rhee, H. W. 2004, “Effect of molecular weight of polymeric additives on formation, permeation properties and hypochlorite treatment of asymmetric polyacrylonitrile membranes”, J.Membr. Sci. 243: 45-57.
2. Tasselli, F., Jansen, J.C. Sidari, F. and Drioli, E., 2005, “Morphology and transport property control of modified poly(ether ether ketone) (PEEKWC) hollow fiber membranes prepared from

PEEKWC/PVP blends: influence of the relative humidity in the air gap", J. Membr. Sci. 243:13-22.

3. Won, J., Kang, Y. S., Park, H. C and Kim, U. Y., 1998, "Light Scattering and Membrane Formation Studies on Polysulfone Solutions in NMP and in Mixed Solvents of NMP and Ethylacetate", J. Membr. Sci. 243: 45-52.
4. Lafreniere, L. Y. Talbot, F. D. F. Matsuura, T and Sourirajan, S., 1987, "Effect of poly(vinylpyrrolidone) additive on the Performance of poly(ether sulfone) Utrafiltration Membranes", Ind, Eng. Chem. Res. 26: 2385-2393.
5. Xu, Z. L. Chung, T. S and Huang, Y., 1999, "Effect of polyvinylpyrrolidone molecular weights on morphology, oil/water separation, mechanical and thermal properties of polyetherimide/polyvinylpyrrolidone hollow fiber membranes", J. Appl. Polym. Sci. 74:2220-2233.
6. Han, M. J and Nam, S. T., 2002, "Thermodynamic and rheological variation in polysulfone solution by PVP and its effects in the preparation of phase inversion membrane", J. Membr. Sci. 202: 55-67.
7. Qin, J. J. Wong, F. S. Li, Y. and Liu, Y. T., 2003, A High Flux Ultrafiltration Membrane Spun from PSU/PVP (K90)/DMF/1,2-propanediol", J. Membr. Sci. 211: 139-145.
8. Sanchez, B. T. Ortiz-Basurto, R. I and Fuente, E. B., 1999, "Effect of Nonsolvents on Properties of Spinning Solutions and Polyethersulfone Hollow Fiber Utrafiltration Membranes", J. Membr. Sci. 152: 19-28.
9. Zaidi, S. K and Kumar, A., 2004, "Effects of Ethanol Concentration on Flux and Gel Formation in Dead end Ultrafiltration of PEG and Dextran", J. Membr. Sci. 237:189-197.
10. Ochoa, N. A., Pradanos, P., Palacia, L., Paglearo, C., Marchese J. and Hernandas, A., 2004," Pore Size Distributions Bsed on AFM Imaging and Retention of Multidisperse Polymer Solutes: Characterisation of Polyethersulfone UF Membranes with Dopes Containing different PVP", J. Membr. Sci. 187: 227–237.
11. Hwang, J. R. Koo, S. H., Kim, J. H., Higuchi, A and Tak,T. M., 1996, Effects of Casting Solution Composition on Performance of Poly(ether sulfone) Membrane", J. Appl. Polym. Sci. 60:1343-1348.
12. Kim, J. H and Lee, K. H., 1998, "Effect of PEG additive on membrane formation by phase inversion", J. Membr. Sci. 138: 153-163.
13. Chaturvedi, B. K., Ghosh, A. K., Ramachandhran, V. Trivedi, M. K., Hanra, M. S and Misra, B. M., 2001, Preparation, Characterization and Performance of Polyethersulfone Ultrafiltration Membranes Desalination 133: 3- 40
14. Xu, Z. L and Qusay, F. A., 2004, "Effect of Polyethylene Gglycol Molecular Weights and Concentrations on Polyethersulfone Hollow Fiber Ultrafiltration Membranes", J. Appl. Polym. Sci. 91: 3398-3407

15 Idris, A., Zain, N, M and Noordin, M. Y., 2007, "Synthesis, Characterization and Performance of Asymmetric Polyethersulfone (PES) Ultrafiltration Membranes with Polyethylene glycol of Different Molecular Weights as Additives. Desalination 207: 324-339

16 Munari, S., Bottino, A., Capannelli, G., Moretti, P. and Bon, P, 1988., "Preparation and Characterization of Polysulfone Polyvinylpyrrolidone Based membranes. Desalination. 70(1-3): 265-275.

17. Zhang, Z., Wang,Y. Y., Wang, C. L and Xiang, H., 2008, "Synthesis and Characterization of a PVA/LiCl Blend Membrane for Air Dehumidification", J. Membr. Sci. 308:198-206.
18. Lee, H. J. Won, J. H and Kanga,Y. S., 2002, "Solution Properties of Poly(amic acid)-NMP Containing LiCl and their Effects on Membrane Morphologies" J. Membr. Sci. 196: 267-277.
19. Ani, I and Iqbal, A., 2007, "Viscosity Behavior of Microwave-Heated and Conventionally Heated Poly(ether sulfone)/Dimethylformamide/Lithium bromide Polymer Solutions ", J. Appl. Polym. Sci. 108:302-307.
20. Sabde, A. D., Trivedi, M. K., Ramachandran, V., Hanra, M. S and Misra, B. M., 1997, "Casting and characterization of cellulose acetate butyrate based UF membranes ", Desalination. 114: 223-232.
21. Singh, S., Khulbe, K. C., Matsuura, T and Ramamurthy, P., 1998, "Membrane Characterization by Solute Transport and Atomic Force Microscopy", J. Membr. Sci. 142: 111-127.
22. Ohya, H., Vladislav, V., Kudryavtsev, Svetlana I. Semenova. (19996). Polyimide membranes: applications, fabrications, and properties. Gordon & Breach, Chapter 5, pp 201-206.
23. Barth, C., Gonçalves, M. C., Pires, A. T. N., Roeder, J and Wolf, B. A., 2000, "Asymmetric Polysulfone And Polyethersulfone Membranes: Effects of Thermodynamic Conditions During Formation on their Performance", J. Membr. Sci. 152: 19-28.
24. Iqbal, A., Ani, I., Nasrul, F. C. P., 2009, "Novel Method of Synthesizing Poly(Ether Sulfone) Membranes Containing Two Solvents and A Lithium Chloride Additive and their Performance", J. Appl. Polym. Sci., Articles online in advance of print.

25 Wang, D., Li, K and Teo.W. K, 1996, "Polyethersulfone hollow fiber gas separation membranes prepared from NMP/alcohol solvent systems", J. Membr. Sci., 115: 85-108.

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