

Structural control of polysulfone membrane by using dimethylacetamide and water-pressure for water treatment

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(Received 21 January 2020 • Revised 7 April 2020 • Accepted 12 April 2020)

Abstract—A method for separating sodium alginate through polysulfone (PSf) support by dimethyl acetamide (DMAc) and hydraulic treatment was studied. After exposing the PSf support to DMAc solvent, water pressure was applied onto the polymer support. As a result, the sponge-type structures were connected to each other and the porosity of the modified PSf increased. In addition, the support pressurized for 3 minutes at 8 bar had the highest value of 133 L/m²h and removal rate of 95.0% for sodium alginate filtration test. When the PSf support was immersed in an organic solvent, the interaction between the chains of the PSf was weakened, while when water pressure was applied, pores were generated. These results were confirmed by SEM, FT-IR and porosimeter data.

Keywords: Polysulfone, Porosity, Dimethylacetamide, Water-pressure

INTRODUCTION

Many studies about water treatment method have been conducted over the years. Yoon et al. fabricated vertically aligned carbon nanotube membrane and compared it with a commercial ultrafiltration (UF) membrane [1]. The CNTs were observed by thermal chemical vapor deposition and it were moved from silicon wafer to tape. Then, the synthesized CNTs were fixed onto cast and epoxy resin was used to stuff vacant spaces [1]. Finally, it was cut by a microtome, and vertically aligned CNT membrane was made. As a result, the membrane showed about three-times higher water-flux than commercial UF membrane [1]. And Deng et al. utilized porous MCM-41 silica nanoparticles to make thin-film nanocomposite [2]. The water-flux increased to 46.6 L/m² by addition of MCM-41. Salt rejection of NaCl and Na₂SO₄ was a high value of about 98% [2]. Kwak et al. prepared hyper-branched poly(amidoamine) and polysulfone composite membrane to remove Cd(II) from water [3]. They modified the hyper-branched poly(amidoamine) by using palmitoyl chloride and it was mixed with the polysulfone by phase inversion method [3]. The Cd(II) removal efficiency was 51%. Under acidic conditions, the prepared membrane recovery ratio was 86% [3]. Chung et al. made polyacrylonitrile (PAN) thin film composite membrane and applied forward osmosis to purify oily waste-water [4]. It was cast onto a glass plate with a casting knife and dipped into NMP/water mixed solution. The PAN-TFC membranes were fabricated by polyamide layer deposition onto hydrolyzed PAN support. Water-flux was quite high and oil rejection was almost 100% [4]. In addition, Chung et al. made hyperbranched polyethyleneimine (HPEI) and isophthaloyl chloride (IPC) composite nanofiltration (NF) membrane by interfacial polym-

erization [5]. The substrate was comprised of macrovoid layer in sandwich structures and the NF membrane showed high water permeability [5]. Nunes et al. prepared nanostructured hydrophobic polyazole membranes to achieve water recovery with low-energy [6]. Aromatic fluorinated polyoxadiazoles and polytriazoles were synthesized by using phase inversion and electrospinning process. Desalination tests were conducted with sea water. Salt selectivity was of 99.95% and water flux was 85 L m⁻² h⁻¹ [6]. In addition, Marais et al. fabricated supported ionic liquid membranes (SILMs) by immobilizing ionic liquids in porous Matrimid membrane [7]. They used water vapor-induced phase inversion method and applied the membranes for separating water and volatile organic compounds (VOCs). [C₄C₁im][BF₄] showed best sorption capacity and selectivity. The membrane permeability increased in the following order: cyclohexane < ethanol < water [7]. Pillay et al. made woven fabric microfiltration (WFMF) membranes by adding silver nanoparticles (AgNPs) with modified chemical reduction method [8]. The coated membranes with hydrophilic and higher water permeability showed bacteria removal efficiency of 84-91% [8]. However, the efficiency of the coated membranes was 100% [8]. Sun et al. prepared hierarchically multifunctional TiO₂ nano-thorn membrane [9]. TiO₂ nano-thorn spheres were hydrothermally synthesized and assembled on a cellulose acetate membrane. Commercial TiO₂ P25 powder was assembled on the cellulose acetate membrane to compare with the TiO₂ nano-thorn membrane [9]. Humic acid and methyl blue were used as pollutants. Removal rate of MB and HA was better in the hierarchical TiO₂ nano-thorn membrane than the P25 deposited membrane [9]. Dankovich et al. utilized ascorbic acid and made copper nanoparticles in paper filters instead of expensive silver nanoparticles [10]. They fabricated the copper nanoparticles (CuNPs) by *in situ* preparation in paper. In the filtrate water, the copper concentration was below the recommended limit in drinking water (1 ppm) [10]. Pant et al. applied pollutant fly ash in fly ash/polyurethane (FA/PU) nanocomposite multifunctional mem-

