

Effect of Peg on Polysulfone Support and Reverse Osmosis Membrane Property

Jin Wang¹, Zhijie Zhang¹, Jiarui Li¹, Jiani Zhu¹, Xiaorong Meng², Xiaojun Li³ and Xudong Wang^{1*}

1 School of Environmental and Municipal Engineering, Xi'an University of Architecture and Technology, Xian 710000, China

2 School of Chemistry & Chemical Engineering, Xi'an University of Architecture and Technology, Xian 710000, China

3 Xi'an Thermal Power Research Institute CO., LTD, Xian 710000, China

Corresponding author e-mail:18629407889@126.com

Abstract. A study on the thin film composite on polysulfone support membranes prepared by different casting solution was conducted. The following conclusions can be drawn from this work, the membrane flux increased with increasing PEG concentration and the pore size and the porosity on the membrane surface became bigger by the increase PEG concentration; the permeability of thin film composite membrane was effected by the membrane continuity and the amount of polyamide formed within PSf membrane pores.

1. Introduction

Water resources become to a crucial problem directly related to the sustainable development of the society and economy after human civilization entering a new century [1]. Recently, reverse osmosis (RO) has become a promising water technology, utilizing the selective permeability of semi permeable membrane to eliminate impurity and the supply the clean water [2-3].

The typical RO TFC membranes consist of two parts [4-5]: (1) support substrate(50 m), the polysulfone (PSF) ultrafiltration membrane is the most common use for supporting, (2) thin barrier layer (200 nm), the desalination layer is generated during the interfacial polymerization (IP) interaction formed on the substrate. Researchers focus on the properties of thin barrier layer and neglect the effect of PSF substrate on the water permeability and salt rejection of RO membrane. Until recently, the importance of supporting membrane received more attention [6-8]. Ghosh et al reported that the pore structure and chemistry have a significant influence on interfacial polymerization reaction [7]. However, the manually preparation of PSF supporting membrane could no guarantee the identical casting speed and residence time nascent membrane both in air and coagulation bath [9-10].

In the paper, the preparation of PSF supporting membrane is precisely controlled by a semi-automatic film casting machine, the effect of concentration of PEG-600 on the structure and chemistry property of both supporting membrane and ultra-thin barrier layer additive was investigated, the optimal preparation parameters was confirmed which could provide valuable data and theory foundation on processes optimization of RO membrane.



2. Experimental

2.1 Materials and Chemicals

Polysulfone (PSf) P-3500 was supplied by Solvay. DMF (liquid, analytical reagent grade), polyethylene glycol (PEG, 600Da) m-phenylenediamine (MPD, powder), triethylamine (TEA, liquid, 99.5%), D(+)-10-Camphorsulfonic acid (CSA, powder, 99.0%) and trimesoyl chloride (TMC, powder) was purchased from Sigma-Aldrich. Isopar G used as organic solvent was obtained from Exxon Corp.

2.2 Experimental

2.2.1. Polysulfone (PSf) Membrane Formation

The PSf was measured and separated into 2 pieces and then dried at 125 °C for 3 hours to get rid of the moisture in the PSf particle. A piece of PSf was added into an airtight bottle in which a specified amount of DMF was in a stirring state at 25 °C. The solution was heated to 80 °C after PSf completely dissolved and the rest of the PSf was added and agitated for several hours. PEG was finally added into the above solution when the effects of the PEG additive were studied. The specific composition of casting solutions was provided in Table 1. The casting solution was kept still overnight for degassing. The membrane was formed by spreading the solution over the non-woven support fabric using semi-automatic film casting machine with a gap of 120 µm and then, the non-woven support was immediately immersed into a DI water bath. The PSf membrane was washed thoroughly and stored in the DI water.

