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Hydrophilization of hydrophobic membrane surfaces for the enhancement of water flux via adsorption of water-soluble polymers

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Abstract. In this study, to improve the water flux of porous hydrophobic membranes, various water-soluble polymers including neutral, cationic and anionic polymers were adsorbed using 'salting-out' method. The adsorbed hydrophobic membrane surfaces were characterized mainly via the measurements of contact angles and scanning electron microscopy (SEM) images. To enhance the durability of the modified membranes, the water-soluble polymers such poly(vinyl alcohol) (PVA) were crosslinked with glutaraldehyde (GA) and found to be resistant for more than 2 months in vigorously stirred water. The water flux was much more increased when the ionic polymers used as the coating materials rather than the neutral polymer and in this case, about 70% of 0.31 L/m^2·h (LMH) to 0.50 LMH was increased when 300 mg/L of polyacrylamide (PAAm) was used as the coating agents. Among the cationic coating polymers such as poly(styrene sulfonic acid-co-maleic acid) (PSSA_MA), poly(acrylic acid-co-maleic acid) (PAM) and poly(acrylic acid) (PAA), PSSA_MA was found to be the best in terms of contact angle and water flux. In the case of PSSA_MA, the water flux was enhanced about 80%. The low concentration of the coating solution was better to hydrophilize while the high concentration inclined to block the pores on the membrane surfaces. The best coating condition was found: (1) coating concentration 150 to 300 mg/L, (2) ionic strength 0.15, (3) coating time 20 min.

Keywords: hydrophobic membrane; hydrophilization; water-soluble polymers; salting-out; poly(vinyl alcohol); poly(styrene sulfonic acid-co-maleic acid); poly(acrylic acid-co-maleic acid)

1. Introduction

The adsorption of biological compounds such as proteins on membrane surfaces which is driven by different protein-surfaceforces, including van der Waals, hydrophobic and electrostatic forces, is important in the fields of separation science (Matsumoto *et al*. 2003). Thephysical adsorption of natural polymers such as proteins on hydrophobic surfaces is referred to as a part of 'fouling phenomena', which is a major drawback of the continuous flux decline due to the adsorption in question, pore blocking, precipitation and cake formation in membrane-based water purification processes (Mulder 1996). The low surface tension energies of hydrophobic membrane surfaces give rise to several problems of easy wetting, ease of initial flux, adsorption or spreading

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(Kozlov *et al*. 2003). Therefore, it is required that the surface energy should be increased through the introduction of polar functionality using chemical modification (Belfer *et al*. 2001, Gancarz *et al*. 2000), gas-discharge treatment (plasma, corona, etc.) (Gancarz *et al*. 2000, Kim *et al*. 2002, Wavhal and Fisher 2003), γ-radiation (Kang *et al*. 2001) UV irradiation (Choi *et al*. 2007, Kou *et al*. 2003), and coating (Akhtar *et al*.1995, Stengaard 1988, Hvid *et al*. 1990, Li *et al*. 2000). Since, however, these chemical approaches are limited to lab scale to date because of the complicated production equipments, strict operation requirements and high costs, the coating or impregnating with hydrophilization agents, such as alcohols (Molisak-Tolwinska *et al*. 1998), surfactants (Kang and Shah 1997), or amphiphilic polymers (Bacheer *et al*. 2004) is more favorable method to endow the hydrophilicity with hydrophobic membranes (Yang *et al*. 2009).

