Experimental Design Applied to Fabrication of PSf Membranes via NIPS Method

Part 1: Influential Parameters on Membrane Porosity and Mechanical Strength

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Abstract— **This work involves non solvent induced phase separation method for fabrication of polysulfone (PSf) flat sheet membranes. N-Methyl-2-Pyrrolidon (NMP) serves as the solvent while poly (ethylene glycol) (PEG 20000) is used as additive. A full-factorial experimental design was employed for individual and mutual assessment of parameters in the membranes. In this case, the individual and mutual impacts of such parameters as the polymer concentration, PEG concentration and the coagulation bath composition were investigated on the final structure and function as well as the performance of membranes. The structural analysis included measurement of porosity and observation of SEM images. In order to assess the performance of membranes, mechanical strength measurement was applied. Comparing F-values in the table of data of analysis of variance (ANOVA) indicates that the significance of parameters differs in porosity analysis from tensile strength. The effective parameters in the porosity analysis include, in terms of priority, coagulation bath composition, polymer concentration and PEG concentration while in tensile strength analysis, PEG concentration overtakes polymer concentration. This issue could contribute to simultaneous optimization of porosity and mechanical strength.**

Key words: Micro-porous membrane, Design of Experiments (DOE), porosity, mechanical strength, non solvent induced separation method (NIPS).

I. INTRODUCTION

WIDESPREAD scientific endeavors have been undertaken for membrane processes to replace traditional and customary ones [1]. The final structure and function of membrane depend on the utilized materials and conditions of either formation or fabrication [2]. Polysulfone is one of the most popular materials because of its excellent resistance to inorganic acids and bases, withstands repeated exposure to steam sterilization and good thermal and mechanical properties [3, 4]. It is clear that the mechanical properties of a membrane depend on the structure and distribution of its pores. Finger-like macrovoid is an improper character of membrane if mechanical strength is aimed at, as it causes the membrane's mechanical strength to decline [5,6]. The point is that the viscosity of the polymer solution is closely associated with the density of finger-like macrovoids and this association could deeply affect the structure and function of the fabricated membranes. Several studies conducted so far show that the dope solution viscosity significantly affects the exchange rate of solvent and nonsolvent [1, 7-9]. Studies show that other parameters like the polymer concentration and the presence of additives have to be taken into account as factors affect the viscosity of dope solution. For instance, kinetic examinations show that the additives influence the rate of solvent-nonsolvent exchange in the dope solution as viscosity varies. Therefore, in order to create a spongy structure, reduce finger-like macrovoids and increase bulk porosity, such additives as poly(vinyl pyrrolidone) (PVP) and PEG are used [7,10-18]. Zheng *et al.* [17] studied thermodynamic, rheological and kinetic aspects, caused after adding PEG 200, in the solutions used in formation of polysulfone membranes. The results showed that adding PEG 200 can increase thermodynamic instability and alter rheological properties in the dope solution. Peng *et al.* [5] studied again the impact of polymer concentration and dope solution viscosity on the reduction of finger-like macrovoids in polysulfone hollow fiber membranes. They concluded that the polymer concentration needs to be above a critical level in order to achieve a symmetric structure devoid of finger-like macrovoids. Coagulation bath conditions also constitute a significant parameter affecting the final structure of the membrane. Wijmans *et al.* [19] continued to study the effect of adding a solvent in formation of polysulfone membranes and found that the structure of the membrane surface changed as the bath composition changed from pure water to a water-solvent bath. In the absence of solvent, the outer surface was non-porous; however, the existence of solvent in the coagulation bath caused porosity on the surface. In addition to porosity, the membrane mechanical strength is a key factor in membrane function assessment, notably in high-pressure processes and membrane contactors. Since increase in porosity reduces the mechanical strength of membrane and vice versa, the factors affecting porosity behave differently and they are likely to significantly decrease the mechanical strength following a little bit of increase in the porosity.

Although numerous studies have been conducted on the effect of various parameters on mechanical strength and porosity, however; no accurate study is available regarding

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influential factors.

As mentioned in the previous paragraphs, several articles discussed on the impact of various influential parameters on the membrane structure and performance, however; there is no good conclusion as to how to optimize the membrane porosity and membrane mechanical strength as two main features of membrane functions.

