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Surface modification of PVDF membranes for water treatment via hydrophilic thermal cross-linking method

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ABSTRACT

Surface modification of poly(vinylidene)fluoride flat and hollow fiber membranes was performed via thermal cross-linking of acrylic acid. Two-stage cross-linking method was developed which enabled the interfacial reaction for effective cross-linked layer formation at surface. Hydrophilization of membranes at surface as well as at the inside of the pore was conducted by suction mode for solution application. Scanning electronic microscopy (SEM) images proved the formation of hydrophilic cross-linked layer to improve the performances of the membrane and antifouling characteristics. Modification of the membranes enhanced the stability of the membrane, and the chemical resistances were much improved. Mini pilot plant test proved the stability of the modified membranes in terms of flux and trans-membrane pressure (TMP) build up.

Keywords: Surface modification; PVDF membrane; Water treatment; Thermal cross-linking

1. Introduction

Poly(vinylidene)fluoride (PVDF), one of the most popular engineering polymers, has attracted continuous interests in recent years because it exhibits excellent chemical and thermal stabilities [1]. It has been widely used in diverse fields, such as biochemical, food, textile, and environmental industries. As a well-known membrane material, PVDF membrane has also been intensively studied for its applications to water and wastewater treatment, and seawater desalination due to its excellent chlorine resistance [2,3]. However, serious biofouling problem on the PVDF membrane surface usually limited its applications to biomedical processes [4,5]. However, PVDF is hydrophobic polymer and hydrophilic modification of PVDF membrane is much required for its performance enhancement. It is generally acknowledged that hydrophilic surfaces are more likely to reduce the nonspecific adsorption of organic molecule, when living systems encounter the membrane surfaces.

Therefore, so many work has been devoted to PVDF membrane modification to improve its surface hydrophilicity [6,7]. Among all the methods of modification, grafting is one of the promising methods [9]. In recent

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decays, a large number of methods have been researched for hydrophilic modification of hydrophobic membrane surface, including physical and chemical methods [10]. Polymer surface hydrophilization has been achieved using different techniques that include both physical and chemical processes [8]. The physical methods modifying the membrane surface with hydrophilic material or coating with hydrophilic compounds are simple. But physical method is not a permanent method and it can be washed out during the operation. Graft polymerization is one of the chemical modification techniques and it can impart a variety of functional groups to a polymer [11].

Surface modification via graft polymerization can be achieved by plasma treatment or UV irradiation process. But UV irradiation may damage the surface over long-time exposures and plasma treatment is performed in vacuum process with expensive cost. Furthermore, all of the current grafting methods are incapable of easily modifying the inner wall of pore because the radicals are primarily generated on the outer surface. Both techniques have geometrical limitations especially for hollow fiber membranes. Therefore, these techniques are not appropriate to used in industrial application. Thermal-induced grafting method is attractive because it is much simpler method than others. It does not require any special equipments and it is a quite cheap process. Thermal energy can be uniformly transferred to every part of the sample. Therefore, grafting is effective at inside of pores as well as the surface and has no geometrical limitations.

In this work, surface modification of PVDF membrane was performed by thermal cross-linking of acrylic acid for both flat sheet and hollow fiber membranes. Although grafting on PVDF was not expected, highly cross-linked polyacrylic acid layer formation was performed by using cross-linking agent. To attain the uniform surface modification, two-stage cross-linking reaction method was performed. Performance enhancement was achieved by thermal cross-linking of acrylic acid and antifouling characterization and stability test were performed.

2. Experimental

2.1. Materials

Durapore flat sheet PVDF membrane was purchased used from Millipore Co. whose pore size was 0.28 m and thickness was 200 m. PVDF hollow fiber membrane was supplied from Econity Co., whose pore size was 0.20 m and outside and inside diameters were 1,200 and 700 m, respectively. Acrylic acid was purchased from Aldrich Co. and used as a hydrophilic monomer without further purification. Azobis(isobutyronitrile)(AIBN, Junsei Chemical Co.) was used for thermal initiator and hydroxymethyl acrylamide(HMA,, Aldrich Co.) was used as a cross-linking agent. Bovine serum albumin (BSA, A2153, Aldrich Co.) was used for investigating the antifouling property of the PVDF membranes. Ethyl alcohol anhydrous (Carlo Erba Co.) was used as solvent.

2.2. Thermal cross-linking process

One-stage thermal cross-linking process was conducted by contacting the membrane with solution comprised of 20% acrylic acid solution with 1% AIBN in ethanol. In this one-stage process homopolymerization took place as well as the polymerization at surface. Two-stage process was developed in this work, and membrane was first contacted with 1% AIBN ethanol solution, and ethanol was dried leaving AIBN on the membrane surface. AIBN coated PVDF membrane was then contacted with 20% acrylic acid in DI water. Since AIBN was not miscible with water, interfacial polymerization of acrylic acid was performed at the membrane surface.