As recognized, most commercial ultrafiltraion and microfiltration membranes are hydrophobic materials which are more sensitive to bio-materials such as proteins than hydrophilic ones, and hydrophilic surfaces preferentially adsorb water rather than solutes (Zhang *et al*. 2008). As for the hydrophilic coating materials, poly(vinyl alcohol)(PVA) which is known as the highly hydrophilic, nontoxic, and bio-compatible polymer and excellent film-forming properties of good mechanical strength, long-term temperature and pH stabilities, have been widely used (Zhang *et al*. 2008, Gholap *et al*. 2005, Serizawa *et al*. 2002, Kozlov *et al*. 2003, Coupe and Chen 2001, Barette *et al*. 2001). Typically, Zhang *et al*. (2008) described an approach for the hydrophilic modification of the hydrophobic polypropylene non-woven fabric by dip-coating PVA. The results showed that after PVA modification, the polar groups such as C-O, C-O-C were introduced to the surface, the hydrophilicity was improved, and water static contact angles were decreased from 86 ± 1° to 43 ± 3°, the amount of bovine serum albumin static adsorption was decreased by 83.4%. Gholap *et al*. (2005) studied the irreversible adsorption of PVA onto highly hydrophobic poly(vinylidene fluoride)(PVDF) membrane to improve the wettability by the measurement of water flux and contact angle. Water flux was enhanced 4 times higher than the origin flux of ca. 2.0 $L/m^2 \cdot h$ (LMH). (Serizawa *et al*. 2002) investigated the layer-by-layer (several layers stepwise adsorption) adsorption of PVA and poly(methyl methacrylate)(PMMA) from NaCl-containing aqueous and organic solutionsonto a quartz crystal (QC) microbalance substrates. They concluded that not only interactive polymer combinations but also combinations between PVA and hydrophobic polymers were significantly assembled in a stepwise manner, and also that the adsorption of PVA was accelerated by the addition of NaCl on the basis of a hydrophobic effect, resulting in thicker films. Kozlov *et al*. (2003) attempted to coat the surface of poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) using poly(L-lysine). After that, they tried to adsorb poly(vinyl alcohol)(PVA) onto the hydrophobic surfaces of FEP, poly(ethyleneterephthalate), poly(4-methyl-1-pentene), and silicone materials. The resulting polymers showed the low contact angles of 40-68° and the coating thicknesses of 1-5 nm. For the irreversible adsorption of PVA, they crosslinked the coated PVA using glutaraldehyde, and after that also claimed that the adsorbed layers were stable in water at 80°C. Outside of PVA coating, the interfacial polymerization/crosslinking which is a mature technology to prepare stable thin film composite membranes for reverse osmosis was applied to endow the hydrophilicity with microporous polypropylene membrane. Polyethyleneimine was coated on polypropylene membrane first and sequentially crosslinked with p-xylylene dichloride. The resulting membranes showed the significant increase of the surface hydrophilicity, a sharp decrease of water contact angle, and double increase of pure water flux (Yang *et al*. 2009). Serizawa *et al*. (1999) demonstrated the stepwise fabrication of ultrathin films that were composed of polyvinylamine (PVAm) by the repetition of its adsorption from an aqueous solution under a controlled pH conditionat a lower temperature, and subsequent drying processes.

In our laboratory, the hydrophobic commercially available membranes such as microporous polysulfone (PSf), polyvinylidene fluoride (PVDF), and polyethylene (PE) membranes were hydrophilized using water-soluble ionic polymers of PVAm, poly(vinyl sulfonic acid) (PVSA), and poly(styrene sulfonic acid) (PSSA) through the physical adsorption by the 'salting-out effect' and after that, characterized by several analysis tools, a contact angle measurements, agravimetric measurement, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). Typically, a contact angle of 47° was observed at ionic strength (IS) = 0.1 $Mg(NO)_2 \cdot 6H_2O$ and PVAm 2,000 mg/L for a PSf membrane. The weight changesby adsorption were varied with adsorption time in the cases of PVSA and PSSA, while the weight change for PVAm approached the equilibrium rapidly after the initial adsorption time (Cheong *et al.* 2013).

In this study, PVA as the neutral polymer, poly(styrene sulfonic acid-co-maleic acid) (PSSA_MA), poly(acrylic acid-co-maleic acid) (PAM) and poly(acrylic acid) (PAA) as the cation exchange polymers, and polyacrylamide (PAAm) as the anion exchange polymer were adsorbed, using the 'salting-out effect', onto hydrophobic membrane surfaces such as PE and PVDF dense membranes, and PSf ultrafiltration membrane. After physical adsorption of the mentioned water-soluble polymers through various adsorption time, drying, and crosslinking patterns, and blended solutions of hydrophilizing materials, etc., the resulting membranes were characterized using a mainly contact angle measurements, and scanning electron microscopy (SEM) and water flux measurements.

2. Experimental

2.1 Materials

PSf (Udel®) and PVDF (Solef®) were obtained from Solvay Plastics Co., respectively. PVA(Mw 89,000-98,000, 99+% hydrolyzed), PSSA_MA(Ave. Mw. ~20,000), PAM (Ave. Mw. ~50,000), PAA (Ave. Mw. ~100,000) and PAAm (Ave. Mw. 10,000 in water solution) were purchased from Sigma-Aldrich Co. (Milwaukee, USA). 1-Methyl-2-pyrrolidinone used as solvent was also obtained from Sigma-Aldrich Co. (Milwaukee, USA) and the ultra-pure water was provided by YOUNGLIN INSTRUMENT, Aqua MAX™. Porous PSf (Ave. pore size 0.1 μm) and PVDF (Ave. pore size 0.1 μm) membranes were provided from Woongjin Chemicals Co. and Waters Co., respectively. All reagents and solvents were used without further purification.

