

## Facile pore control by NMP-dipping method with water-pressure

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**Abstract**—Polysulfone (PSf) membrane by treated NMP solvents with water forces was studied for pore control and separation of sodium alginate. For the preparation of modified PSf membranes, it was exposed to specific solvents and then treated by water-forces. PSf membrane treated only with NMP could show the separation of sodium alginate above 6 bar since the pore-size was not proper for water transport. However, the membrane treated with NMP and water forces showed the separation performance of sodium alginate from 2 bar. Furthermore, the highest flux (211 L/m<sup>2</sup>h) and rejection (99.3%) at 8 bar was observed. FT-IR and TGA analysis showed no chemical or physical changes after NMP and exposure to water forces. The modified pore size in polysulfone membrane was confirmed by the porosimeter.

Keywords: Polysulfone, NMP, Water Pressure, Dipping Method, Pore Size

### INTRODUCTION

Globally, the interest in water shortage and water pollution continues to increase [1-4]. To address these pollution and water shortage issues, research has been conducted to purify waste-water and preserve freshwater sources [5-9]. Several effective techniques have been studied, including adsorption, chemical precipitation, ion exchange, coagulation, electrodialysis, electrolysis and reverse osmosis. In addition, global efforts to improve current water treatment processes and develop new energy and cost-effective technologies to continuously produce clean water through wastewater regeneration and seawater desalination have been accelerated [2,10,11]. Among these methods, membrane filtration has offered several advantages while maintaining high process efficiency [5,8,12,13]. Small installation space, low energy consumption, wide application range, low chemical usage and simple operation have made the membrane filtration process a more advantageous and convenient process compared to the competition technology.

Due to these advantages, the researches on membrane filtration have been actively conducted. A mesoporous 3D wood film decorated with palladium nanoparticles has been reported for efficient wastewater treatment [14]. The 3D Pd NPs/wood membrane reached 1×10<sup>5</sup> L/m<sup>2</sup>h and showed high Methylene blue (MB) removal efficiency (>99.8%). A new graphene oxide (GO)-based nanofiltration membrane on a highly porous polyacrylonitrile nanofibrous mat (GO@PAN) was prepared by vacuum suction method [15]. Water flux at very low pressure (1.0 bar) significantly increased. In addition, GO@PAN membrane showed the high rejection performance of 56.7% for Na<sub>2</sub>SO<sub>4</sub> and nearly 100% for Congo Red. GO membranes incorporating MOF and coated with chitosan have been studied [16]. These GO membranes have a 344% increase in water flux com-

pared to the normal GO membrane and a 99% dye rejection rate. They also has the excellent antifouling and self-healing ability. The nafion/polyvinylidene fluoride (PVDF) nanofiber membranes prepared by electrospinning showed a high porosity of more than 80% and negatively charged into sulfonate groups to improve antifouling against negatively charged oily contaminants [17]. Furthermore, many water treatment membranes and methods for improving existing water treatment membranes have been studied. For example, a facile in-situ chemical deposition method was applied to obtain nanoporous ZrO<sub>2</sub> membranes with controllable pore size [18]. By controlling the content of the precursor, it was possible to control the MWCO. Nanoporous polymeric membranes (NPMs) by using soluble molecular coordination complexes as pore-forming agents were studied [19]. This method could greatly improve the porosity of the membrane, and the pore size could also be adjusted by using different complexes with pore formers.

In our group, the membrane was prepared by adding an inorganic additive Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O to the cellulose acetate (CA) polymer [20]. These CA membranes showed a rejection rate of over 75% for sodium alginate. In addition, our group reported an effective way to separate sodium alginate through PSf membranes treated with tetrahydrofuran (THF) and water pressure [21]. This membrane showed a high water flow of 259 L/m<sup>2</sup>h in sodium alginate filtration test. It also showed 98.8% sodium alginate rejection [21].

We studied the effect of solvent species on pore control and membrane performance, compared with previous study to utilize the THF. NMP solvent was chosen since it was expected to affect the physical structure of PSf. By comparing the PSf treated with NMP and PSf treated NMP with water pressure, it was expected that the pore size could be adjusted according to the membrane treatment method, resulting in the change of separation performance.