Thermal cross-linking reaction was performed by two modes; solution polymerization and surface polymerization. Solution polymerization was performed by heating the monomer solution at 70˚C for 30 min while leaving the membrane in the solution. For surface polymerization, membrane was taken out from the monomer solution and placed in an oven at 70˚C for 30 min. The yield of cross-linking was calculated from the following equation:

$$D_{\mathrm{g}}\ (\%) = (W_{\mathrm{f}} - W_{\mathrm{i}})/(W_{\mathrm{i}} \times 100)$$

where W_{i} and W_{f} represent the weight of the membrane before and after cross-linking [12].

2.3. Membrane characterization

FT-IR/ATR spectra of the surface of the membranes were obtained using a FT/IR-6200 (Jasco, Co.) with ATR cell. Scanning electronic microscopy (SEM) was performed with a Stereoscan 440(Leica Co.) to investigate the changes in the surface morphology of the membranes. BSA was used as organic material to evaluate the protein fouling characteristic of the PVDF membranes. The membrane was immersed in 0.2% BSA solution for 12 h and mass of adsorbed BSA was measured. A dead-end filtration method was employed to test the water flux of PVDF membranes. For kaolin test for flux recovery of the membrane, back-flush treatment was performed for 10 min after 1-h operation.

3. Result and discussion

3.1. Effects of thermal cross-linking method

The schematic mechanism of two-stage thermal cross-linking on the surface of PVDF membrane was shown in Fig. 1. AIBN solution in ethanol was soaked into the PVDF membrane, and ethanol was evaporated leaving AIBN on the PVDF membrane surface. PVDF membrane was then contacted with AA solution in water. Since AIBN was not miscible with water, cross-linking reaction happened only at the surface during the curing process.

Fig. 2 shows that two-stage cross-linking was more effective than one-stage cross-linking in terms of graft yield and contact angle both for surface and solution polymerization processes. Solution polymerization could provide more monomer from bulk phase than the surface polymerization. Therefore, solution polymerization achieved more graft yield and lower contact angle due to more cross-linking of acrylic acid than surface polymerization.

Fig. 3 shows that more pure water permeation rate and greater pore size were achieved for two-stage thermal cross-linking than one-stage one as expected from the results in Fig. 2. Even though solution polymerization achieved more cross-linking than surface polymerization, pure water permeation rate of solution polymerization was lower than that of surface polymerization. Too much polymerization inside the pore caused the pore size reduction and decrease in pure water permeation rate. Therefore, two-stage thermal cross-linking via surface polymerization was the most effective method.

3.2. FT-IR/ATR spectroscopy

Surface characterization of the hydrophilized PVDF membranes was carried out by ATR spectroscopy. Fig. 4 shows the spectra of several PVDF membrane samples. It is known that absorption peaks in the range of 610–650 cm^{-1} for C–F bonding. For the AA-modified surfaces, absorption bands were observed at 1,715 cm^{-1} corresponds to the carboxyl group [13]. These results are consistent with the supposition that the monomer was successfully grafted onto the membrane surface.

3.3. Surface morphology

Fig. 5 shows surface morphology of one-stage and two-stage thermal cross-linking samples. The sample prepared by one-stage solution polymerization showed less uniform coating layer was formed, which caused the pore blocking. Surface polymerization sample had similar surface structure to bare PVDF membrane, but there were slight decreases in surface pore size and porosity. The sample prepared by two-stage thermal cross-linking formed quite uniform