2.2 Dense membrane synthesis

10wt% PSf and PVDF solutions were prepared by dissolving preweighed quantities of each powder in 1-Methyl-2-pyrrolidinone and heating at 60°C for at least 6 h. Then homogeneous membranes were cast onto a glass plate using a Gardner knife. The membranes were allowed to dry in a thermoset oven at 80°C for more than 24 h. The resulting membrane thickness was about 25~30 μm.

2.3 Surface Adsorption (*Kim et al. 2011*, *Cheong et al. 2013*)

To adsorb the PSSA, PVSA and PVAm onto the several dense membranes and porous PE membranes, the 'salting-out' effect was used. Here, NaCl and $Mg(NO_3)_2 \cdot 6H_2O$ were used as salts.

First, the membrane materials to be adsorbed were soaked in water in a 500 mL beaker which already contained the adsorption materials. The concentration, 150-2,000 mg/L, and ionic strength, 0.1-0.15, of each salt were investigated for porous PE membranes andvarious 8 cm × 8 cm dense membrane samples. After adsorption for the desired adsorption time, the resulting sampleswere soaked in the crosslinking bath, usually 30wt% acetone aqueous solution containing 5vol% glutaraldehyde (GA) for 12 h at 40°C if necessary (Lee *et al*. 1999, Kang *et al*. 2014), and then washed with deionized water several times and then dried at room temperature.

2.4 Membrane characterization

Since the wettability of the adsorbed membrane surfaces by hydrophilic materials is greater than that of the original membrane surfaces, contact angles were measured to compare the surface characteristics. In this study, the static contact angles were measured to realize the changes in the membrane surface characteristics following the adsorption of the hydrophilic polymers, and as a result, the wettability was measured using water. A goniometer (CA-X, Kyowa, Kaimenkagaku Co., Tokyo, Japan) was employed to measure the angles at which the liquid interface meets the solid surface after dropping 1 μL ultrapure water on the membrane surface. Measurement of the static contact angle was duplicated over 10 times and then the values within the standard deviation of ± 8% taken and averaged.

2.5 Membrane performance (*Cheong et al. 2013*)

The adsorbed membrane performance was determined in terms of water flux by a permeation apparatus (Fig. 1) using a hollow membrane cell with an effectivearea of 32.1 cm^2. The membrane performance determination was carried out at a desired operating pressure at 25°C under a constant flow rate of 1.2 L/min. Water flux was determined by direct measurement of the permeate flow.

$$\text{Flux [LMH]} = (\text{permeate (liter)}/\text{membrane area (m}^2)) \times \text{time (h)} \qquad (1)$$

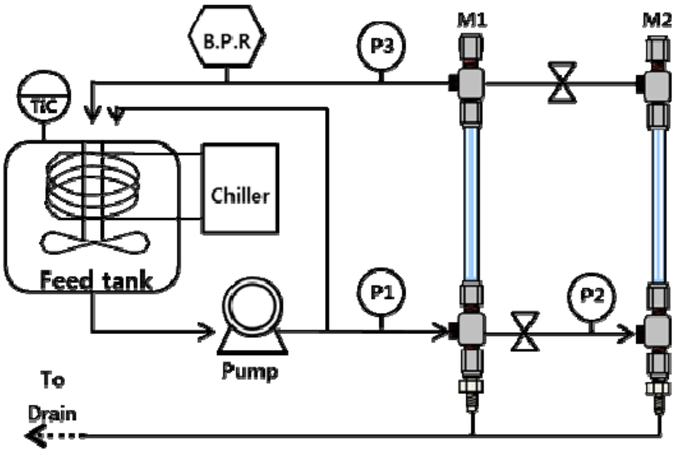


Fig. 1 Performance test apparatus for the adsorbed hollow fiber membranes

3. Results and discussion

The ‘salting-out effect’ is defined as the separation of an organic phase from an aqueous phase by adding a salt (Kim *et al.* 2011, Cheong *et al.* 2013, Hey *et al.* 2005). The solubility of organic molecules in aqueous solution can be also controlled by the addition of inorganic salts. At this point the solubility of then on-electrolyte can be reduced by the addition of the salt due to the salting-out effect. Likewise, when the salt concentration is increased in polymer aqueous solution, some of water molecules are attracted by the salt ions, which may decreases the number of water molecules available to interact with the charged part of hydrophilic, water-soluble polymers, leading to the polymer-polymer interactions are stronger than the water-salt interactions, that is, the polymers coagulateby forming hydrophobic interactions with each other, preferentially leading to physical adsorption on hydrophobic polymer surfaces. Therefore, the salting-out effect can be strengthened by altering the quantity of salts added, andthe quantity of salts required is governed by the ionic strength, which is a function of the concentration of all ions presentin a solution as follows

$$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2 \tag{2}$$

c_i is the concentration of ion i, z_i is the charge of ion i, and Σ is the sum taken over all ions in the solution.