Design of experiments (DOE) is a branch of knowledge helping to measure the impact of influential factors (X1, X2, X3,...) on the outputs (Y1, Y2, Y3,...) under Yi = F(Xi) equation. Some objectives of an experimental design include minimizing the number of tests, saving time and costs, taking into account the persistent and interactional impact of operational parameters and determining significant variables [20]. It is important to know that porosity and tensile strength analysis lie on the extremes. Therefore, measuring the significance of influential parameters would help to calculate the optimum porosity and tensile strength. In other words, a precise control of influential parameters would avoid sharp decline in the tensile strength while we are going to increase membrane porosity. Full factorial design of experiments was preferred as the one of the most popular method in order to minimize errors. The main objective of this study is to assess the significance of such influential factors as the polymer concentration, PEG additive and coagulation bath composition on porosity and mechanical strength of polysulfone membranes. Moreover, the individual and mutual significance and impact of influential parameters have been examined in order to simultaneously optimize porosity and mechanical strength as the structural and functional features of membranes. The next article would probe other factors like water permeability until a useful strategy is presented for simultaneous optimization of the features of membranes in the light of the significance and impact of influential parameters.

II. Materials and Methods

A. *Materials*

Polysulfone (ρ =1250 (kg/m³), T_g=190°C) purchased from Slovay, N-Methyl-2-Pyrrolidon (NMP) (ρ = 1030 (kg/m^3)) purchased from Daejung and poly (ethylene glycol) (PEG) (Mw = 20000(g/g mol)) purchased from Merck. All chemical and reagents were used with no more treatment, unless otherwise described.

B. *Membrane fabrication*

Proper amounts of polymer, additive and solvent are measured for weight and placed in a closed glass container. The mixture was stirred with a magnet stirrer to give a homogenous solution and then enough time was given for bubbles to be completely released. Then a portion of the achieved solution was poured onto flat plate glass and spread out using an automatic casting knife at the speed of 5 mm/sec. The thickness of all membranes was kept constant at 150 micrometers. The glass plate containing polymeric solution was then immersed into the non-solvent coagulation bath for sufficient period of time where phase separation took place to give a porous structure. Coagulation bath solution was changed every 24 hours.

C. *Scanning Electron Microscopy (SEM)*

In order to create cross-section and outer-surface images of the membranes, a scanning electron microscope (SEM LEO 440-I) method was used. The samples were broken in liquid nitrogen after being dried in the ambient temperature. The samples were then stuck on specific holders, gold-sputtered and imaged.

D. *Porosity of membrane*

In this method, the samples were cut in specific sizes before being weighed in a digital balance. After noting their dry weights, the samples were dipped into isobutanol for 24 hours until all their pores were filled with isobutanol. For each membrane, four samples were taken for porosity analysis. The porosity of membranes was calculated using the following equation [21]:

$$\varepsilon = \frac{(w_w - w_d)/\rho_w}{(w_w - w_d)/\rho_w + (w_d/\rho_p)} \times 100 \text{ ,} \qquad (1)$$

where w_w is the mass of wet membrane in g, w_d is the mass of dry membrane in g, ρ_w and ρ_p are the density of isobutanol and polysulfone in (g/cm^3), respectively. In the determination of the membrane porosity, it was ensured that all the pores in the membranes were completely filled with isobutanol.

E. *Mechanical Strength Measurement*

The mechanical strengths of the membranes were measured by STM-5 tensile machine. The samples were cut into 8.0×1.5 cm×cm in length and width, respectively. The effective length was 5 cm and two 1.5 cm edges were stuck in the machine. The thickness of each sample was measured by a micrometer. The tensile speed was 50 mm/min for all samples. Four trials were conducted for each sample and the mean values were reported.

F. *Experimental Design*

From among numerous parameters affecting membrane features, three parameters including polymer concentration, PEG additive concentration and NMP solvent concentration in the coagulation bath were selected to examine the factors affecting porosity and mechanical strength. The results are available in Table I.

Once the tests were conducted, the following calculations were carried out for a statistical analysis of results and study of the impact of parameters:

1- Variance analysis table

2- Degree of freedom for each factor (D_f)

3- Total response squares including sum of squares (AdjSS) and mean square (AdjMS)

4- Variance ration (F-value) and contribution ration (P-value).

To study the individual and mutual impacts of influential parameters on the process, F and P values are required for each impact. P-value is used to assess the impact of a single parameter on a specific response, i.e., when P-value is less than 0.05, the relevant parameter is effective and the more P-value nears zero, the more significant the impact. F-value helps to find out the impact of all parameters on a specific response.