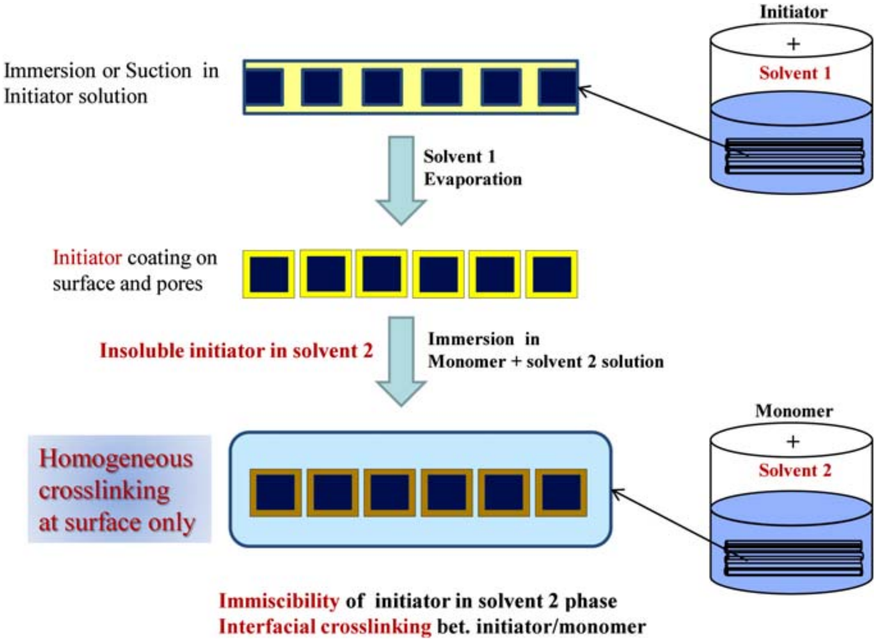

Fig. 1. Mechanism of two-stage cross-linking.

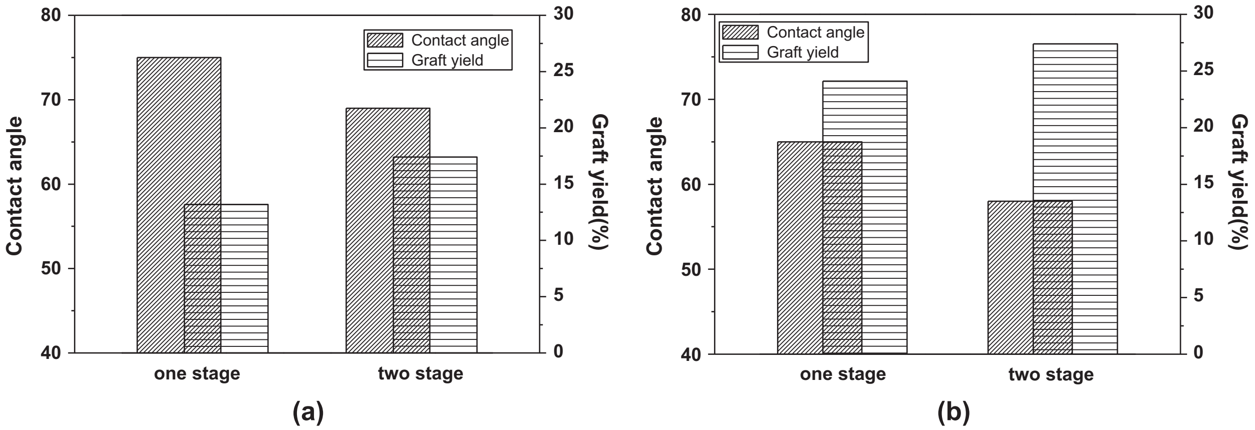

Fig. 2. Effect of cross-linking method (a) surface polymerization (b) solution polymerization. (one-stage grafting: AA/AIBN/EtOH = 20/1/80, two-stage grafting: AIBN/EtOH = 1/100 and AA/DI water = 20/80, at 70℃ for 4 h).

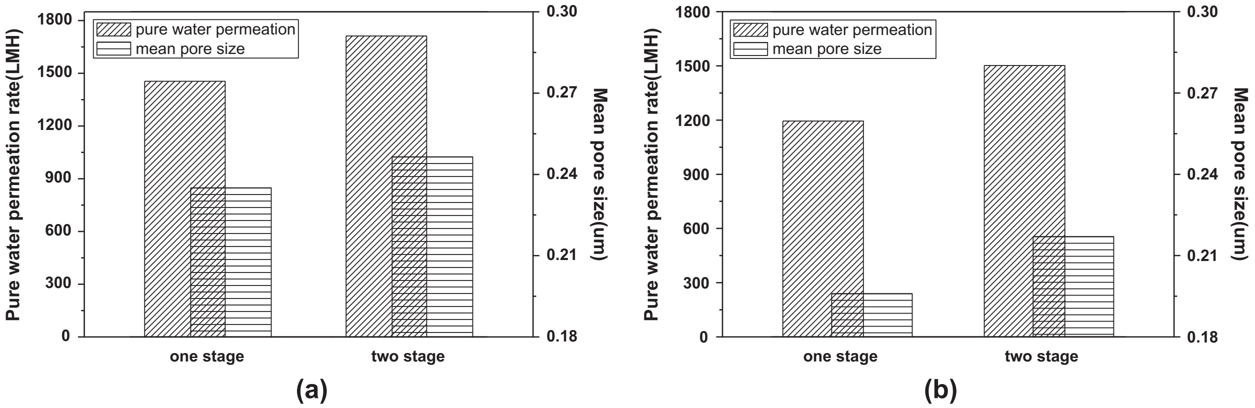

Fig. 3. Effects of cross-linking method on the pure water flux and mean pore size (a) surface polymerization (b) solution polymerization.

coating layers. The sample via solution polymerization had more dense coating layer than that from surface polymerization, which reduced the pore size. These results are in good agreement with the results in Figs. 2 and 3.