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brane by using electrospinning process [11]. The fly ash particles (FAPs) were doped with silver. PU solution with FAPs and Ag metal precursor was made as spider-web-like membrane [11]. This membrane can be utilized for removing carcinogenic arsenic (As) and toxic organic dyes [11]. Kuznicki et al. prepared clinoptilolite-based phosphate composite membranes with high temperature autoclave steaming and dry pressing [12]. They conducted water desalination under different salinity levels between 25–95 °C (1 atm feed pressure). When Na feed salinity and temperature were 1,400 ppm and 95 °C, water flux and Na⁺ removal efficiency were 15 kg/m² h and over 95% [12]. Pan et al. reported the pristine graphene oxide and reduced graphene oxide nanosheets [13]. They blended pristine graphene oxide and reduced graphene oxide with sodium alginate matrix to acquire two different kinds of hybrid membranes. Pervaporation test was conducted by using ethanol/water mixture [13]. Especially, rGO-filled membranes showed higher separation performance than pGO-filled membranes. When rGO content was 1.6 wt%, separation factor and permeation flux were 1,566 and 1,699 g/(m²h) [13]. Ho et al. synthesized thin-film reverse osmosis membranes for seawater desalination [14]. They added o-amino-benzoic acid-triethylamine salt into m-phenylenediamine solution to react with trimesoyl chloride [14]. Membrane support was nanoporous polysulfone. The water-flux and salt rejection was 1.81 m³/m²/day and 99.41%, respectively [14]. Madaeni et al. made mixed matrix polymeric membrane with polyethersulfone and polyaniline/iron (II, III) oxide nanoparticles by the phase inversion method [15]. The membrane with 0.1 wt% nanoparticles showed the highest Cu(II) ion removal. However, pure water flux was the lowest when containing 0.1 wt% nanoparticles [15]. This is due to membrane surface pore blockage of the nanoparticles [15]. Lee et al. fabricated sodium alginate (SA)/polyvinyl alcohol (PVA) composite membranes with various SA/PVA blending ratio [16]. Then, calcium ions (II) were complexed with the membranes [16]. There were many parameters, such as operating temperature, annealing time and PVA content. They separated the water-methanol mixture by vapor permeation (VP) method and conducted a separation test between 40–70 °C [16]. The only water component penetrated through SA/PVA (90/10) annealed complex membrane at 40–60 °C [16]. Wang et al. synthesized two types of sulfonated aromatic diamine monomer and used it to make thin-film composite (TFC) nanofiltration (NF) membranes [17]. Microporous polyphenylsulfone (PPSU) support was utilized by an interfacial polymerization method with trimesoyl chloride (TMC) solution, amine solutions containing 6FAPBS/6FBABDS with piperazine [17]. The NF membranes were applied to dye treatment tests with rhodamine B, methyl orange aqueous solutions. The membranes showed the increased water-flux by the sulfonated aromatic diamine monomers without compromising dye rejection [17]. Tsuru et al. synthesized thin polyamide NF membranes on UF polysulfone support [18]. They used acetone and hexane to control thin dense layer and “nanopores” by co-solvent assisted interfacial polymerization (CAIP) [18]. Sodium chloride solutions were utilized for permeation tests. The membrane containing 2 wt% acetone showed about four-times higher water-flux than a membrane containing no acetone co-solvent [18]. Chang et al. modified commercial ceramic microfiltration membranes by nano-TiO₂ coating [19]. The nano-