TABLE I
FACTORS AND LEVELS TO BE USED IN FABRICATION OF FLAT PLATE MEMBRANES

Factors for flat sheet membranes	Levels
Polymer concentration (wt.%)	12, 15, 18
PEG concentration (wt.%)	0, 5, 10
NMP concentration in coagulation bath (wt.%)	0, 60

III. RESULTS AND DISCUSSIONS

The results from analyses are fully available in Table II.

A. *Porosity Analysis*

Table III shows the results from data of analysis of variances (ANOVA) for porosity. P value calculations show that all parameters, except for PEG and polymer concentrations mutual impact, are influential on the membrane porosity. F-value is maximal for coagulation bath composition and therefore this parameter is the most influential one. Polymer concentration and PEG concentration come next so that the less F-value, the less degree of importance of parameters. The important point deduced from Table III is the ignorable impact of mutual parameters compared with individual parameters on the porosity.

1) *Effects of Coagulation Bath Conditions on Membrane Porosity*

As Figure 1 shows, the membranes formed in water bath are more porous than those formed in combined water-solvent bath.

This diagram shows identical results for three polymer concentrations in which the trends for all polymer concentrations are similar.

As Sukitpaneenit *et al.* [21] pointed out; the most significant factor in reducing porosity after adding solvent is the decline in finger-like macrovoids. It could be also deduced that in both cases, any increase in NMP results in the membrane porosity decline.

Since the formation of pores in the membrane structure is justified based on the penetration rate of non-solvent into the polymer solution [5], it could be concluded that quick penetration of non-solvent into the polymer solution is an important factor in the formation of finger-like macrovoids. It is clear that the presence of any impurity in the bath could reduce its chemical potential and subsequently the non-solvent thrust. Therefore, the non-solvent penetration rate declines as the solvent concentration increases in the non-solvent coagulation bath. Given the absence of water in the polymer solution, the concentration gradient of water between non-solvent bath and polymer solution is high at the moment the polymer solution is entering the bath and consequently water will penetrate more quickly, raising the possibility of formation of finger-like macrovoids in the membrane structure. However, in the combined water-solvent bath, the solvent reduces water chemical potential as well as the transfer of water into the polymer solution and finally, the size and density of finger-like macrovoids decline. SEM images in Figure 2 confirm this deduction.

TABLE II
OBTAINED RESULTS FROM PERFORMED ANALYSIS ON THE MEMBRANES

Sample #	PSf Conc. (wt. %)	PEG Conc. (wt.%)	NMP Conc. (wt.%)	Porosity (%)	Tensile (Mpa)
1	12	0	0	86.401	3.022
2	12	0	60	83.540	6.780
3	12	5	0	90.323	1.802
4	12	5	60	85.725	4.375
5	12	10	0	91.165	1.147
6	12	10	60	86.210	2.739
7	15	0	0	85.622	4.497
8	15	0	60	80.528	7.105
9	15	5	0	88.611	2.902
10	15	5	60	82.325	5.561
11	15	10	0	89.512	2.341
12	15	10	60	83.389	4.471
13	18	0	0	82.455	4.765
14	18	0	60	78.025	8.070
15	18	5	0	85.205	3.615
16	18	5	60	80.661	6.546
17	18	10	0	85.980	2.925
18	18	10	60	81.720	6.056

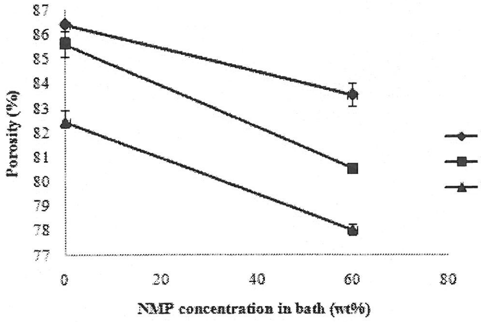
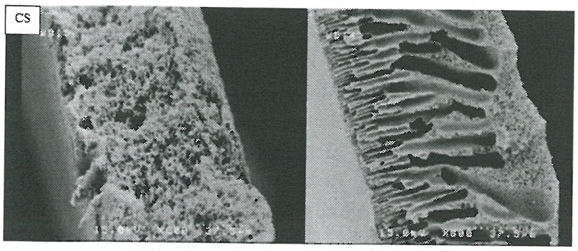


Fig. 1. Diagram of Porosity vs. NMP concentration in coagulation bath for three different polymer concentrations in absence of additive.

