Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.912159

54 (2015) 2911–2919
June

Taylor & Francis
Taylor & Francis Group

Preparation of a PVDF hollow fiber blend membrane via thermally induced phase separation (TIPS) method using new synthesized zwitterionic copolymer

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Received 10 December 2013; Accepted 9 March 2014

ABSTRACT

Antifouling properties of PVDF hollow fiber membrane were improved by the addition of a new synthesized zwitterionic copolymer. This copolymer was synthesized using methyl methacrylate and the zwitterionic monomer 3-(methacryloylamino)propyl-dimethyl(3-sulfopropyl) ammonium hydroxide) (MPDSAH). The copolymer was used as additive in the preparation of a poly(vinylidene fluoride) (PVDF) hollow fiber membrane via thermally induced phase separation. With addition of the copolymer, the crystallization temperature and spherulite growth rate of the polymeric solution decreased sharply. Quartz crystal microbalance with dissipation monitoring results showed that bovine serum albumin (BSA) interactions with the prepared PVDF/copolymer film sharply decreased with addition of the synthesized copolymer. BSA filtration results showed that the membrane had higher antifouling resistance than a membrane without the copolymer additive.

Keywords: Poly(vinylidene fluoride); Zwitterion copolymer; 3-(methacryloylamino)propyl -dimethyl(3-sulfopropyl) ammonium hydroxide; Thermally induced phase separation; Blend hollow fiber membrane

1. Introduction

Poly(vinylidene fluoride) (PVDF) is a semi-crystalline polymer that has attracted much attention because of its good mechanical strength, chemical stability against vigorous chemicals, and thermal stability [1–3]. Because of these properties, it could be used for membrane preparation, but it is easily fouled by protein [4–6]. Fouling decreases the membrane permeability and subsequently increases the processing costs. A number of studies have been performed to overcome the fouling problem, including polymeric phospholipid coatings [7], plasma treatment [8], grafting [9], chemical modification of the surface [10], and blending with hydrophilic polymers [5,11,12]. Among membrane preparation methods, blending is the simplest because it requires just one step and further processing is not needed. Because of the interactions between PVDF's fluorine atoms and carbonyl groups of the partner polymer [13], PVDF is highly miscible with oxygen-containing polymers. Consequently, several polymer blends have been investigated, such as PVDF/poly(vinylpyrrolidone) (PVP) [14], PVDF/poly

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(ethylene glycol) (PEG) [15], PVDF/poly(acrylonitrile) (PAN) [16], and PVDF/poly(methyl methacrylate) (PMMA) [17].

It is well reported that surfaces covered with zwitterions are resistant to protein adsorption [18–24]. Therefore, zwitterions could be useful for the preparation of antifouling membranes. Jiang and co-workers [18,19,25,26] showed that when a copolymer including a zwitterionic monomer and PES or PAN was used as a hydrophilic additive to prepare a PES or PAN blend membrane, the antifouling properties were much better than without the copolymer. Wang et al. [25] prepared a sulfobetaine copolymer by reacting *N*,*N*-dimethyl-*N*-methacryloxyethyl-*N*-(3-sulfopropyl) (DMMSA) with butyl methacrylate (BMA), and used it as an additive for the preparation of a PES blend membrane. This membrane showed considerably low irreversible fouling during protein filtration, and the good antifouling properties were observed over a wide pH range (4–8). In this study, the concentration of the sulfobetaine copolymer detected at the membrane surface was higher than that in the membrane bulk. In another study from the same group, Sun et al. [19] synthesized a random copolymer, poly((2-dimethylamino ethyl methacrylate)-acrylonitrile), (PAN–DMAEMA) as a novel additive for PAN blend membrane preparation. The fouling of the blend membrane was remarkably low, and reversible, compared with a control PAN membrane. Subsequently, they found that when PAN was blended with the random copolymer poly(acrylonitrile-([3-(methacryloylamino)propyl]-dimethyl(3-sulfopropyl) ammonium hydroxide)) (PAN–MPDSAH), membrane fouling was very low and reversible [26]. Li et al. [27] showed that a novel amphiphilic zwitterionic copolymer, poly(vinylidene fluoride)-graft-poly(sulfobetaine methacrylate) (PVDF-g-PSBMA), greatly improved the surface hydrophilicity and surface antifouling properties of PVDF-blended membranes when it was used as an as amphiphilic additive in the membrane preparation.