### EXPERIMENTAL

#### 1. Materials

Porous polysulfone support was obtained from Toray Chemical

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Korea Inc. N-Methyl-2-pyrrolidone (NMP) and sodium alginate purchased at Daejung Chemicals & Metals Co., Ltd.) was used as the solvent and target material for separation, respectively.

## 2. Fabrication Process

N-methyl-2-pyrrolidone (NMP) was diluted as 15 wt% in water solvent. The porous PSf membranes were immersed in NMP/H<sub>2</sub>O mixture solvent for 1 hour. Then, the NMP/H<sub>2</sub>O solvent-treated PSf was washed by distilled water for removal of solvents. The washed PSf membranes were exposed to water-pressure at 8 bar for 5 min to generate and expand the pores in polymers. The water pressure-treated PSf membranes were utilized to separate sodium alginate (200 ppm) from water at various pressures from 1 to 8 bar.

## 3. Characterization

The IR peak shift was measured by a VERTEX 70 Fourier transform infrared (FTIR) spectrometer; 64-200 scans were signal averaged with a resolution of 4 cm<sup>-1</sup>. The thermal stability of PSf supports by change of chain stiffness was analyzed by thermogravimetric analysis (TGA; Universal V4.5A, TA instruments). The pore sizes of the PSf supports were examined using a mercury porosimeter (Autopore IV9500, Micromeritics).

## RESULT AND DISCUSSION

### 1. Separation Performance: Water Flux and Rejection % for Sodium Alginate

Sodium alginate separation experiment was performed with pore-controlled PSf. Fig. 1 shows the separation performance of sodium alginate solution for various pressure. In the case of neat PSf, the water did not penetrate until the water pressure reached 10 bar. However, as shown in Fig. 1, PSf treated with NMP was not observed for flux up to 5 bar and PSf treated with NMP and water pressure was observed from 2 bar. Both supports showed high flux at 8 bar ((1) PSf treated NMP: 202 L/m<sup>2</sup>h and (2) PSf treated NMP and water pressure: 211 L/m<sup>2</sup>h). Therefore, it could be thought that the pore size of the PSf increased through the pore control method. Flux was observed at PSf treated with NMP and water pressure at lower pressure than PSf treated with NMP. As a result, it was deter-

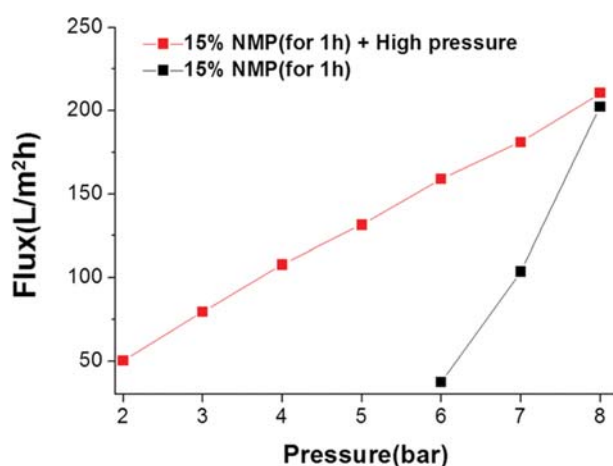


Fig. 1. Separation performance for sodium alginate by PSf membrane treated with NMP and PSf membrane treated with NMP and water pressure at 8 bar for 5 min: water flux.

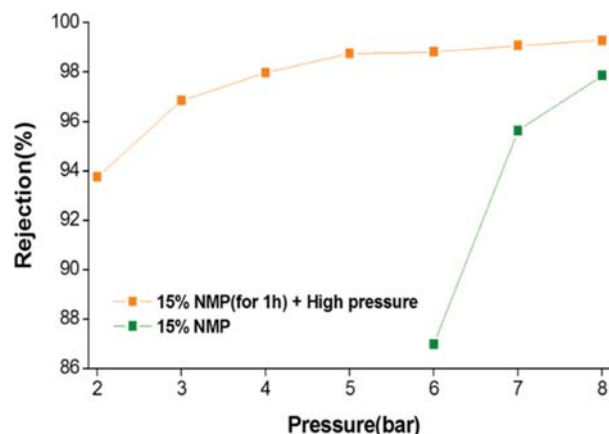


Fig. 2. Separation performance for sodium alginate by PSf membrane treated with NMP and PSf membrane treated with NMP and water pressure at 8 bar for 5 min: rejection %.

mined that the pore size could be selected according to the pore treatment method.