coating increased membrane surface hydrophilicity. The membranes were used to separate oil-in-water emulsions [19]. Under the specific operation parameters, the modified membrane had better stable flux than the unmodified one [19]. The filtrate oil concentration was not higher than 10 mg/L when feed oil concentration was less than 4 g/L [19]. Kariduraganavar et al. made crosslinked poly(vinyl alcohol) (PVA) membrane with various amounts of gelatin (Ge) [20]. After finishing membrane preparation, pervaporation separation was conducted by using water-isopropanol mixtures between 30–50 °C [20]. A membrane with 10 mass% of Ge showed high separation selectivity of 1791 with high water flux.

In this study, polysulfone with sponge-like pore structure was used as a support. To modify the existing pore structure, dimethyl acetamide, an organic solvent that can weaken the polysulfone chain, was used. Therefore, when the PSf support was immersed in DMAc, the interaction between the polymer chains inside the PSf was expected to be more flexible than before. In addition, when water pressure of 8 bar is applied to the PSf support for various times, the sponge-like pores will connect with each other and grow. These results confirmed the performance of the modified PSf using SEM, FT-IR, TGA and porosimeter. In addition, a filtration test on sodium alginate was performed at a pressure of 2 bar to see if it could be used for microfiltration membranes.

EXPERIMENTAL

1. Materials

Polysulfone received from Toray Chemical Korea Inc. was used and N, N-dimethyl acetamide (Aldrich Chemical Co.) was selected as the immersion solvent. For filtration experiments, sodium alginate (Daejung Chemicals & Metals Co., Ltd) and distilled water were used.

2. Fabrication Process

After preparing a 13 wt% aqueous DMAc solution, the polysulfone support was immersed for 4 hours. Thereafter, a pressure of 8 bar was applied using a filtration device, and distilled water was used. Various times of hydraulic pressure were controlled from 30 seconds to 10 minutes and water molecules were infiltrated into the DMAc-treated PSf support. Thereafter, a 200 ppm aqueous sodium alginate solution at a pressure of 2 bar was filtered using a DMAc-treated PSf support. On the other hand, the neat PSf support not treated with DMAc did not filter the water molecules even when exposed to an external water pressure of 10 bar.

3. Characterization

TGA (Universal V4.5A, TA) was used to confirm the thermal stability of the PSf support. Mercury pore system (Autopore IV9500, Micromeritics) was used to measure the pore size of the PSf support, and scanning electron microscopy (SEM) (JSM-5600LV, JEOL) was used to examine the cross section of the PSf support. FT-IR spectrometer (VERTEX 70/70V, Bruker Optics) was used to investigate the chemical structure change of the support.

RESULTS AND DISCUSSION

1. Separation of Sodium Alginate

Fig. 1 shows the filtration test of sodium alginate solution for vari-

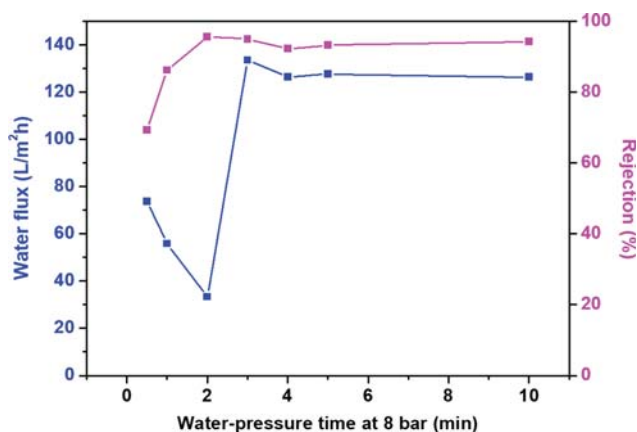


Fig. 1. Filtration test of sodium alginate at 2 bar by a membrane pressurized at 8 bar.