Fig. 2 shows the effect of the coating time of PVA as the hydrophilization agent on PE dense film at IS = 0.1 NaCl. And the coated film was crosslinked with GA as illustrated in ‘Experimental’ section. It is known that the contact angle of pure PVA film is about 35° (Pemberton and De Jaeger 1996). As can be seen, the contact angle decreased sharply and then slowly decreased even though there does not look big difference to about 41° which is bigger than the 35° of untreated PVA film.

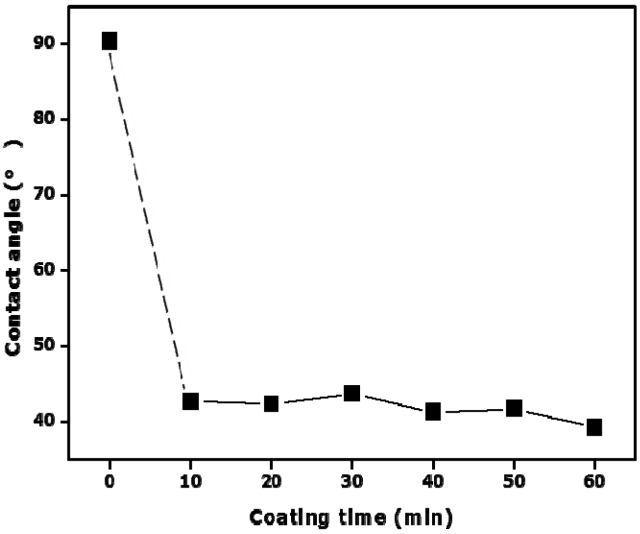
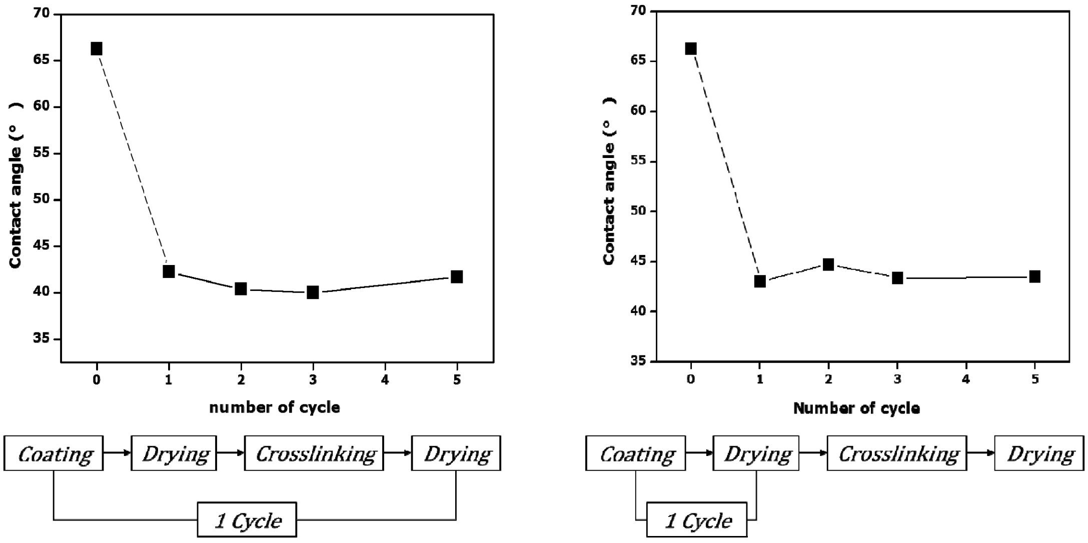


Fig. 2 Effect of the coating timeon PE dense film at IS = 0.1 NaCl using PVA 1000 mg/L as the hydrophilization agent and crosslinked with GA



(a) (b)

Fig. 3 Effect of the number of coating on PSf dense film at IS = 0.15 NaCl using PVA 2000 mg/L as the hydrophilization agent for 20 min and crosslinked with GA

It is considered that the adsorption takes place almost completely at the initial stage. The contact angle, 41.3°, of PVA on the PE surface is a little bit higher than the value of pristine PVA, 35°. This may be due to the loss of –OH group in PVA and hence the hydrophilicity of PVA on the surface decreases after reacting with GA (Hyder 2008).

