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Effects of water as non-solvent additive on performance of polysulfone ultrafiltration membrane

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Abstract. In this work, polysulfone ultrafiltration membranes were prepared via simple phase inversion with distilled water as non-solvent additive. The main reason for the addition of water in polysulfone dope solution preparation was to enhance the membranes structure. In the dope, 15 wt. % of polysulfone was used and water was varied up to 6 wt. %. The effects of water on morphology, porosity and tensile properties were investigated in detail. From the porosity test, results showed that the addition of water has improved membrane porosity up to 53 %. The FESEM images revealed that membrane morphology has also been modified. However, the tensile properties of membrane decreased as water content increased which may be due to the porosity interaction between polysulfone/NMP with water.

Introduction

Membrane formation via phase inversion with modification of material preparation and processing parameter has been intensively studied nowadays [1-3]. The modification and improvement of membrane structure are directly influenced by the thermodynamic and kinetics behaviour of the membrane during its formation process. In fact, thermodynamic and kinetics are more complex in phase inversion technique as it involve the diffusion and convection with at least three different components e.g. polymer, solvent and nonsolvent [4, 5].

Basically, the process of immersion precipitation involves polymer transformation from dope solution to solid state which known as phase inversion. Generally polymer solution is cast on a suitable support and immerse in a coagulation bath containing nonsolvent. The exchange of solvent and non-solvent in coagulation bath were lead to the formation of precipitation [4]. This process is based on thermodynamic principle, since the starting point is a thermodynamically stable solution which is subjected to demixing. The most frequently used polymer in membrane making process via phase inversion is polysulfone. Polysulfone (PSf) membrane relatively has great mechanical properties, resistance to extreme pH conditions as well as thermally stable. PSf has a T_g of 195 ˚C and soluble in chloroform, dimethylformamide, N-methyl-2-pyrrolidone (NMP) and dimethylacetamide (DMAC). Preparation of PSf via phase inversion method was done by many researchers [2, 6, 7]. Hansen has compiled the solubility data of polysulfone with various solvent based on dispersion, polar and hydrogen bonding parameter. In fact, this solubility parameter is helpful in the selection of best solvent for polysulfone [8].

The capability of non-solvent to act as additives was reported in numbers of papers [4-7]. Wang et al. [8] has studied the effects of water as non-solvent additive on polyethersulfone hollow fiber membrane. They found that pressured normalized fluxes and ideal selectivity of polyethersulfone membrane was increased with water, ethanol and propanol of non-solvent additives. They also reported that the membrane performance with water as additive is higher as compared to alcohol or propionic acid. Whereas, Aroon et al. [4] investigated the effects of ethanol and glycerol as non-solvent additives on the performance of polysulfone gas separation membrane. The non-solvent additives has moved the binodal curve and brought it closer to polymer-solvent

axis which in turn increased the permeability and selectivity of membrane. The effects of non-solvent additives on PVDF hollow fiber membrane has also been reported by Mansourizadeh and Ismail [7]. They found that PVDF/ethanol form finger-like structure which led to a high permeability and low wetting resistance membrane as compared to PVDF/glycerol and PVDF/phosphoric acid.

Generally, the function of water as non-solvent bath in phase inversion process is well understood [9]. However, to date, the previous work on water as non-solvent additives did not provide definitive information on membrane mechanical properties. Thus in this study, the effects of water as non-solvent additive on polysulfone membrane were investigated emphasis on mechanical property.

Experimental

Materials. Dope solutions were prepared using polysulfone (UDEL P1700) as polymeric material and N,N, methyl pyrrolidone (NMP) (MERCK) as solvent. Distilled water was used as non-solvent additive and non-solvent bath. All chemical purchased in this study was used without further purification.