In Fig. 6, cross sectional and outer surface images of PVDF membrane modified by two-stage thermal cross-linking process was compared with those of pristine one. It was confirmed from cross sectional images that coating layer of 1 micron thickness was formed on the outer surface of the modified membrane. Surface image of the modified membrane also showed the formation of coating layer on the surface, which reduced the pore size and surface porosity.

3.4. Antifouling test with BSA aqueous

Antifouling characteristics of the membranes were compared in Fig. 7. Pristine PVDF membrane showed great amount of BSA adsorbed greater than 400 g/cm^2. When it was modified by one-stage thermal

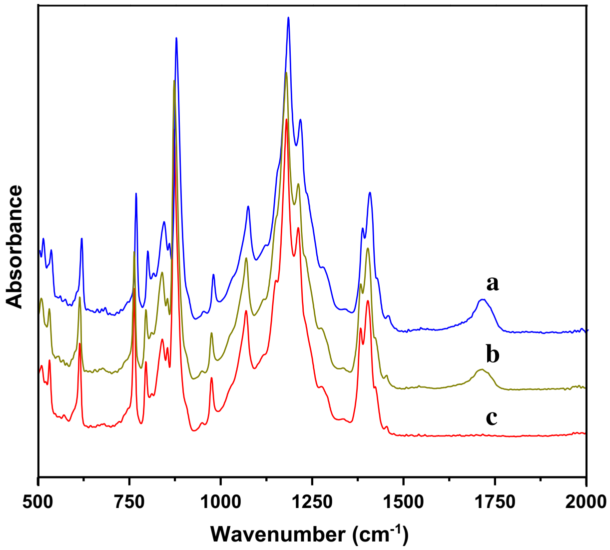

Fig. 4. ATR spectra of (a) two-stage solution polymerization, (b) two-stage surface polymerization, (c) pristine PVDF membrane.

cross-linking via solution polymerization, it achieved the minimum BSA adsorption, even though too much thermal cross-linking resulted in the pore blocking as was proved in Fig. 3. Similar trend was observed for two-stage thermal cross-linking via solution polymerization. However, surface polymerization via two-stage thermal cross-linking showed less BSA adsorption than that via one-stage thermal cross-linking. Therefore, two-stage thermal cross-linking via surface polymerization was the best process in terms of membrane permeation performance as well as the membrane fouling.

3.5. Flux variation for backwash process

Flux variations for backwash process were examined for DI water and Kaolin solution. As shown in Fig. 8(a), initial flux of DI water through the modified membrane was slightly lower than that of the pristine membrane due to the pore size reduction as mentioned in Fig. 3. However, modified membrane maintained initial flux, while pristine membrane underwent more flux decline. When Kaolin solution was tested, flux of the pristine membrane was much reduced and serious flux decline was observed. Back wash treatment could not properly restore the flux. Modified membrane showed much improved flux and more effective flux restoration than pristine membrane. When HMA, the cross-linking agent was used, more cross-linking was attained to reduce the flux as shown in Fig. 8(b). However, slope of the flux decline was reduced and modified membrane showed more stable flux for Kaolin solution permeation.

Various membrane chemical cleaning processes were attempted by using several chemicals, and chemical resistance was examined. When pristine