Table1. Specific Composition of Casting Solutions and Membrane Number

Membrane	Casting solution (wt.%)			Membrane	Casting solution (wt.%)		
	Polysulfone	DMF	Additive		Polysulfone	DMF	Additive
PSf-1	15	85	-	PSf-4	18	82	-
PSf-2	16	84	-	PSf-5	15	80	5
PSf-3	17	83	-	PSf-6	15	70	15

2.2.2. TFC membrane formation

The PSf membrane was immersed into an aqueous solution contained MPD and other additives for 15 s. The excess aqueous solution was then eliminated from the skin surface via an air knife. After then, the membrane was immersed into the TMC-Isopar G solution for 15 s to initiate the polymerization reaction. The resulting TFC membranes were subsequently heat cured for 6 min at 90 °C. The TFC membranes were finally washed thoroughly to remove any residual solution from the surface by DI water.

2.2.3. Characterization of polysulfone and polyamide membrane

Separation performance of PSf membrane and TFC membrane was evaluated using a cross-flow filtration system with an effective membrane area of 70 cm² at 25 °C. For the PSf membrane, the pure water flux was performed under the pressures of 0 and 0.3 MPa, respectively. For the TFC membrane, the flux and the selectivity were characterized by a 2000 ppm NaCl feed solution under 1.55 MPa. Salt rejections were determined from the conductivity of the feed and permeate water.

The surface and cross-sectional morphology of membranes is visualized by scanning electron microscopy, SEM (Nova Nano SEM 430, FEI Company, Hitachi, Japan). The chemical structure of PA-TFC membranes was characterized using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR).

3. Result and Discussion

3.1. Effect of PSf Concentration on PSf Membrane

The water flux changes of PSf membranes prepared with different PSf concentration are presented in Figure 2. It indicated that the flux of the PSf membrane decreased significantly with the increasing PSf concentration under both 0 MPa and 0.3 MPa, the PSf-1 membrane was the most permeable membrane with the flux of 960 LMH (0 Mpa) and 2400 LMH (0.3 Mpa), whereas the PSf-4 membrane has the lowest flux values of 415 LMH (0 Mpa) and 1048 LMH (0.3 Mpa), respectively. As shown in SEM micrographs, a typical asymmetric membrane structure was observed in all the cross-sectional images, the top-layer of the membrane was dense and the sub-layer where macrovoids existed was sparse. Furthermore, the membrane structure became denser and the quantity of the macrovoids was suppressed with the increasing PSf concentration, the membrane changed to sponge-like structure with few macrovoids when PSf concentration reached 18%. The changes of the membrane structure and permeability could be attributed to the transport rates, the inflow rate of non-solvent (water) and the outflow rate of the solvent (DMF).

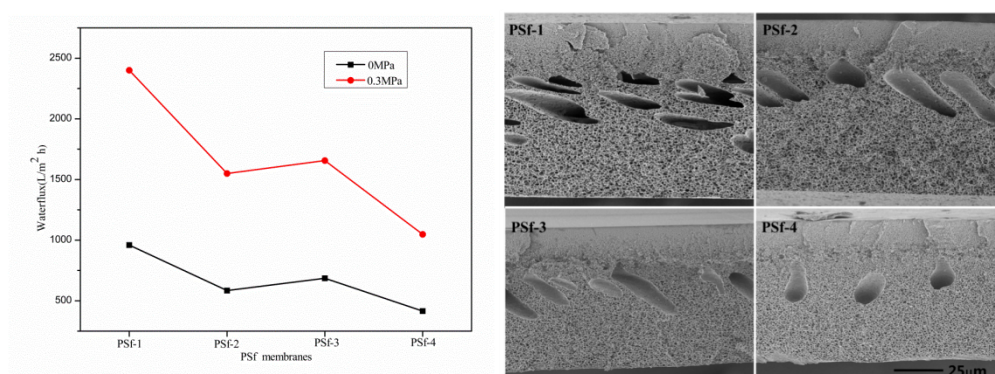


Figure 1. Effect of Polysulfone Content on PSf Membrane Permeability (left), Cross-section Images of PSf Membrane with Different Casting Solution (right)