Membrane preparation. For dope preparation, PSf were added slowly into a solution consist of NMP and was stirred until they were completely dissolved. The desired amount of water slowly added into polymer dope under constantly agitation. In cases when local precipitation occurred, agitation was continued until the solution became homogeneous again. Flat sheet membranes were prepared by casting a polymer solution (15 wt % of polysulfone) with different non-solvent additive content on a glass plate. Dope solution was cast on a glass plate with casting knife gap setting of 100 μm at an appropriate casting shear. The thin film was then immersed in water bath until the membrane sheet peel off naturally [10]. The procedures were performed in 25 °C and relative humidity HR 84%.

Scanning Electron microscopy (SEM) examination. Scanning Electron microscope (SEM) was used to examine the morphology of the flat sheet membrane. The membrane were immersed in liquid nitrogen and fractured carefully. Then the samples were coated by sputtering gold before testing.

Porosity and tensile properties. In order to determined membrane porosity, the membrane was first immersed in distilled water for 24 hour at 25 °C. The surface of membrane was then being wiped carefully with tissue paper before weighed in electronic balance, W_w. This wet membrane was dried in over at 60 °C before being weighted again in dry state, W_d. Membrane porosity was determined using following equation [11]:

$$\varepsilon = \frac{W_w - W_d}{\rho_w \times V} \quad (1)$$

where W_w is weight of wet membranes (g), W_d is weight of dry membranes(g), ρ_w is density of pure water at room temperature (g/cm^3) and V is volume of membrane in wet state(cm^3). In order to minimize experimental error, each membrane was measured five times and average was calculated.

Tensile properties were determined by Universal Tensile Machine (Shimadzu). The measurements were carried out at room temperature and a strain rate of 1mm/min was employed. The reported were average of five samples as per standard ASTM D822.

Results and discussions

NMP is a good solvent for polysulfone, therefore it is expected that PSf/NMP mixtures are thermodynamically stable with different PSf concentrations. However, due to crystallization of small oligomer fraction of polysulfone, PSf solution will become turbid after a certain time and precipitated to white-colored form [12] . Therefore in this work, the solution/dope of PSf/NMP were tested immediately once homogenous solution is formed.

Morphology of flat sheet membranes . There are many factors that influenced the formation of membrane structure prepared via phase inversion method. As for example, one of the most critical part during the stirring processis the entrapped bubble that lead to void formation in membrane structure which in turn reduce/affect the membrane performance. Thus it is important to place the dope in ultrasonic bath in order to remove all the bubble. During membrane formation, the addition of small additive i.e water can influence membrane properties [4, 13, 14]. Basically in the phase inversion process, the formation of asymmetric membrane structure depends on the thermodynamic and kinetic effects of dope formulation [15]. In fact, the addition of this small amount of water can reduce thermodynamic miscibility of dope solution and results in faster precipitation of dope and tending to form macrovoid with finger–like structure and sponge-like membrane structure for the slow precipitation process [16].

The SEM images of membrane cross-section are depicted in Figure 1. From the images, it is significant that by increasing water content, the finger-like structure size is increased. This is due to the instantaneous demixing of PSf in NMP solution is increases. It is also shown that as water content in PSf/NMP solution is increased, the dope system is near to cloud point and enhances the formation of phase separation. Therefore, only small amount of water is needed for demixing process. Generally nucleation and growth droplets formed when the stability of solution is being disturbed during the demixing process. Once formed, the droplet has potential to grow because of the presence of a concentration towards the droplet [15]. The figure also displays the sponge-like shape around the finger-like structure which may due to the slow precipitation inside membrane layer. Basically the precipitation process started from the outer surface due to the thermodynamic instability between water in the coagulation bath and the dope. Then it is followed by the diffusion of solvent into the coagulation bath and nonsolvent into the cast film [9]. After the external coagulant penetrates into the membrane depth, the droplets were formed and solidification occurred near the outer surface. This mechanism will drive the solidified walls to extend the droplets along the depth direction, which resulted in finger-like shapes formation. However, since slow solidification was occurred near the inner surface in this work, the wall between droplets was difficult to formed, thus many small droplets combined to form larger droplets which then results in sponge-like shape structure [17].