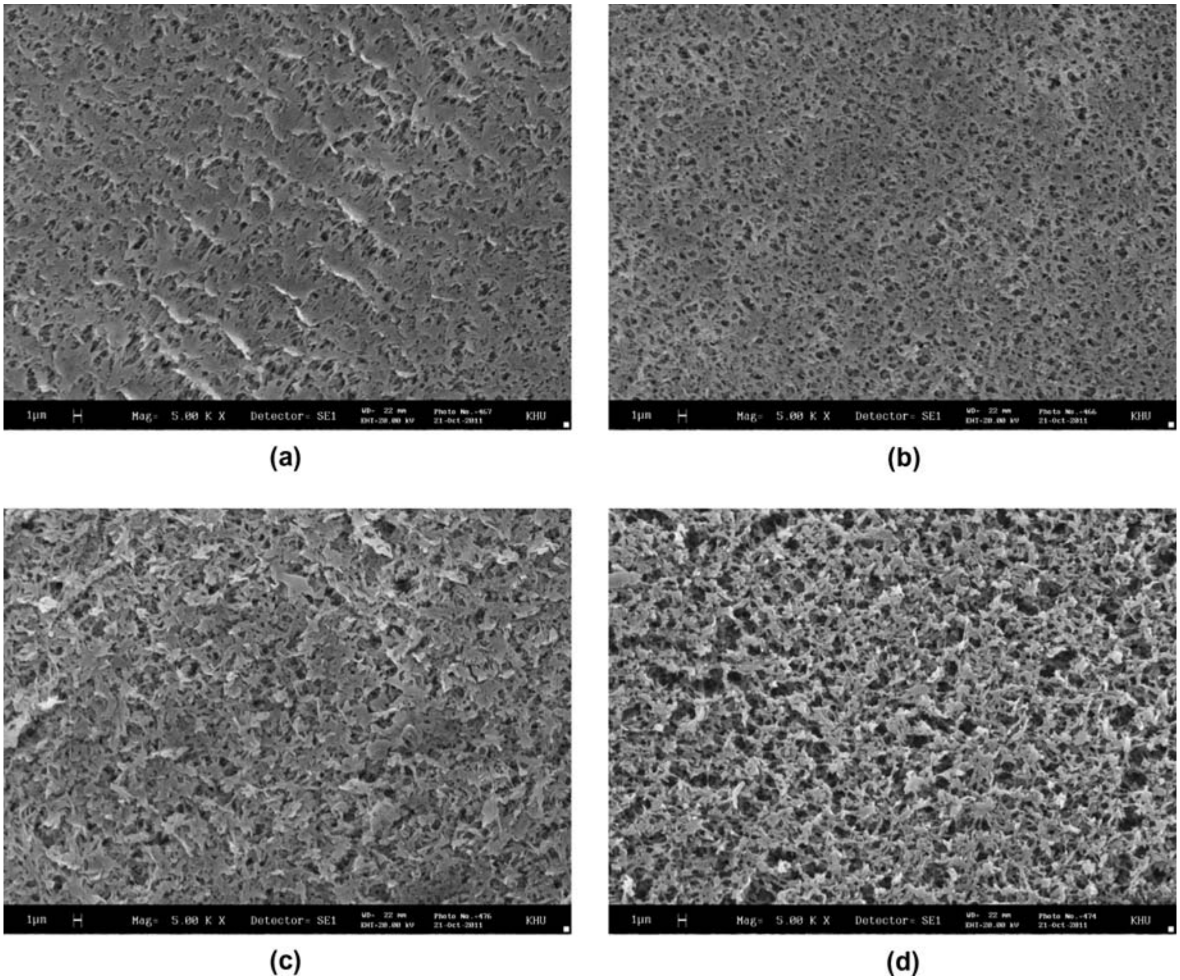

Fig. 5. Surface SEM images for (a) one-stage solution polymerization, (b) one-stage surface polymerization, (c) two-stage solution polymerization and (d) two-stage surface polymerization.