3.2. Effect of Additive Concentration on PSf Membrane

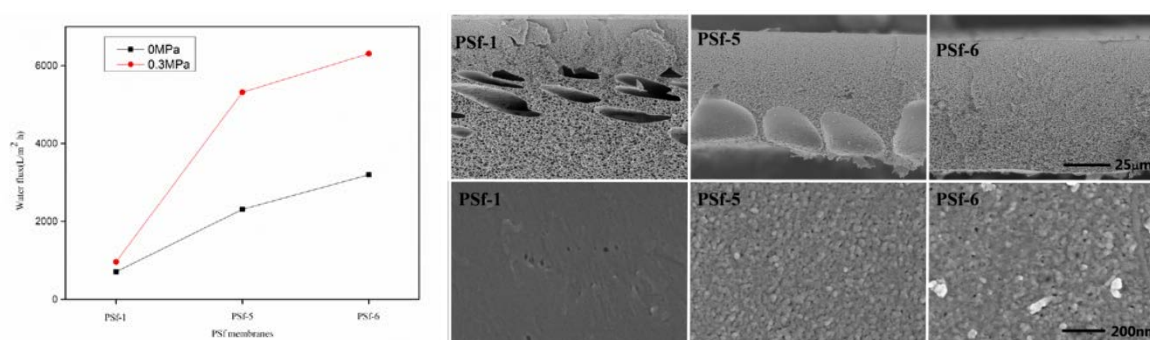


Figure 2. Effect of Additive Content on PSf Membrane Permeability (left); Cross-section and Surface Images of PSf Membrane with Different Additive Concentration (right)

The flux changes of the PSf membrane after adding PEG-600 were presented in Figure 3. From the plot we could clearly observed that the membrane flux increased with increasing the concentration of PEG. The structure of membrane still showed a dense top-layer and sparse sub-layer feature. Moreover, the pore size and the porosity on the membrane surface became bigger by the increase PEG concentration. The structure changes of the membranes could also be considered as the result of the

different diffusion rates. It could be observed from Table 1. That the viscosity of the casting solution increases with increasing the ratio of PEG to DMF. According to the literature, PEG possesses the nonsolvent characteristic for PSf comparing with NMP, the addition of PEG result in the inter-molecular aggregations and entanglements of the polymer chains.

3.3. Effect of PSf Membrane on TFC Membrane

The surface morphology and chemical composition of the TFC membrane on the PSf-1 support membrane are analyzed by SEM and ATR-FTIR as shown in Figure 3.(a) and (b). We could observe a nodular membrane surface under the experimental condition which is different from the classic ridge-and-valley surface features in the literatures. In order to further characterize TFC thin-film layer, ATR-FTIR spectroscopy was used to identify the main functional groups, indicated that a successful polymerization process had occurred.