Another important point is that the outer surface porosity increases, if solvent is used in the coagulation bath. This phenomenon can be justified by the fact that since polymer is more incompatible with non-solvent, as soon as polymer solutions are placed in the non-solvent bath, polymer chains take orientation so as to avoid penetration of non-solvent. In this way, in the first moments, the solvent exit occurs more rapidly than entrance of non-solvent after the polymer solution is placed in the bath. Therefore, the concentration of polymer-rich phase on the outer surface increases. Given the beginning of phase separation from the outer surface, high concentration of polymer-rich phase in the outer surface means porosity has declined. In the mixed water-solvent bath, the polymer-lean phase would see its concentration rise on the surface and subsequently porosity increases. SEM images in Figure 3 confirm these important conclusions. It is concluded that existence of solvent in the coagulation bath decreases finger-like macrovoids and increases surface pores. Given the point that changes in the condition of coagulation bath brings about reduction in porosity, it could be concluded that finger-like macrovoids contribute further to total porosity, i.e., their reduction in the mixed bath leads to decline in porosity in the mixed solvent-water bath compared with pure water bath.



(a) (b)

Fig. 2. SEM images from cross sections (CS) of 15 wt.% PSf membrane in absence of PEG as additive, (a) Coagulation bath containing NMP and water, (b) Coagulation bath containing only water.

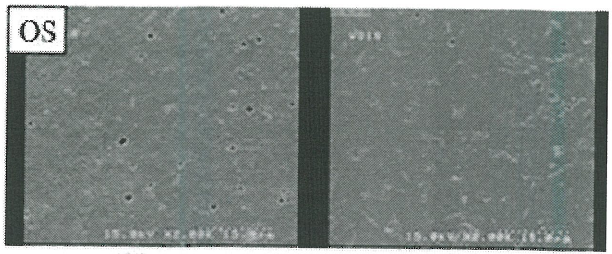
2) Impact of Polymer Concentration

The variance analysis table shows that polymer concentration is the second most influential parameter on the membrane porosity. Figure 4 illustrates changes in the membrane porosity for different polymer concentrations.

As the Figure 4 shows, polymer concentration and membrane porosity are inversely proportionate. Reduction in porosity could be attributed to decline in both surface porosity and finger-like macrovoids. As polymer concentration raises, the viscosity of polymer solution increases, the non-solvent penetration rate into the solution slows down and finger-like macrovoids formation becomes less likely. On the other hand, when the dope solution enters a non-solvent bath, incompatibility between polymer and non-solvent and the difference in their interaction parameter causes the polymer chains take directions so as to keep non-solvent away from the solution. The density of polymer chains increases as the polymer concentration goes up and finally, at the end the concentration of polymer-lean phase on the outer surface becomes less and therefore pores change in terms of quantity and size. Figure 5 shows SEM images taken from the outer surfaces and cross-sections of membranes for two different polymer concentrations. These images show well that the surface porosity and density of finger-like macrovoids are more for 12% concentration than that of 15% concentration.

3) Additives and Membrane Porosity

The concentration of additive is the third important parameter affecting the membrane porosity. As Figure 6 shows, porosity increases when PEG concentration rises. This diagram has been sketched for 15% concentration. Similar trends could be achieved for 12% and 18% concentrations using the data in Table II.



(a) (b)

Fig. 3. SEM images from outer surfaces (OS) of 15wt.% PSf membrane in absence of PEG as additive, (a) Coagulation bath containing NMP and water, (b) Coagulation bath containing only water.

Since the PEG exits from the membrane structure, its dissolution in water results in the formation of pores in the membrane. Therefore, membrane porosity increases when PEG concentration increases. This conclusion matches well with the finding from the literatures [6]. However, the curves in Figure 6 show two different slopes for two PEG concentration ranges which have not been mentioned in any published articles.

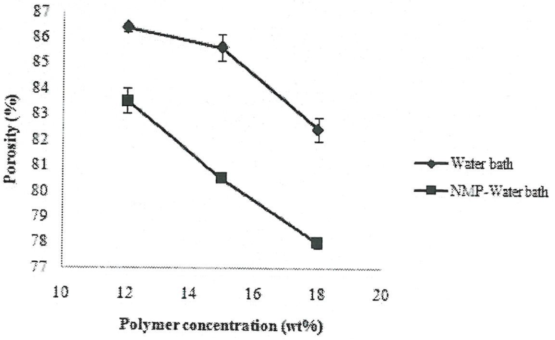


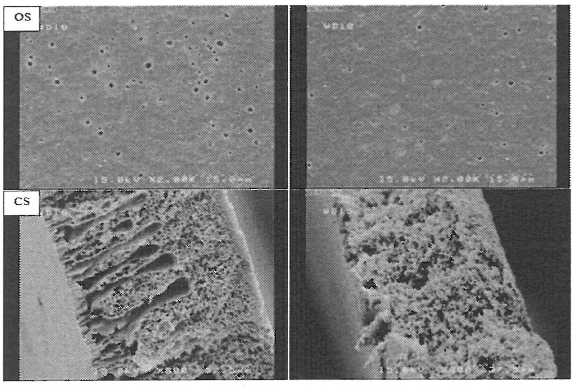
Fig. 4. Diagram of Porosity vs. Polymer concentration in two types of coagulation bath; pure water and mixture of NMP -Water in absence of PEG.