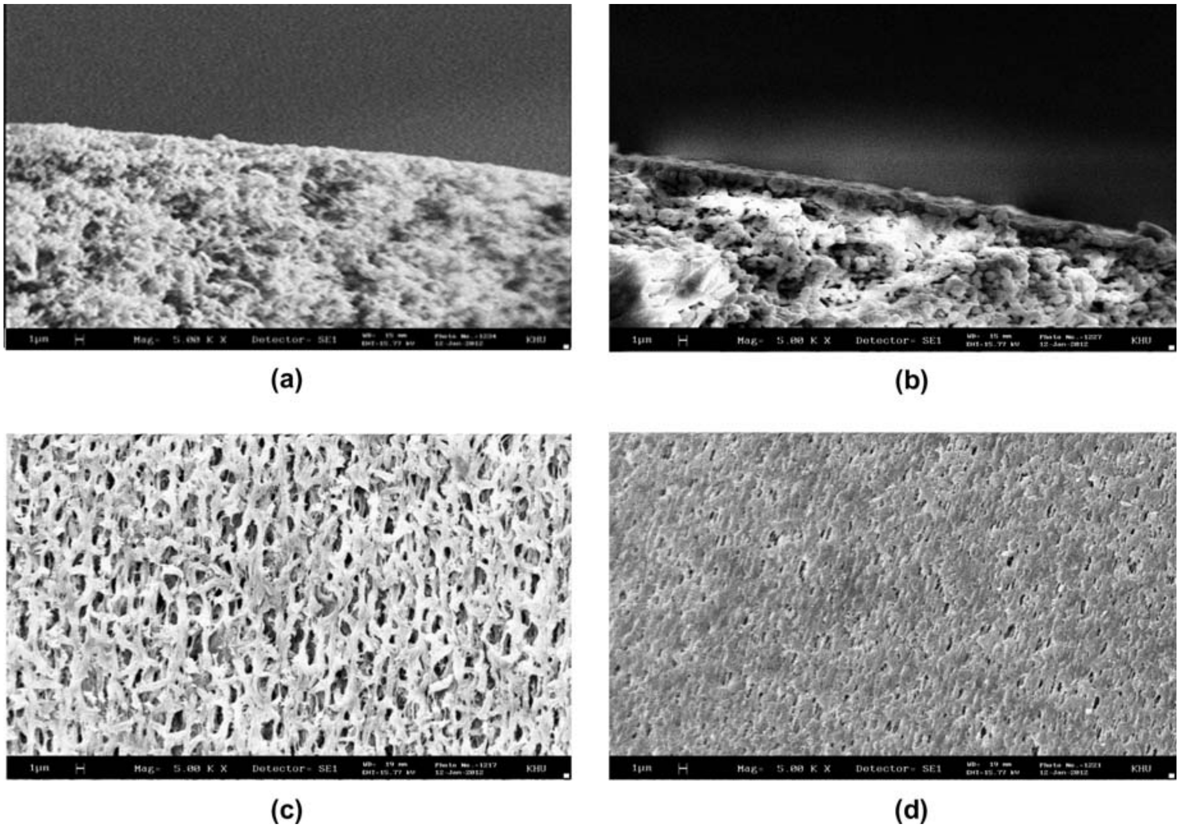

Fig. 6. SEM images for cross sections of (a) pristine membrane, (b) two-stage cross-linked membrane and top surfaces of (c) pristine membrane and (d) two-stage cross-linked membrane.

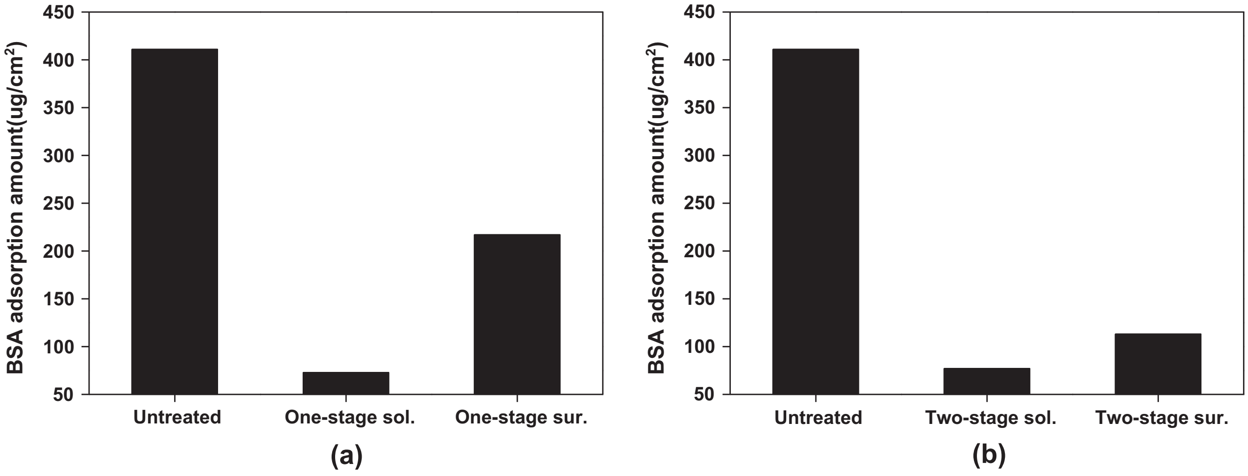

Fig. 7. Amount of BSA adsorbed on the sample via (a) one-stage cross-linking and (b) two-stage cross-linking.

membranes were tested membrane performances were deteriorated after contacting the chemicals as shown in Fig. 9(a). When the membrane was modified by two-stage thermal cross-linking, performance of the membrane was little affected by the chemical contacting as shown in Fig. 9(b). Therefore, thermal cross-linking also enhanced the chemical resistance of the membrane as well as the coating layer.