Fig. 2 showed sodium alginate rejection with water pressure. Rejection of PSf treated with NMP was 87% at 6 bar and 97.9% at 8 bar. The rejection of PSf treated with NMP and water pressure was 93.8% at 2 bar and 99.3% at 8 bar. Both membranes showed increased rejection with increasing pressure with high rejection. Generally, as the pore size and porosity increased, the water flux increased while the rejection % decreased. However, for the PSf membrane treated by NMP without water-pressure, rejection phenomena were observed above at 6 bar. Since a smaller pore size was generated in the PSf membranes treated by NMP and water-pressure, the rejection % was enhanced with the increased water flux by the increased porosity. Therefore, this pore control method was thought to be useful for making water treatment membrane for separation of sodium alginate as suggested in Scheme 1.

### 2. FT-IR: Chemical Structural Changes

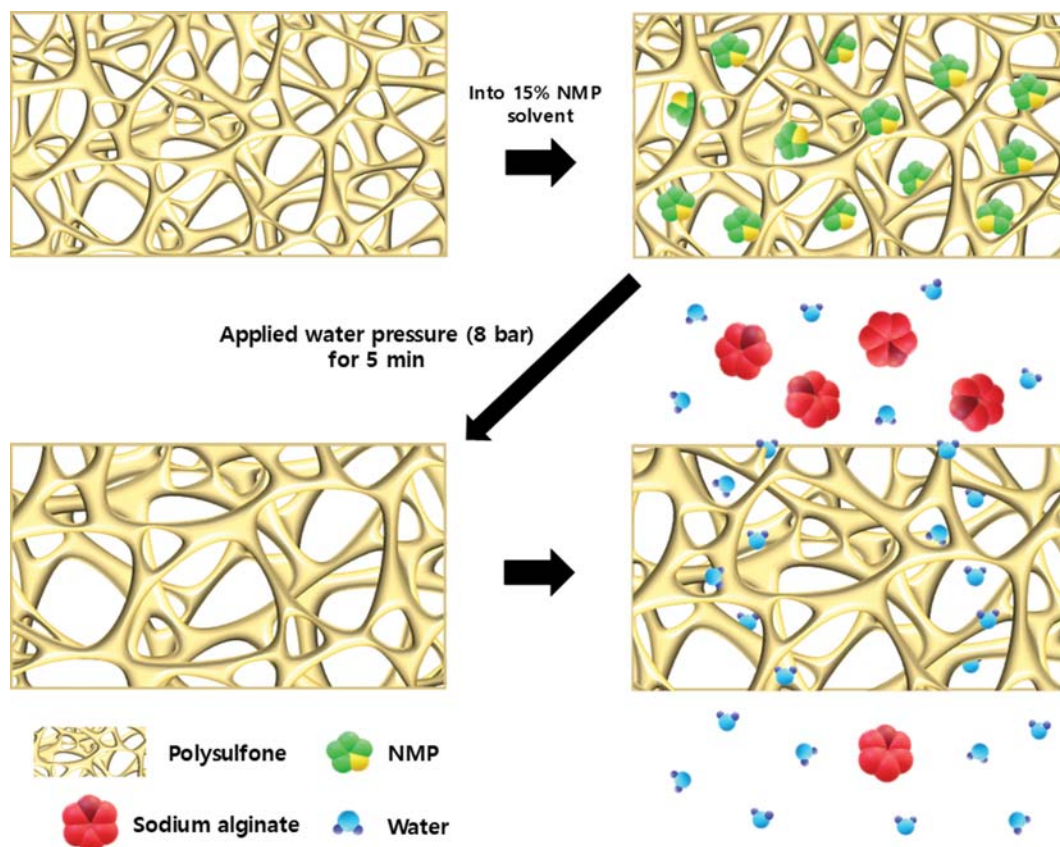
The FT-IR spectra for the neat PSf and pore-controlled PSf are shown in Fig. 3. The IR spectra of the neat PSf and the pore-controlled PSf were nearly identical. Therefore, the pore size was able to be adjusted without changing the chemical structure of PSf even after immersion in 15% NMP solution for 1 hour and water treatment.