ous times. Membrane used in the test was subjected to PSf modified by DMAc at 8 bar; it showed flux with the rejection rate depending on time applied at 8 bar. The rejection test was conducted at 2 bar pressure. The best results were at 3 minutes for the flux data and 2 minutes for the rejection data. The rejection data values were 95.5% at 2 minutes and 95.0% at 3 minutes; thus, it was determined to be similar at both times. The most important point was as follows: it was confirmed that no water was penetrated into the clean PSf supports not immersed in DMAc until the water pressure was 10 bar. On the other hand, DMAc-treated PSf supports with a water pressure of 8 bar could filter the water molecules. As shown in Fig. 1, PSf support modified with DMAc could filter the sodium alginate at 2 bar while exhibiting high water flow and rejection values. From these results, it was considered that treatment of the PSf support by DMAc and water pressure was highly effective for sodium alginate separation.

2. Thermal Stability and Mechanical Strength of PSf Support

TGA was performed to investigate the thermal and mechanical stability of PSf as shown in Fig. 2. TGA showed that the major reductions were observed at 350 °C for both samples. Therefore, it could be thought that the thermal stability was not significantly

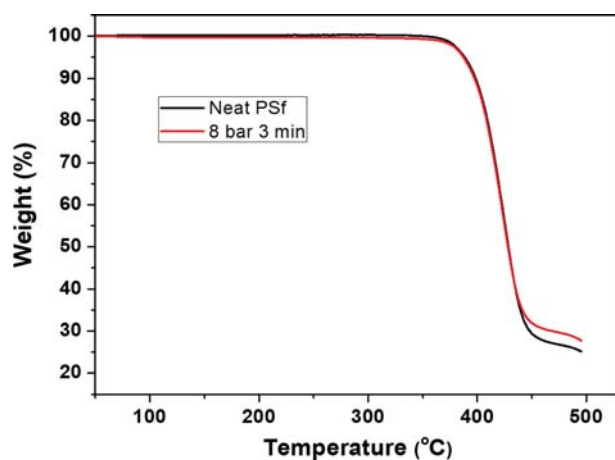


Fig. 2. Thermogravimetric analysis: neat PSf support and PSf treated with DMAc at 8 bar for 3 min.

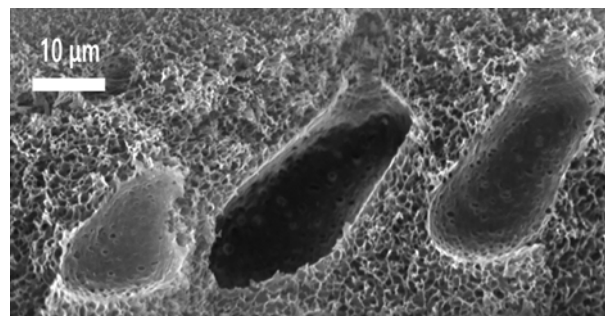


Fig. 3. SEM image: cross-sectional PSf support treated with DMAc at 8 bar for 3 min.

diminished even when modified with DMAc. The final residual weight also showed a higher value for the modified PSf. These results showed that the mechanical strength was improved due to the change in physical properties due to the connection of pores in the PSf support.

3. Cross-sectional Morphology of PSf

The cross section of the PSf support was observed by SEM. Fig. 3 shows the sponge-like structure of the PSf support with large pores and numerous small pores. However, the PSf supports treated with DMAc appeared to have larger pores than pure PSf supports. Therefore, it could be determined that the PSf support treated by DMAc and hydraulic pressure caused the pores to be connected for sponge-type pores.

4. Porosity Change of PSf

Fig. 4 shows the porosity of the PSf support treated with DMAc. Pore size distribution shows a wide range (0-15,000 nm) for the treated polysulfone support. The PSf supports treated with DMAc show a high porosity of 24.0%. As compared to the 21.0% porosity of pure PSf support, it was demonstrated that the pore size of the PSf support was controlled by organic solvents and external forces as shown in Table 1.