Fig. 3 illustrates the effect of the number of coating of PVA on PSf dense film surface for two types of the coating pattern. Fig. 3(a) indicates the case of the coating pattern likewise, ‘coating, drying, crosslinking and drying’ in sequence which this whole sequence is one cycle while the coating pattern of Fig. 3(b) of ‘coating and drying’ is one cycle and then crosslinking and drying processes have been done at final stage. (Referred to Fig. 3) In both coating patterns, there was no big difference in the contact angles. And it is considered that there is nothing to do with the number of coating as well. However, as the number of coating increases, the coating layer thickness would increase so that the surface pores may be blocked, as a result, the flux would be reduced.

To observe the effect of the number of coating, SEM images were taken for Fig. 3(b) case as shown in Fig.4. Pores on the surface of 1 cycle coating are rarely observed while the surface of 2 cycles coating is seen very denser than that of 1 cycle coating so that it is hardly to find pores as can be seen in Fig. 4. However, for the cross section, it is obvious to find the coating layer for the 1 cycle or 2 cycles coated PSf membrane even if it is difficult to differentiate which costing layer thickness is thicker. Apparently, the used IS (0.15), PVA concentration (2,000 mg/L) and coating time (20 min) are overdosed for the purpose of the hydrophilization. Each condition should be used lower to hydrophilize the porous hydrophobic membranes.

The physical adsorption on the hydrophobic surfaces would lead to return to the original state by the long-time rinsing since the adsorbed materials are water-soluble polymers. Therefore, the adsorbed layer should be crosslinked to avoid washing-out and then it needs to investigate the

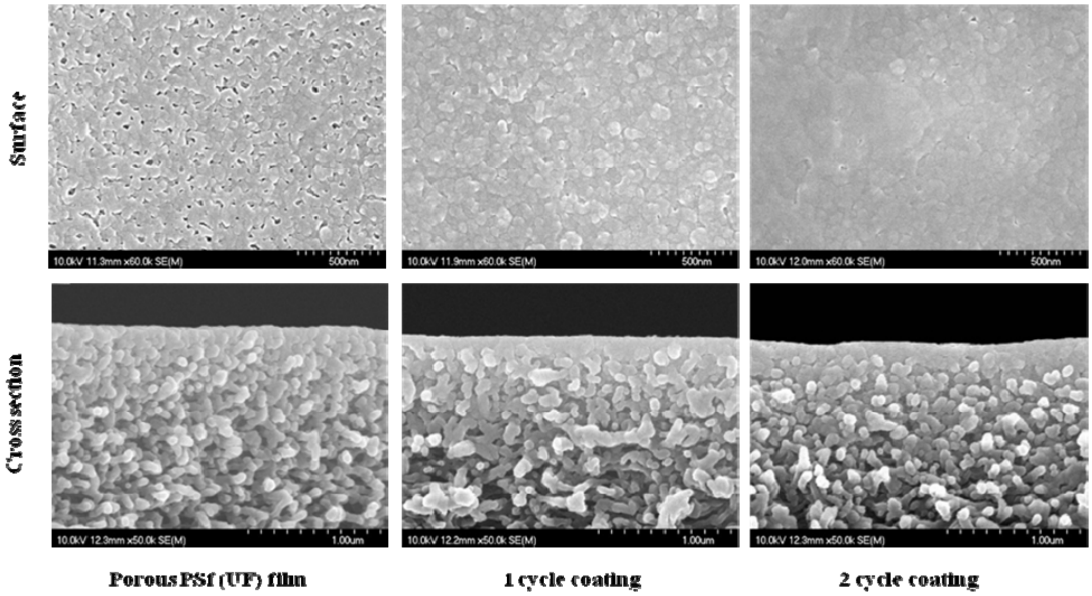


Fig. 4 SEM images for 1 and 2 cycles coating on PSf UF film at same conditions as illustrated in Fig. 3