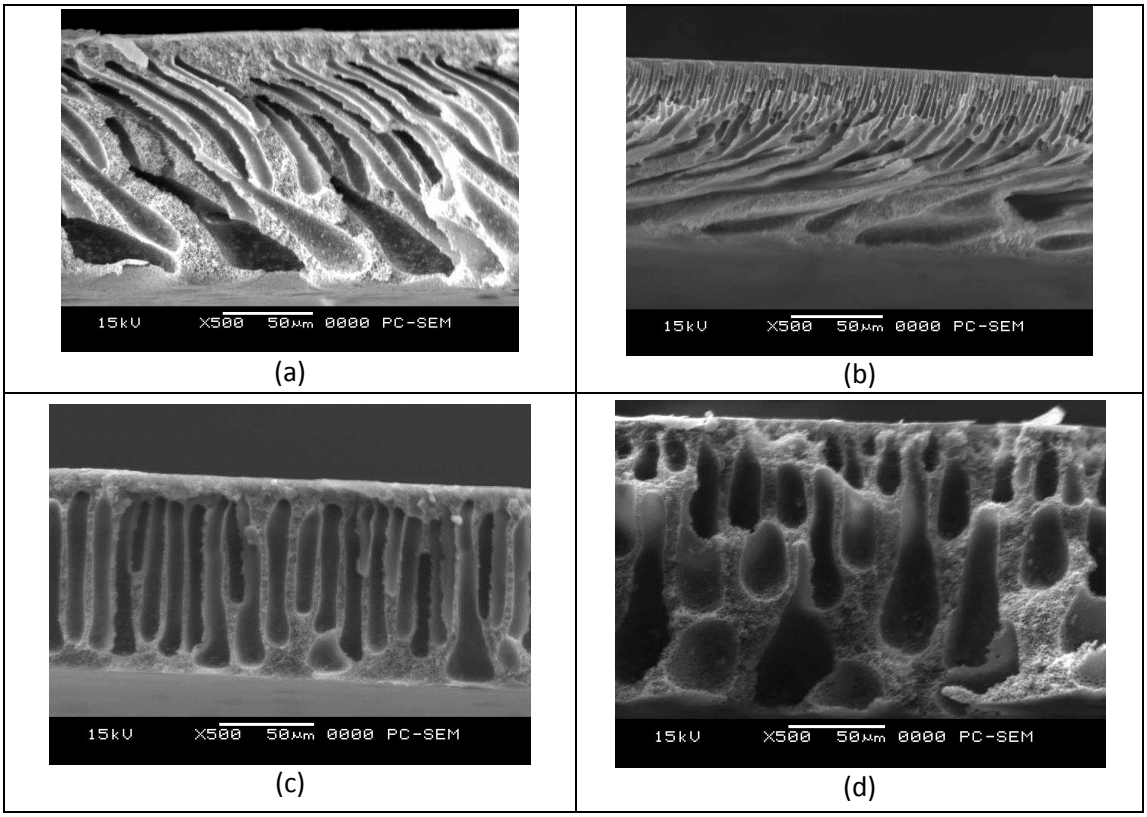

Figure 1: SEM photograph of 15 wt. % of PSf membrane with different weight percentage of water a)0% water b)2% water c)4% water d)6% water

Porosity and Tensile properties. In general, membrane porosity has a direct relationship to the flux permeation, rejection and also mechanical properties of membrane, and can be considered as a key specification factors for the membrane performance. Basically the porosity can be simply defined as weight of water trapped in 1 m^3 of membrane structure. Figure 2 shows the porosity and tensile properties of membrane with different water content in the membrane. It was significant that as the water content increased from 37 % to 53%, the porosity of membrane also increased. This could be directly due to formation of large finger-like and macrovoid structure as shown previously in Figure 1. This phenomena was explained in detail by Zhang et al. [18]. Indeed, they also proved that membrane porosity is strongly related to the kinetic parameter of membrane formation due to faster coagulation process. The tensile strength results of presented in this figure also shows that there is a slight decreases of tensile strength from 4.1 MPa to 3.61 MPa as the water content is increased from 0 wt. % to 6 wt. % of water. The same trend could be found in other documented research papers [19] and as reported, this is due to the existence of porosity that weakens the strength of membrane structure.