As shown in Figure 6, when PEG concentration varies between 0 and 5%, the slope is higher than when it varies between 5 and 10%. In order to justify this phenomenon, we may say that the porosity measured in this way is a general index showing porosity in depth and porosity on the surface and therefore this phenomenon could be attributed to the possible formation of finger-like macrovoids in low PEG concentrations. PEG is intrinsically hydrophilic, affecting the rate and speed of solvent-nonsolvent exchange in the polymer solution, phase separation and subsequently the final structure of the membrane. Since one of the most important factors

TABLE III
OBTAINED RESULTS FROM ANALYSIS OF VARIANCE OF DATA FOR POROSITY

Parameters	DF	AdjSS	AdjMS	F	P
NMP concentration in bath	1	207.026	207.026	1741.44	0.000
Polymer concentration	2	143.528	71.764	603.660	0.000
PEG concentration	2	83.244	41.622	350.110	0.000
Polymer concentration* NMP concentration in bath	2	4.974	2.487	20.920	0.000
PEG concentration* NMP concentration in bath	2	2.009	1.005	8.450	0.003
Polymer concentration* PEG concentration* NMP concentration in bath	4	1.398	0.349	2.940	0.049
Polymer concentration* PEG concentration	4	0.450	0.112	0.950	0.460
Error	18	2.140	0.119		
Total	35				

contributing to formation of finger-like macrovoids is the rapid penetration of non-solvent into the polymer solution, the presence of PEG in lower viscosities of polymer solutions (concentration 0 to 5%), could increase penetration of water into the polymer film due to its hydrophilic characteristics. This issue would result in formation of bigger finger-like macrovoids that are behind higher porosity for a lower range of PEG concentration. In the same way, the viscosity of the polymer solution rises significantly as PEG concentration varies from five to ten percent and the non-solvent penetrates the polymer film more slowly. The result is that finger-like macrovoids are smaller in higher PEG concentrations. SEM images in Figure 7 show how PEG concentration affects formation of finger-like macrovoids.



(a) (b)

Fig. 5. SEM images of outer surfaces (OS) and Cross sections (CS) of PSf membrane in different polymer concentrations; (a) 12 wt.% PSf and (b) 15wt.% PSf.

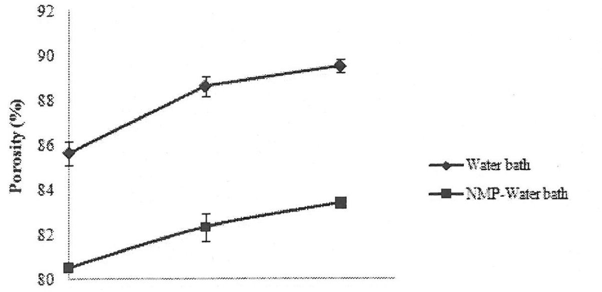


Fig. 6. Diagram of Porosity vs. PEG concentration of 15 wt.% PSf membrane in two types of coagulation bath; pure water and mixture of NMP –Water.

The images show quite well that the finger-like macrovoids get bigger as PEG concentration varies from 0 to 5%. However, the pores get smaller when concentration varies between 5 and 10%. Given the fact that when viscosity is high in polymer solution, the phase separation slows down as non-solvent penetration rate falls, more time is required for the growth of polymer-lean phase. In other words, the time difference between the beginning and end of phase separation causes polymer-lean phase to reach sufficient growth. Outer surface pores get bigger as the growth of polymer-lean phase lasts longer. Therefore, higher PEG concentration in the solution and subsequently higher viscosity lead to formation of bigger pores on the outer surface and the total porosity increases. This result matches well the findings by Kim and Lee [13]. Figure 8 illustrates the effect of PEG concentration on the surface porosity.