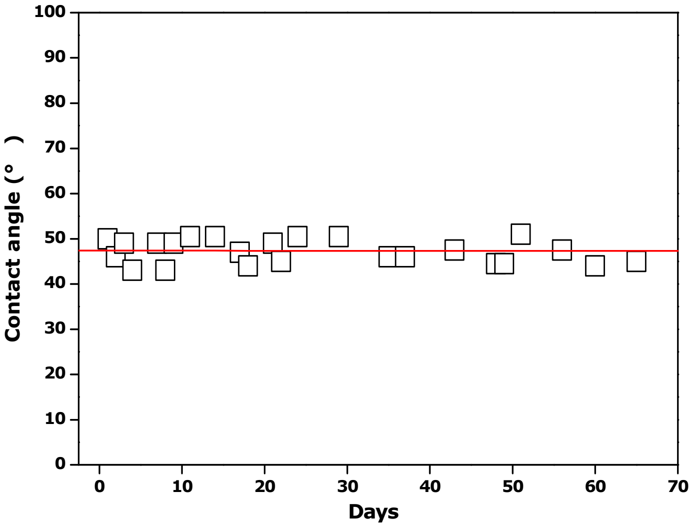
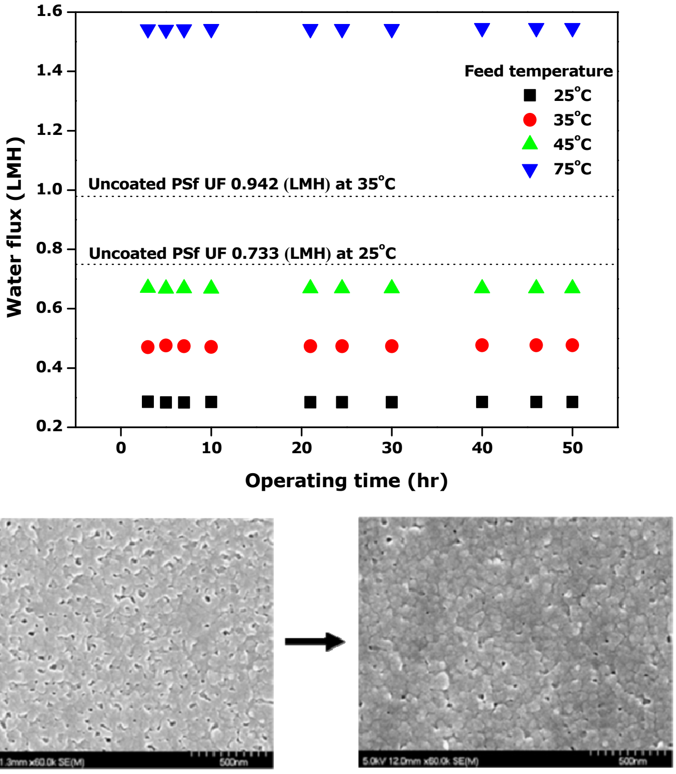


Fig. 5 Durability test results by soaking the PVA adsorbed PVDF dense film followed by the adsorption of 5 cycles illustrated in Fig. 3(a) in water at room temperature after the crosslinking with GA at 40°C for 12 h

disappearance of the coating layer. Next Fig. 5 illustrates the durability test results of the adsorbed coating layer of dense PVDF film using PVA by the contact angle measurement. To obtain the sturdy coating layer, the 5 number of the coating cycles have been done and also the crosslinking time and temperature have been also lengthened. The adsorbed crosslinked PVDF samples were shredded to 2 cm × 2 cm size and soaked them in water and stirred steady vigorously. Then one by one was taken out to measure the contact angle after drying. The initial contact angle value varied from 44° to 50° for a week and this value was maintained consistently to two months passing by. Overall contact angle values are within the ranges of between 44° and 51°. It can be said that the adsorbed coating layer is fairly durable.

However, since this indirect method of the contact angle measurement is too short to realize the durability and the temperature is also room temperature, the real water flux experiments would need to study using the coated UF/MF membranes at the elevated operating temperature.

Fig. 6 shows the water flux of PSf UF membrane coated with 1,500 mg/L PVA at IS = 0.1 NaCl. The water fluxes of the uncoated PSf membranes are shown ca. 0.73 LMH and 0.94 LMH at 2 atm, respectively, while the fluxes of the coated membranes at same temperatures are half-time lower. From these results, the coating conditions may be overdosed since the water flux is lower than expected. However, the most important thing of this figure is that the coated membrane has the durability at high temperature, 75°C since the water flux is shown very consistent at low to high temperatures for fairly long operating time. It is noteworthy that the adsorbed PVA looks not to be desorbed at high temperature of 75°C even if PVA is water-soluble but nevertheless crosslinked. The below SEM images prove the porosity of the coated UF membranes lowered due to the 'salting-out effect'.