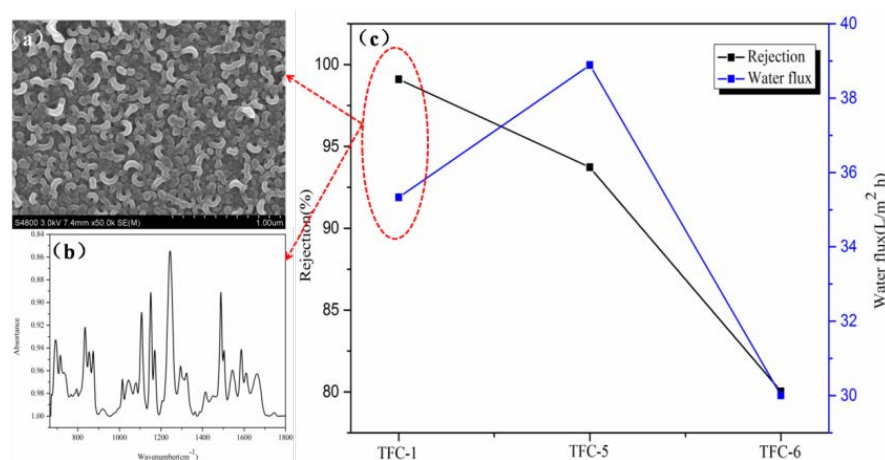


Figure 3. Influence of PSf Membranes on TFC Membranes. (a) The Surface Image (TFC-1); (b) The ATR-FTIR Spectra (TFC-1); (c) The Permeability Performance of TFC Membranes

Figure 3.(c) resents the changes of TFC membranes permeability synthesized on different support layer surface. It clearly appeared that the PSf membrane has significant effect on the TFC membrane performance. According to Figure 6.(c), the TFC-5 membrane possessed the highest water flux 10.7 LMH with 94.8% salt rejection, TFC-1 membrane had the highest salt rejection 99.1% and the flux was just little lower than that of TFC-5. For the PSf membrane prepared with PEG, the aqueous solution diffuse into the surface pores more easily because of the lager pore size and hydrophilic. However, when the polymerization reaction began, MPD diffused slowly out of the pores due to favorable interactions with polar functional groups of PEG. As a result, amount of polyamide formed deeper within PSf membrane pores and no continuous and complete polyamide formed on the surface especially when the PEG was added to 15%. This factor increased the overall path length for water transport and caused the less salt rejection and water flux.

4. Conclusion

The concentration of PEG additive lead to a structural change from dense top-layer and sparse sub-layer feature to a symmetric, sponge type with no macro-void structure, which could be considered as the result of the different diffusion rates.

The polyamide formed deeper within PSf membrane pores result in the increased the overall path length for water transport and the less salt rejection and water flux.

5. Acknowledgments

This work was financially supported by National Natural Science Foundation of China (Grant No. 51804240), Key Industrial Chain Project of Shaanxi Province (Grant No. 2017ZDCXL-GY-07-03).

6. References

- [1] Global risks 2015, Insight Report, 10th Edition, World Economic Forum, (2015)
- [2] Li D, Wang H. Recent developments in reverse osmosis desalination membranes [J], Journal of Material Chemistry, 2010, (20):4551-4557.
- [3] Lee K, Arnot T, Mattia D, A review of reverse osmosis membrane materials for desalination -Development to date and future potential [J], Journal of Membrane Science, 2011, 370:1-22.
- [4] Prakash R A, Joshi S V, Trivedi J J. Structure-performance correlation of polyamide thin film composite membranes: effect of coating conditions on film formation [J]. Journal of Membrane Science, 2003, (211):13-24.
- [5] Ng L, Mohammad A, Leo C. Polymeric membranes incorporated with metal/metal oxide nanoparticles: A comprehensive review [J], Desalination, 2013, (308): 15-33.
- [6] Kang G D, Gao C J, Cao Y M. Study on hypochlorite degradation of aromatic polyamide reverse osmosis membrane [J], Journal of Membrane Science, 2007, (300): 165-171.
- [7] Asim G, Eric H. Impacts of support membrane structure and chemistry on polyamide-polysulfone interfacial composite membranes [J], Journal of Membrane Science, 2009, (336):140-148.
- [8] Asim G, Jeong K, Huang B. Impacts of reaction and curing conditions on polyamide composite reverse osmosis membrane properties[J], Journal of Membrane Science, 2008, (311): 34-45.
- [9] Puyam S, Joshi S, Trivedi J. Probing the structural variations of thin film composite RO membranes obtained by coating polyamide over polysulfone membranes of different pore dimensions [J], Journal of Membrane Science, 2006, (278):19-25.
- [10] Kenneth M, Vassilis G, Gun T. Study of membrane compaction and its influence on ultra-filtration water permeability [J], Journal of Membrane Science, 1995, (100):155-162.