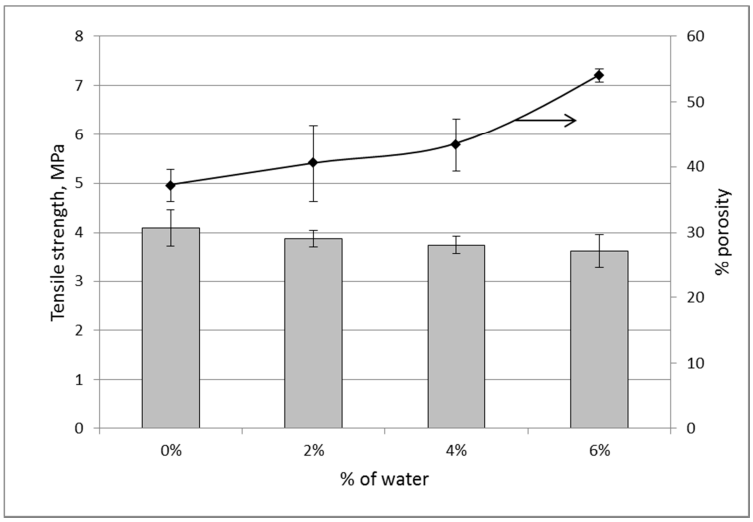

Figure 2: Porosity and tensile property of PSf membrane a different water content

Conclusions

In this work, the effect of different water content as non-solvent additive on polysulfone membranes was investigated. The results revealed that the additions of water improved the membrane porosity evidenced by SEM analyses and porosity test. Meanwhile, the tensile properties of membrane reduced as water content increased which may be due to the porosity interaction between PSf/NMP with water.

Acknowledgements

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References

[1] Ghaemi, N., etc., Journal of Membrane Science, 2011. 382(1-2): p. 135-147.

[2] Hamid, N.A.A., etc., Desalination, 2011. 273(1): p. 85-92.

[3] Idris, A., N. Mat Zain, and M.Y. Noordin, Desalination, 2007. 207(1-3): p. 324-339.

[4] Aroon, M.A., etc, Separation and Purification Technology, 2010. 72(2): p. 194-202.

[5] Boom, R.M., etc., Polymer, 1993. 34(11): p. 2348-2356.

[6] Khayet, M., etc., Desalination, 2002. 148(1-3): p. 321-327.

[7] Mansourizadeh, A. and A.F. Ismail, International Journal of Greenhouse Gas Control, 2011. 5(4): p. 640-648.

[8] Wang, D., K. Li, and W.K. Teo, Journal of Membrane Science, 2000. 176(2): p. 147-158.

[9] Mulder, M.: Basic principles of membrane technology(Kluwer Academic. London 1996)

[10] Basri, H., A.F. Ismail, and M. Aziz, Desalination, 2011. 273(1): p. 72-80.

[11] Chakrabarty, B., A.K. Ghoshal, and M.K. Purkait, Journal of Membrane Science, 2008. 309(1-2): p. 209-221.

[12] Wijmans, J.G., etc., Polymer, 1985. 26(10): p. 1539-1545.

[13] Karimi, M., etc., Journal of Membrane Science, 2007. 292(1-2): p. 80-91.

[14] Han, J., etc., Journal of Membrane Science, 2010. 365(1-2): p. 311-318.

[15] Guillen, G.R., etc., Industrial & Engineering Chemistry Research, 2011. 50(7): p. 3798-3817.

[16] van de Witte, P., etc., Journal of Membrane Science, 1996. 117(1-2): p. 1-31.

[17] Xu, A., etc., Journal of Membrane Science, 2008. 311(1-2): p. 153-158.

[18] Zhang, Z., etc., Desalination, 2011. 269(1-3): p. 239-248.

[19] Ma, Y., etc., Desalination, 2011. 272(1-3): p. 51-58.

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