PSf(UF) membrane

Coated and crosslinked

Fig. 6 Water flux for PSf UF membrane coated with 1,500 mg/L at IS = 0.2 NaCl for 20 min and crosslinked with GA at 40°C for 12 h according to operating time and feed temperature and SEM images of pristine and coated membranes

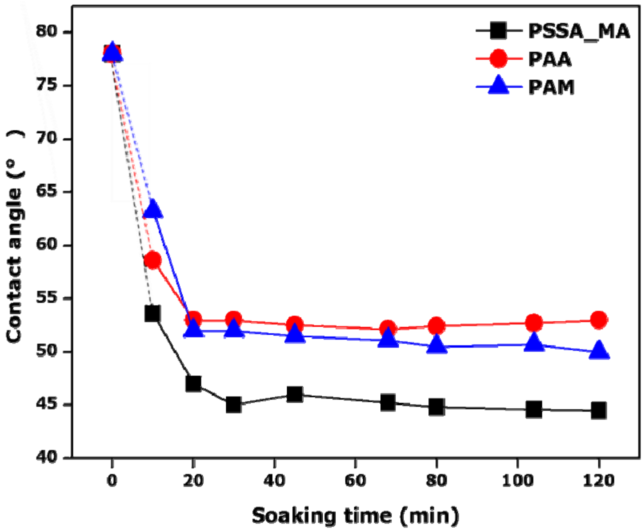


Fig. 7 Effect of the coating timeon PVDF dense film at IS = 0.15 NaCl using PSSA_MA, PAA, and PAM 300 mg/L as the hydrophilization agents

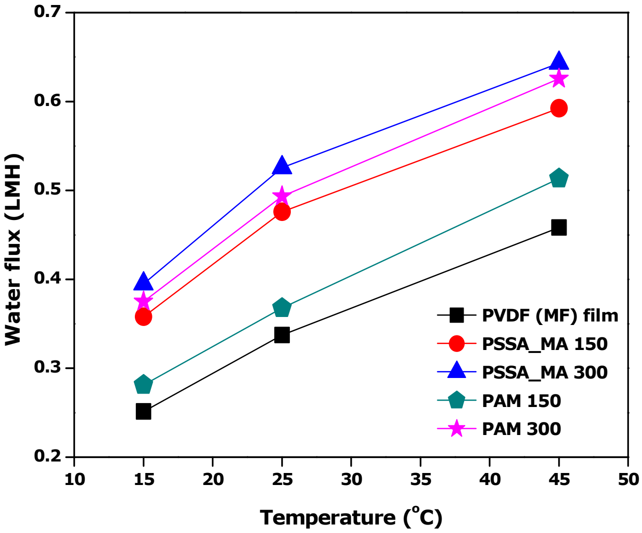


Fig. 8 Water flux of porous PVDF membranes coated with PSSA_MA, PAA, and PAM 300 mg/L at IS = 0.15 NaCl for 20 min

Until now the hydrophilic characteristics of the membranes coated with the neutral polymer of PVA were discussed. From now on, when the ionic polymers of cationic and anion exchange polymers were used as the coating materials, the characteristic changes in terms of the contact angles and water flux will be investigated.

At the same coating condition, the contact angle for PSSA_MA is shown the lowest value among the three hydrophilization agents. After 20 min coating, the contact angles are stabilized to 52° for PAA and PAM and 45° for PSSA_MA. Since PSSA_MA has both sulfonic acid group and carboxylic acid group in each repeating unit while PAA and PAM have only carboxylic acid groups in their repeating unit, its hydrophilicity may be higher than those of PAA and PAM.

Fig. 8 illustrates the water flux for PSSA_MA and PAM coated on porous PVDF membranes which concentrations are 150 and 300 mg/L at other conditions same as previous figure case, respectively. The flux at same concentration, 150 mg/L of coating agents in the soaking solution is shown surprisingly that PSSA_MA is much superior to PAM and this tendency maintains even at higher concentration of 300 mg/L. According to Semenova *et al.* (1997), fixed ion and counter ion have a very strong influence on the interaction of polymers with water. Table 1 presents the sorption of saturated water vapor in polymers. Water sorption increases with the increase of acidity of ionic groups by changing carboxylic groups to sulfonate group which pKa values are 1.1 and 4.2, respectively. Therefore, as in Fig. 7, the contact angle of PSSA_MA coated PVDF film is lower than that of PAA or PAM coated film. Nevertheless, in Fig. 8, the increase of hydrophilicity leads to the increase of water flux resultantly. With coating of PSSA_MA 300 mg/L, the water flux was enhanced about 70%. However, since these polymers are water-soluble, it is doubtful about the durability even if the flux data was shown at higher temperature, 45°C. Therefore, the ionic polymers could not be used in commercial process even though the water flux is higher than neutral water-soluble polymers as the coating material.