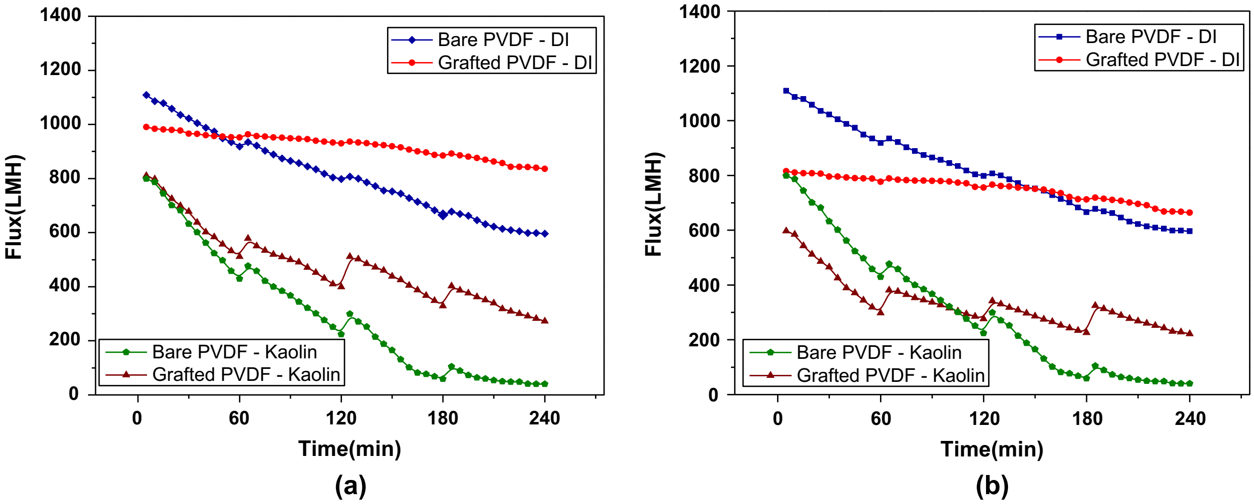

Fig. 8. Flux variation for backwash process with hydrophilized PVDF hollow fiber (a) grafted without cross-linking agent (b) grafted with cross-linking agent.

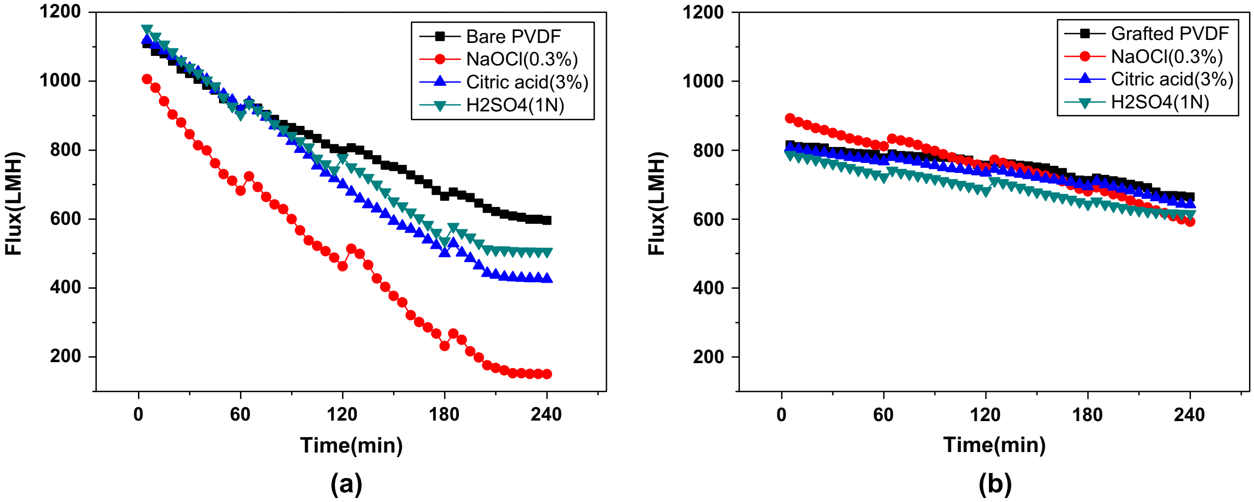

Fig. 9. Test of chemical resistance of coating layer on the pure water permeation rate (a) pristine membrane (b) two-stage cross-linked membrane.

3.5.1. Mini pilot test

Pristine and two-stage cross-linked PVDF membranes were potted to make hollow fiber module effective surface area of which was 0.24 m^2. Both hollow fiber modules were installed in water purification site in Bupyoung, Korea. Permeation tests were performed for 7 days via dead-end filtration mode. Feed water was supplied from Han River without any further purification system, whose turbidity was 7–12 NTU. Operation cycle time was 30 min, which consisted of operation for 27 min, back washing at 1.5 times greater than normal operation for 1 min, and drain and refill for 1 min, respectively.

Variations of flux and trans-membrane pressure (TMP) with time for pristine membrane module and modified membrane module are compared in Fig. 10. Test was performed at harsh conditions of much higher flux and TMP than the normal operation to accelerate the flux decline and TMP build up. At initial stage, there was little difference between the modules. However, after 48 h pristine membrane module showed more flux decline and TMP build up than the modified membrane module. Therefore, it was proved that thermally cross-linked membrane showed better performance and stability than the pristine membrane for real system application.