5. Change of Structure in PSf

FT-IR spectroscopy was used to investigate the PSf supports for the change of chemical structure as shown in Fig. 5. In the un-

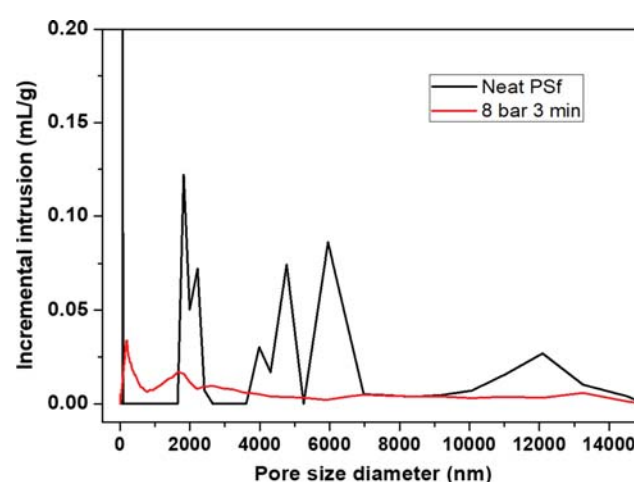
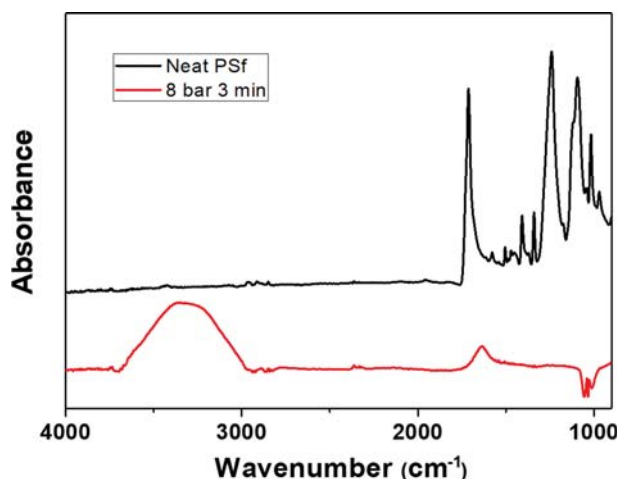


Fig. 4. Porosity analysis for the untreated and treated PSf support.

Table 1. Performance comparison of neat polysulfone and the treated polysulfone support: water flux, rejection % for sodium alginate and porosity

	Neat polysulfone	Treated PSf supports by DMAc and water-pressure
Water flux	Not permeable	133 L/m ² h
Rejection % for sodium alginate	Not selective	95%
Porosity	21%	24%

**Fig. 5. FT-IR spectra of the PSf support.**

treated PSf support with DMAc and water-pressure, distinctive peaks of PSf (O=S=O, stretching) were found at 1,500–1,000 cm⁻¹. However, after treatment with the DMAc and water-pressure at 8 bar for 3 min, the distinctive peaks disappeared. Instead, at 8 bar 3 min, a broad peak at 4,000–3,000 cm⁻¹ appeared. It could be thought that the broad peak indicated O-H bonds since the water-molecules remained even though the samples were exposed to vacuum oven. FT-IR spectra showed that there were obvious structural changes of neat PSf support after the treatment with DMAc and water-pressure, judging from the fact that both water-molecules and DMAc could be easily attached on the surface of polymer chains.

CONCLUSION

We report a method of modifying PSf support with an organic solvent to form sponge-like structure, which is used to filter sodium alginates. DMAc was found to weaken the PSf chains and increase the flexibility of polymer chains. Therefore, when external hydraulic pressure (8 bar and 3 minutes) was applied to polymer support, the sponge-like pores were connected to each other, reaching a high porosity of 24.0%. In addition, with a high water flow of 133 L/m²h and a sodium alginate rejection rate of 95.0%, these proposed treatment methods are expected to be applied to water-purification technology to separate large pollutants.

ACKNOWLEDGEMENTS

This work was supported by a 2018 Sangmyung University research fund.

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