### 3. TGA: Thermal Stability of Polysulfone

Thermal stability was investigated by TGA. Fig. 4 shows the TGA analysis of neat PSf and pore-controlled PSf. All of the three PSf films show major weight changes at about 380 °C, and the overall graphs of the neat PSf and pore-controlled PSf are similar, indicating no significant structural changes as observed in the IR results. Therefore, it was concluded that thermal stability was not affected even after NMP and hydraulic treatment. The improved thermal stability of PSf treated with NMP above 500 °C was due to the effect of physical changes resulting from the merged pores.

### 4. Porosimeter: Pore Size Change

Fig. 5 shows the pore size of neat PSf and after PSf treated with NMP and water pressure. Compared to neat PSf, the pore diameters of about 1,500 and 7,000 nm became abundant, which indicated that the area plasticized by NMP was widened by water pressure. In detail, the plasticized regions in polymer chains by NMP were



Scheme 1. Sodium alginate separation using PSf membrane treated with NMP and water pressure at 8 bar for 5 min.

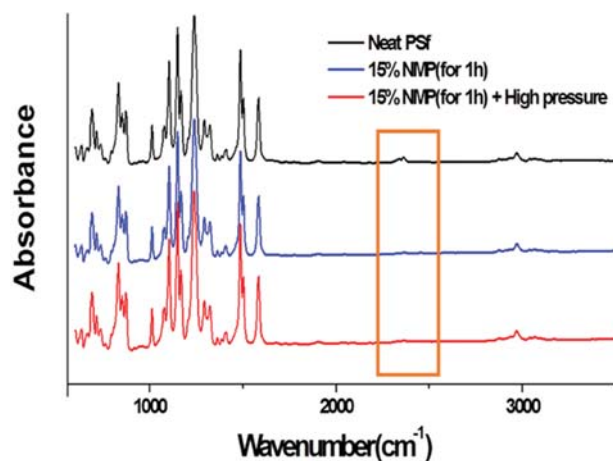


Fig. 3. FT-IR analysis for the neat PSf support and PSf membrane treated with NMP and water pressure at 8 bar for 5 min.

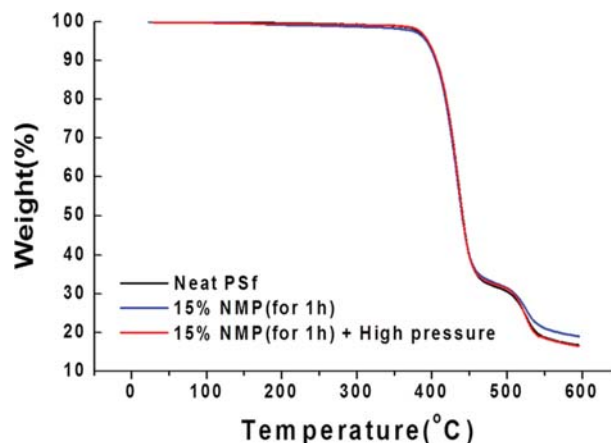


Fig. 4. Thermogravimetric analysis of PSf supports: neat PSf support, PSf treated with NMP and PSf membrane treated with NMP and water pressure at 8 bar for 5 min.

easily torn out by physical forces when exposed to water-pressures. It was also shown that pores below 1,000 nm were not affected by solvent and water pressure. Therefore, it was confirmed that the pore size could be easily adjusted through solvent and water pressure.

## CONCLUSION

By treating with NMP and water pressure, PSf can be used for

separation of sodium alginate. In addition, the pore size is adjustable with NMP alone without water pressure. Both pore-controlled PSf successfully could separate the sodium alginate with flux above 200 L/m<sup>2</sup>h and rejection above 97%. Pore of plasticized part by immersion in NMP increased to the size suitable for separating sodium alginate. IR and TGA analysis confirmed that there was no change in chemical structure and thermal stability. The porosimeter analysis showed little change in pore size below 1,000 nm, and a change in

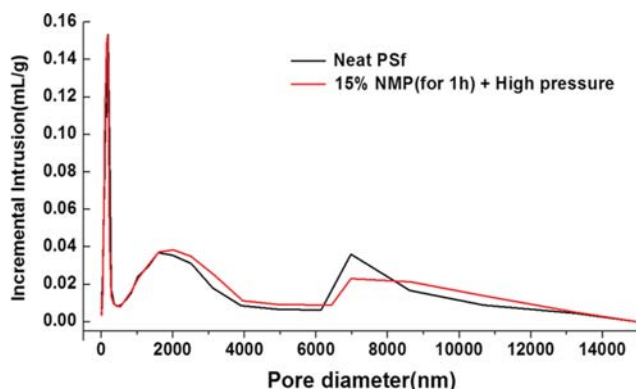


Fig. 5. Porosimeter data for the neat PSf support and PSf membrane treated with NMP and water pressure at 8 bar for 5 min.