When the PEG concentration varies between 5 and 10%, two important factors contribute to porosity. The first one is fewer finger-like macrovoids and the second one is more surface pores. These two factors affect one another and justify slower trend of porosity rise for 5 to 10% PEG concentration.

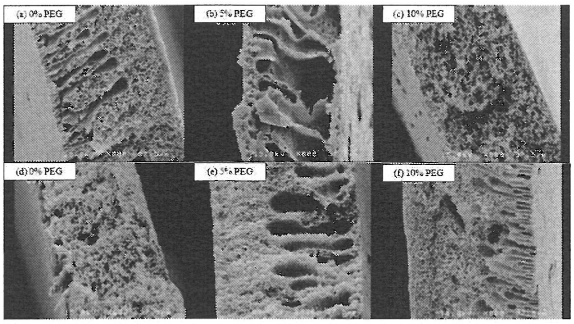


Fig. 7. SEM images of cross sections (CS) of 12 wt.% (a, b, c) and 15 wt.% (d, e, f) PSf membranes in mixed coagulation bath containing NMP and water in presence of various PEG concentrations, 0 wt.%, 5 wt.% and 10 wt.%.

B. Mechanical Strength Analysis

Table IV shows the results from data of analysis of variance (ANOVA) for mechanical strength. As it shows, the coagulation bath composition is still the most influential parameter on the mechanical strength. However, the difference is that PEG concentration is more significant than polymer concentration. Obtained results in this table also show that the parameters are individually more influential than mutual. This is very important finding when simultaneous modification of membrane porosity and membrane mechanical strength is the main target. In the following paragraphs the impacts of influential parameters on the mechanical strength will be discussed.

TABLE IV.

OBTAINED RESULTS FROM ANALYSIS OF VARIANCE OF DATA FOR MECHANICAL STRENGTH

Parameters	DF	AdjSS	AdjMS	F	P
NMP concentration in bath	1	67.722	67.722	926.940	0.000
PEG concentration	2	36.364	18.182	248.861	0.000
Polymer concentration	2	24.653	12.327	168.720	0.000
PEG concentration* NMP concentration in bath	2	1.325	0.663	9.072	0.002
Polymer concentration* NMP concentration in bath	2	0.694	0.347	4.750	0.022
Polymer concentration* PEG concentration* NMP concentration in bath	4	1.267	0.317	4.340	0.012
Polymer concentration* PEG concentration	4	1.069	0.267	3.660	0.024
Error	18	1.315	0.073		
Total	35				

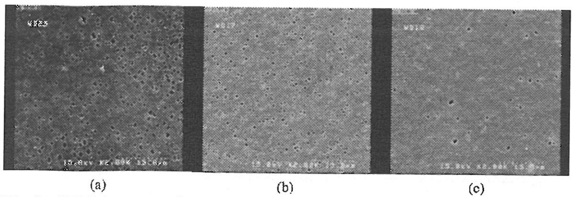


Fig.8. SEM images of outer surfaces of 15 wt.% PSf membrane in mixed coagulation bath containing NMP and water in various PEG concentrations; (a): 10 wt.%, (b) 5 wt.%, (c) 0 wt.%.

1) Bath Conditions Impact on Membrane Mechanical Strength

Figure 9 illustrates changes in the membranes mechanical resistance versus polymer concentrations in two types of coagulation baths. The diagram shows clearly that the membrane mechanical strength is higher in mixed bath than that in pure water bath. Given that porosity and mechanical strength are two features of membranes, they are predicted to be inversely proportionate.

The presence of solvent in the bath is a key to slowing down penetration of non-solvent and subsequently fewer finger-like macrovoids formation. Therefore, the membrane mechanical strength increases as finger-like macrovoids decrease in number.

2) PEG Concentration Effects on Membrane Mechanical Strength

As Figure 10 illustrates, when PEG concentration increases, mechanical strength falls for both states of coagulation bath. This diagram has been sketched for 15% concentration. Similar diagrams however, are achieved for 12% and 18% concentrations using the data in Table II.

Given the fact that PEG concentration increases porosity, it decreases mechanical strength. The diagram in Figure 10 shows different slopes for mechanical strength changes within two PEG concentration ranges. When the PEG concentration varies between 0 and 5%, the slope is steeper. As stated before, within this concentration range, porosity changes more rapidly. Since porosity and mechanical strength lie on the extremes, higher porosity would give out less mechanical strength. When PEG concentration varies between 5 and 10%, the slope is lower. Consequently, mechanical strength would be on a slower downward trend.