To the best of our knowledge, all studies on blended hollow fiber membranes with zwitterionic copolymer additives have used non-solvent induced phase separation method (NIPS) rather than thermally induced phase separation (TIPS). Some studies have investigated preparation of blended hollow fiber membranes by TIPS, but the membranes were prepared without copolymer additives. In our earlier research on the preparation of blended membranes by TIPS, we found that blending PVDF with PMMA had almost no effect on the antifouling properties of the prepared membrane, while PVP-blended membrane showed some promise in improving antifouling properties [28,29]. Based on these results, we concluded it was difficult to find a commercial polymer with sufficiently high hydrophilicity that was also compatible with PVDF to use as an additive for blended membrane preparation by TIPS. Thus, in the present study, we synthesized a random copolymer of the zwitterionic monomer, 3-(methacryloylamino)propyl-dimethy l(3-sulfopropyl) ammonium hydroxide (MPDSAH), with methyl methacrylate (MMA), in the hope it would fulfill the above criteria. As far as we know, MPDSAH as a zwitterion monomer was used for the preparation of the antifouling membranes in some works [26,30–32], and antifouling properties of the membranes prepared from this monomer were comparable with those of the common zwitterionic monomers [32]. MMA with high compatibility with PVDF was selected as a PVDF substitute. On the other hand, since our new synthesized copolymer has PMMA part that is compatible with PVDF, PES, and PSf (polysulfone), it is expected that newly synthesized copolymer can be used as potential additive with antifouling properties not only for PVDF that we used in this study, but also for other types of polymers. To investigate the effect of the synthesized copolymer addition on membrane fouling, a pure PVDF membrane and blended membranes with similar water permeability were prepared by changing dope solution composition and spinning conditions. Effect of each parameter of the hollow fiber membrane preparation on the prepared membrane properties was explained in our previous published papers [28,29,33]. Fouling trends of the prepared membranes was explained based on the quartz crystal microbalance with dissipation monitoring (QCM-D).

2. Experimental

2.1. Materials

PVDF (Mw = 322,000, Solef 6020) was purchased from Solvay Co. (Belgium). MMA and MPDSAH were purchased from Sigma-Aldrich (St. Louis, MO). Diethyl phthalate (DEP, Wako Pure Chemical Industries, Osaka, Japan) was used as a solvent for membrane preparation. Bovine serum albumin (BSA) solution was prepared by dissolving BSA in a buffer solution of sodium dihydrogen phosphate and disodium hydrogen phosphate at pH 7.0. BSA; sodium dihydrogen phosphate, disodium hydrogen phosphate, 2,2′-azobisisobutyronitrile (AIBN), ethanol, 1-methyl-2-pyrrolidone, (NMP), and lithium bromide monohydrate were purchased from Wako Pure Chemical Industries. Polystyrene latex particles (ø 50 nm) were from Duke Scientific Corporation (Thermo Fisher Scientific, Waltham, MA). MMA was purified using a

MFCD00081548 packed column purchased from Sigma-Aldrich. All other chemicals were used without further purification.

2.2. Polymerization and characterization of the poly(MMA-MPDSAH) copolymers

Poly(MMA-MPDSAH) copolymers were synthesized by free radical polymerization of MMA with MPDSAH. In this reaction, the ester group of MMA reacts with the methacryloylamino group of MPDSAH to produce poly(MMA-MPDSAH). The chemical structure of in-house made copolymer was shown in Fig. 1. For polymerization, a mixture of 0.5 mol MMA, 55.6 mmol MPDSAH, and 1.52 mmol AIBN was added to a mixture of 67.5 mL of ethanol and 37.5 mL of Milli-Q water in a three-neck flask. The mixture was refluxed at 80˚C for 8 h under nitrogen gas. After completion of polymerization, the reaction product was precipitated in Milli-Q water and separated by using filter paper (5A, Advantec; Toyo Roshi Kaisha, Ltd., Japan). The obtained copolymer was dried at 40˚C under vacuum, and then analyzed using attenuated total reflection Fourier-transform infrared (ATR-FTIR) (FTIR-8100A, Shimadzu Co., Kyoto, Japan) and elemental analysis (Japan System Engineering). The copolymer was also subjected to gel permeation chromatography (GPC) (Shimadzu) using a Shodex KD-804 column, refractive index detector, 50 mmol/L LiBr in NMP as the eluent, and PMMA as the standard. Thermogravimetric analysis (TGA) was performed using (TGA-50, Microthermobalance, Shimadzu Co., Kyoto, Japan).