Table 1 Sorption of saturated water vapor in polymers at 25°C*

Polymer	Active group	C_{water} (mol/mol)
Polyvinyl alcohol	-OH	0.4
Polyacrylic acid	-COOH	0.7
Sodium polyacrylate	-COONa	4.2
Sodium polyvinylsulfonate	$-SO_3Na$	8.8
Sodium polystyrene sulfonate	$-SO_3Na$	11.3

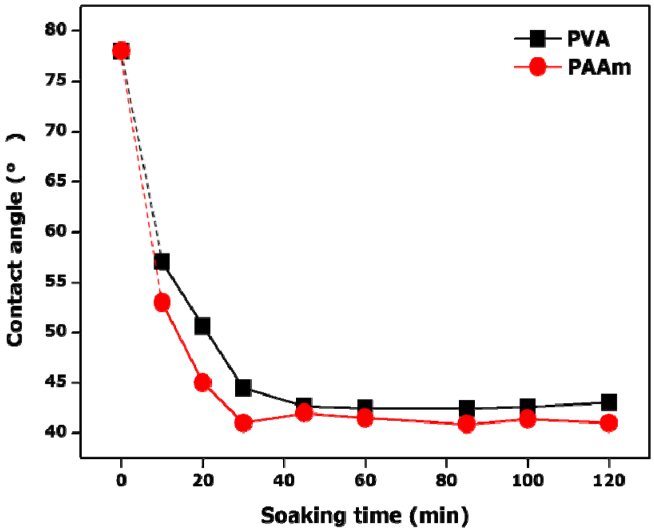


Fig. 9 Effect of the coating timeon PVDF dense film at IS = 0.15 NaCl using PVA and PVAm 150 mg/L as the hydrophilization agents

Fig. 9 shows the contact angle comparison between PVA and PAAm as coating materials. The case of PAAm is a little lower than that of PVA, but they are close each other. The amine group, -NH_2, may be more hydrophilic than the hydroxyl group, -OH. This tendency is also coincident with results described in Figs. 7-8. As seen in Fig. 10, the water flux of PVDF membrane coated with PAAm 300 mg/L is more than that of PAAm 150 mg/L coated PVDF membrane. This may be due the reason that 150 mg/L PAAm may not be enough too low to coat the membrane surface evenly because the contact angles for both PVA and PAAm cases are stabilized after 30 or 40 min which is different from the cationic polymers used as the coating materials appeared in Fig. 7. Therefore, the 20 min coating with 300 mg/L may spread more out than with 150 mg/L and this would lead to more water flux. The water flux of 300 mg/L PAAm coated PVDF membrane was enhance about 70% at 25°C. Apart from the cationic polymers as coating materials, this PAAm (or PVA) can be crosslinked with glutaric acid to improve the durability.

4. Conclusions

To improve the water flux of porous hydrophobic membranes, various water-soluble polymers such as PVA, PSSA_MA, PAM, PAA and PAAm were used as the coating materials and the salting-out method was carried out for the coating purpose. The adsorbed hydrophobic membranes were characterized via the contact angle measurements, SEM image observations and water flux measurements. From these experiments, several conclusions can be drawn as below;

- The contact angles of the membrane surfaces were lowered to the ranges, 40°-45° for PVA, PSSA_MA, and PAAm, and 50°-55° for PAA and PAM.
- Since the contact angles of the PVA adsorbed PVDF dense film followed by crosslinked with GA was maintained consistently for more than 2 months, the durability was verified.
- The water flux was more increased when the ionic polymers used as the coating materials rather than the neutral polymer. Typically, when 300 mg/L of polyacrylamide (PAAm) was used, about 70% of 0.31 LMH to 0.50 LMH was increased.
- PSSA_MA of the highest acidity value among cationic exchange polymers was shown the lowest contact angle value, about 45° and also the highest water flux of about 0.53 LMH whereas the water flux of the pristine PVDF membrane was 0.33 LMH.
- The low concentration of the coating solution was better to hydrophilize while the high concentration inclined to block the pores on the membrane surfaces.
- The best coating condition was found: (1) coating concentration 150 to 300 mg/L; (2) ionic strength 0.15; (3) coating time 20 min.

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