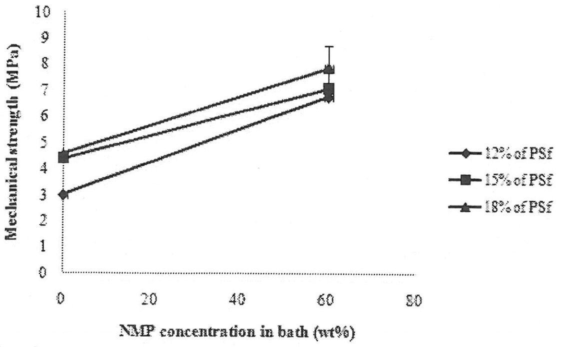


Fig. 9. Diagram of Mechanical strength vs. NMP concentration in coagulation bath for three different polymer concentrations in absence of additive.

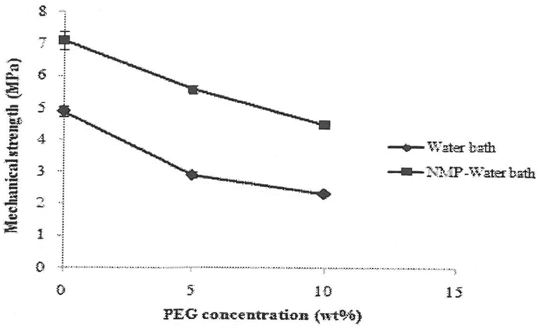


Fig. 10. Diagram of Mechanical strength vs. PEG concentration of 15 wt.% PSf membrane in two types of coagulation bath; pure water and mixture of NMP –Water.

3) Effects of Polymer Concentration on Membrane Mechanical Strength

Figure 11 illustrates mechanical strength versus polymer concentration. This diagram has been sketched for two different compositions of coagulation bath, showing that polymer concentration raises mechanical strength. Similar to the previous cases, it would be due to fewer finger-like macrovoids and surface pores and their smaller size in higher polymer concentrations.

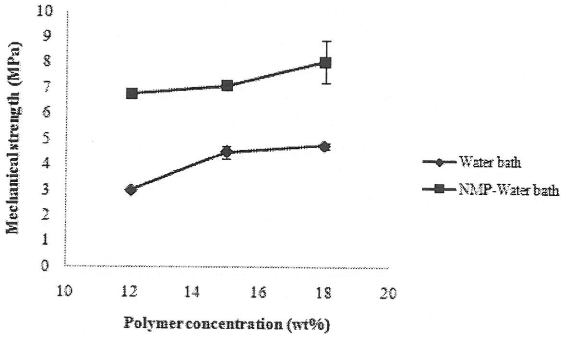


Fig. 11. Diagram of Mechanical strength vs. Polymer concentration in two types of coagulation bath; pure water and mixture of NMP –Water in absence of PEG.

IV. CONCLUSION

Additive PEG concentration, coagulation bath composition and polymer concentration are among the significant parameters affecting the features of membranes. The results showed that the parameters differently affect porosity and tensile strength. The most significant parameters in porosity analysis in terms of priority were bath composition, polymer concentration and PEG concentration, however; order changed to bath composition, PEG concentration and polymer concentration in tensile strength analysis. The difference in the priority of parameters helped prevent excessive decline in the tensile strength when porosity rises, i.e. porosity and tensile strength could be optimized simultaneously due to influential parameters of different degrees of significance. Therefore, porosity and mechanical strength could be simultaneously optimized by modifying influential parameters. In other words, any changes in PEG concentration mainly affect on the mechanical strength and show less impact on the membrane porosity. In order to compensate any decline in membrane porosity we may use lower polymer concentration in which there will be less impact on the membrane mechanical strength.

REFERENCES

[1] S. H. Choi, F. Tasselli, J. C Jansen, G. Barbieri and E. Drioli, "Effect of the preparation conditions on the formation of asymmetric poly (vinylidene fluoride) hollow fibre membranes with a dense skin" *Eur Polym J*, vol. 46, no. 8, pp. 1713–1725, 2010.

[2] P. van de Witte, P. J. Dijkstra, J. W. A. van den Berg and J. Feijen. "Phase separation processes in polymer solutions in relation to membrane formation", *J. Membrane Sci.*, vol. 117, no. 1-2, pp. 1-31, 1996.

[3] H. Ohya, "Fabrication of gradient structure hollow fiber microfiltration membranes using non-solvent induced phase separation", PhD thesis, Tokyo Metropolitan University. Tokyo, Japan, 2009.