pores of 1,500 and 7,000 nm was observed. This suggested treatment is expected to be utilized as the method that can be applied to water treatment by easily adjusting the size of existing pores.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

1. B. E. Mosikatsi, N. Mabuba and S. P. Malinga, *J. Water Process Eng.*, **30**, 100686 (2019).
2. H. Yoo and S. Kwak, *J. Membr. Sci.*, **448**, 125 (2013).
3. X. Song, Y. Wang, C. Wang, M. Huang, S. Gul and H. Jiang, *ACS Sust. Chem. Eng.*, **7**(5), 4889 (2019).
4. E. Virga, J. de Grooth, K. Žvab and W. M. de Vos, *ACS Appl. Polym. Mater.*, **1**(8), 2230 (2019).
5. J. Li, H. Wang, X. Yuan, J. Zhang and J. W. Chew, *Coord. Chem. Rev.*, **404**, 213116 (2020).
6. H. A. Hasan and M. H. Muhammad, *J. Water Process Eng.*, **33**, 101035 (2020).
7. S. Abo-Farha, A. Abdel-Aal, I. Ashour and S. Garamon, *J. Hazard. Mater.*, **169**(1-3), 190 (2009).
8. M. Barrejón, Z. Syrgiannis, M. Burian, S. Bosi, T. Montini, P. Fornasiero, H. Amenitsch and M. Prato, *ACS Appl. Mater. Interfaces*, **11**(13), 12920 (2019).
9. K. Buruga, H. Song, J. Shang, N. Bolan, T. K. Jagannathan and K. Kim, *J. Hazard. Mater.*, **379**, 120584 (2019).
10. P. Karami, B. Khorshidi, M. McGregor, J. T. Peichel, J. Soares and M. Sadrzadeh, *J. Cleaner Prod.*, **250**, 119447 (2020).
11. H. Zeng, Z. Yu, Y. Peng and L. Zhu, *Appl. Clay Sci.*, **183**, 105322 (2019).
12. H. R. Shahriari and S. S. Hosseini, *Chem. Eng. Process-Process Intensification*, **147**, 107766 (2020).
13. A. Vedadghavami, F. Minoei and S. S. Hosseini, *Iranian J. Chem. Chem. Eng. (IJCCE)*, **37**(2), 1 (2018).
14. F. Chen, A. S. Gong, M. Zhu, G. Chen, S. D. Lacey, F. Jiang, Y. Li, Y. Wang, J. Dai, Y. Yao, J. Song, B. Liu, K. Fu, S. Das and L. Hu, *ACS Nano*, **11**(4), 4275 (2017).
15. J. Wang, P. Zhang, B. Liang, Y. Liu, T. Xu, L. Wang, B. Cao and K. Pan, *ACS Appl. Mater. Interfaces*, **8**(9), 6211 (2016).
16. R. Chang, S. Ma, X. Guo, J. Xu, C. Zhong, R. Huang and J. Ma, *ACS Appl. Mater. Interfaces*, **11**(49), 46251 (2019).
17. J. Lee, J. Jung, Y. H. Cho, S. K. Yadav, K. Y. Baek, H. B. Park, S. M. Hong and C. M. Koo, *ACS Appl. Mater. Interfaces*, **6**(16), 14600 (2014).
18. X. Chen, T. Qi, Y. Zhang, T. Wang, M. Qiu, Z. Cui and Y. Fan, *J. Membr. Sci.*, **597**, 117631 (2020).
19. L. Shu, N. Wang, C. Zhao, Y. Meng, S. Ji and J. Li, *ACS Sust. Chem. Eng.*, **7**(2), 2728 (2018).
20. H. Y. Kim, Y. Cho and S. W. Kang, *J. Ind. Eng. Chem.*, **78**, 421 (2019).
21. J. Hwang, J. Choi, J. M. Kim and S. W. Kang, *Macromol. Res.*, **24**(11), 1020 (2016).