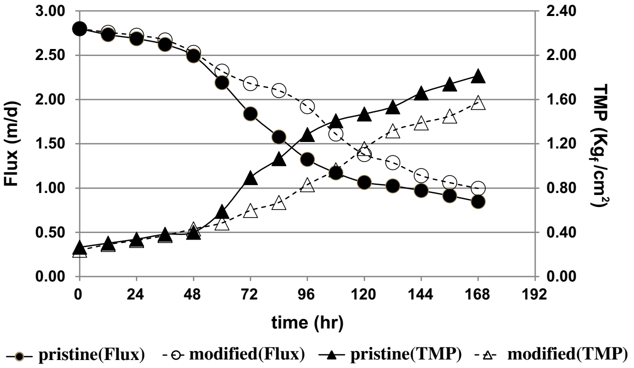

Fig. 10. Comparison of modified and pristine PVDF hollow fiber performance on the flux and trans-membrane pressure (TMP). (Dead-end filtration mode with feed water from Han-River at 7–12 NTU.)

4. Conclusions

Two-stage cross-linking method was more effective than one-stage method due to the interfacial reaction at surface. SEM images proved that the sample prepared by two-stage thermal cross-linking formed quite uniform coating layers. Surface polymerization was more appropriate than solution polymerization which caused excess coating. The sample via solution polymerization was proved to have dense coating layer to reduce the pore size. Two-stage thermal cross-linking via surface polymerization was the best process in terms of membrane permeation performance as well as the membrane fouling. Modified membranes showed more stable flux than the pristine membranes especially for the Kaolin solution, and they were proved chemical resistant to several chemicals in the solution. Long-term test proved the stability of the modified membranes in terms of flux and TMP build up.

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References

[1] R. Souzy, B. Ameduri, B. Boutevin, Synthesis and (co)polymerization of monofluoro, difluoro, trifluorostyrene and ((trifluorovinyl)oxy)benzene, Prog. Polym. Sci. 29 (2004) 75–106.

[2] B.S. Oh, H.Y. Jang, J. Cho, S. Lee, L.E. Lee, I.S. Kim, T.M. Hwang, J.W. Kang, Effect of ozone on microfiltration as a pretreatment of seawater reverse osmosis, Desalination 238 (2009) 90–97.

[3] J. Liu, P.L. Li, Y.D. Li, L.X. Xie, S.C. Wang, Z. Wang, Preparation of PET threads reinforced PVDF hollow fiber membrane, Desalination 249 (2009) 453–457.

[4] J. Mueller, R.H. Davis, Protein fouling of surface-modified polymeric microfiltration membranes, J. Membr. Sci. 116 (1996) 47–60.

[5] J. Wei, G.S. Helm, N. Corner-Walker, X.L. Hou, Characterization of a non-fouling ultrafiltration membrane, Desalination 192 (2006) 252–261.

[6] J.F. Hester, P. Banerjee, Y.Y. Won, A. Akthakul, M.H. Acar, A.M. Mayes, ATRP of amphiphilic graft copolymers based on PVDF and their use as membrane additives, Macromol. 35 (2002) 7652–7661.

[7] Y.C. Chiang, Y. Chang, A. Higuchi, W.Y. Chen, R.C. Ruaan, Sulfobetaine-grafted poly(vinylidene fluoride) ultrafiltration membranes exhibit excellent antifouling property, J. Membr. Sci. 339 (2009) 151–159.

[8] Y. Chang, Y.J. Shih, R.C. Ruaan, A. Higuchi, W.Y. Chen, J.Y. Lai, Preparation of poly(vinylidene fluoride) microfiltration membrane with uniform surfacecopolymerized poly(ethylene glycol) methacrylate and improvement of blood compatibility, J. Membr. Sci. 309 (2008) 165.

[9] C. Makhlouf, S. Marais, S. Roudesli, Graft copolymerization of acrylic acid onto polyamide fibers, Surf. Sci. 253 (2007) 5521–5528.

[10] S. Hu, W.J. Brittain, Surface grafting on polymer surface using physisorbed free radical initiators 38 (2005) 6592–6597.

[11] A. Bhattacharya, B.N. Misra, Grafting: a versatile means to modify polymers Techniques, factors and applications, Prog. Polym. Sci. 29 (2004) 767–814.

[12] W. Yang, B. Ranby, Radical living graft polymerization on the surface of polymeric materials, Macromolecules 29 (1996) 3308–3313.

[13] J. Pieracci, D.W. Wood, J.V. Crivello, G. Belfort, UV-assisted graft polymerization of N-vinyl-2-pyrrolidinone onto poly (ether sulfone) ultrafiltration membranes: comparison of dip versus immersion modification techniques, Chem Mater. 12 (2000) 2123–2133.