[4] D. Nevstrueva, "Preparation of polysulfone membrane", PhD thesis, Lappeenranta University of Technology, Lappeenranta, Finland, 2009.

[5] N. Peng, T. S. Chung and K. Y. Wang, "Macrovoid evolution and critical factors to form macrovoid- free hollow fiber membranes", *J. Membrane Sci.*, vol. 318, no. 1-2, 363–372, 2008.

[6] S. Simone, A. Figoli, A. Criscuoli, M. C. Carnevaleb, A. Rosselli, E. Drioli, "Preparation of hollow fibre membranes from PVDF/PVP blends and their Application in VMD", *J. Membrane Sci.*, vol. 364, no. 1-2, pp. 219–232, 2010.

[7] H. Ohya, S. Shiki and H. Kawakami, "Fabrication study of polysulfone hollow- fiber micro filtration membranes: Optimal dope viscosity for nucleation and growth", *J. Membran Sci.*, vol. 326, no.2, pp. 293–302, 2009.

[8] Q. Yang, T. S. Chung, M. Weber and K. Wollny, "Rheological investigations of linear and hyperbranched polyethersulfone towards their as-spun phase inversion membranes differences", *polymer*, vol. 50, no. pp. 524–533, 2009.

[9] Q. Yang, T. S. Chung and M. Weber, "Microscopic behavior of poly vinyl pyrrolidone hydrophilizing agents on phase inversion poly ether sulfone hollow fiber membranes for hemo filtration", *J. Membrane Sci.*, vol. 326, no. 2, pp. 322–331, 2009.

[10] Y. Liu, G. H. Koops and H. Strathmann, "Characterization of morphology controlled polyether sulfone hollow fiber membranes by the addition of polyethylene glycol to the dope and bore liquid solution", J. Membrane Sci, vol. 223, no.1-2, pp. 187-199, 2003.

[11] B. Chakrabarty, A. K. Ghoshal and M. K. Purkait, "Effect of molecular weight of PEG on membrane morphology and transport properties", *J. Membrane Sci.*, vol. 309, no.1-2, pp. 209-221, 2008.

[12] J. Yan and W. W. Y. Lau, "Effect of internal coagulant on morphology of polysulfone hollow fiber membrane", *Sep. Sci. Technol.*, vol. 33, no. 1, pp. 33-55, 1998.

[13] J. H. Kim and K. H. Lee, "Effect of PEG additive on membrane formation by phase inversion" *J. Membrane Sci.*, vol. 138, no. 2, pp. 153-163, 1998.

[14] G. Arthanareeswaran, D. Mohan and M. Raajenthiren, "Preparation, characterization and performance studies of ultrafiltration, membranes with polymeric additive", *J. Membrane Sci.*, vol. 350, no. 1-2, pp. 130–138, 2010.

[15] S. Deniz, "Characteristics of polycarbonate membranes with poly ethylene glycol prepared via dry/wet-phase inversion methods", *Desalination*, vol. 200, no. 1-3, pp. 42–43, 2006.

[16] I. C. Kim and K. H. Lee, "Effect of poly (ethylene glycol) 200 on the formation of a poly ether imide asymmetric membrane and its performance in aqueous solvent mixture permeation", *J. Membrane Sci.*, vol. 230, no. 1-2, pp. 183–188, 2004.

[17] Q. Z. Zheng, P. Wang and Y. N. Yang, "Rheological and thermodynamic variation in polysulfone solution by PEG introduction and its effect on kinetics of membrane formation via phase-inversion process", *J. Membrane Sci.*, vol. 279, no. 1-2, pp. 230–237, 2006.

[18] C. Shen, Q. Meng and G. Zhang, "Chemical modification of polysulfone membrane by poly ethylene glycol for resisting drug adsorption and self-assembly of hepatocytes" *J. Membrane Sci.*, vol. 369, no. 1-2, pp. 474–481, 2011.

[19] J. G. Wijmans, J. P. B. Baaij and C. A. Smolders, "The mechanism of formation of microporous or skinned membranes produced by immersion precipitation", *J. Membrane. Sci.*, vol. 14, no. 3, pp. 263-274, 1983.

[20] D. C. Montgomery, *Design and Analysis of Experiments (5th ed.)*, New York, Wiley, 1997.

[21] P. Sukitpaneenit, T and S. Chung, "Molecular elucidation of morphology and mechanical properties of PVDF hollow fiber membranes from aspects of phase inversion, crystallization and rheology", *J. Membrane. Sci.*, vol. 340, no. 1-2, pp. 192–205, 2009.