2.3. Crystallization temperature and spherulite growth rate

PVDF/DEP or PVDF/copolymer/DEP mixtures were heated to 200˚C in an oil bath, mixed at this temperature for 3 h, and then cooled to room temperature to obtain a solid. Each sample was then cut into small pieces and placed between a pair of microscope cover slips. A 100 μm thick Teflon film with a square opening in the center was set between the two cover slips to prevent solvent evaporation and to ensure all the samples were of approximately the same thickness. Each sample was heated on a LK-600 PH hot stage (Linkam Scientific Instruments, Guildford, UK) to 200˚C, held at this temperature for 5 min, and then cooled to 25˚C at a controlled rate of 10˚C/min. The crystallization tem perature was determined visually by noting the appearance of spherulites under a BX50 optical microscope (Olympus Co., Japan) equipped with a LK-600 PH hot stage [28]. The spherulite growth rate was also measured using this equipment by recording several snapshots at set time intervals and measuring the spherulite diameter in each photograph.

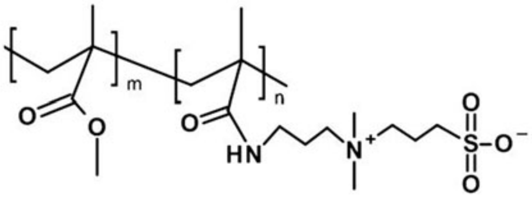

Fig. 1. Synthesized copolymer structure.

2.4. BSA adsorption on polymer films

QCM-D was used to measure the amounts of BSA adsorbed on the PVDF and PVDF/copolymer blend films. Polymer-coated QCM sensors were prepared as follows. Piezoelectric quartz crystal sensors with a fundamental resonant frequency of 4.95 MHz and a diameter of 14 mm (QSX 301; Q-Sense Co., Stockholm, Sweden) were pre-cleaned using an ultraviolet/ozone cleaner (Pro Cleaner 110; BioForce Nanosciences Co., Ames, IA). Then, the sensors were spin-coated with a 1.0 wt% polymer solution at 3,000 rpm for 60 s, followed by drying on a hot plate (KATHERM C-MAG HP4; Kampmann GmbH, Lingen, Germany) at 80˚C for 2 h. QCM-D measurements were conducted in a flow chamber equipped with PVDF or PVDF/copolymer blend-coated quartz crystal sensors. A buffer solution was fed into the flow chamber at a flow rate of 50 μL/min for more than 30 min to stabilize the sensor. Then, 1,000 ppm BSA solution was supplied for more than 30 min. When BSA adsorbed onto the QCM sensor, the resonance frequency of the sensor decreased. The amount of BSA adsorbed per unit surface area of the QCM sensor (Δm) was correlated to the change in frequency (Δf) in accordance with the Sauerbrey equation (Eq. (1)) [34].

$$\Delta m = -C\frac{\Delta f}{n} \tag{1}$$

where C is the mass sensitivity constant (17.7 ng/cm^2/Hz at f = 4.95 MHz) and n is the overtone number (n = 3, 5, 7).

2.5. Membrane preparation

Hollow fiber membranes were prepared by a batch type extruder (BA-0, Imoto Co., Japan). A polymer solution was prepared by adding PVDF, solvent, and the copolymer (Table 1) into a vessel, heating the

Table 1
Hollow fiber membrane preparation conditions

		Membrane type		
		(A)	(B)	(C)
Dope solution	PVDF(Mw:322,000) [wt%]	37	32.5	29
	Poly(MMA-MPDSAH) [wt%]	0	2.5 (7.1*)	5 (14.7*)
	Diethyl phtalate(DEP) [wt%]	63	65	66
Quench bath temperature [℃]		40	0	16
Air gap distance [mm]		5	70	5
Take up speed [m/s]		0.14	0.1	0.1

*Numbers inside the parentheses indicate the copolymer concentration in polymer phase.

vessel to 230℃, and then mixing the solution for 1 h at 90 rpm. After mixing, the vessel temperature was decreased to 190℃ and held at this temperature for 2 h with mixing at 5 rpm to remove air bubbles. The prepared polymer solution was fed into a spinneret by a gear pump under pressure in a nitrogen atmosphere. The spinneret consisted of outer and inner tubes with diameters of 1.58 and 0.83 mm, respectively. The solvent was introduced into the inner tube to make a lumen of the hollow fiber. The hollow fiber was extruded from the spinneret and passed through a quenching bath containing water, which induced phase separation and solidified the membrane. After passing through the quenching bath, the fiber was wound onto a take-up winder. The velocities for introducing the polymer solution and solvent to the spinneret were fixed at 0.085 and 0.18 m/s, respectively. The temperature of the quenching bath, air gap distance, and uptake speed for each prepared membrane are summarized in Table 1. The solvent remaining inside the hollow fiber membrane structure was extracted with ethanol and then the ethanol was removed by immersing the membrane in water.

2.6. Scanning electron microscopy observation

Prepared hollow fiber membranes were freeze dried (FD-1000; EYELA, Tokyo, Japan). The dry membranes were fractured in liquid nitrogen and coated with osmium tetroxide (OsO_4). A thin OsO_4 layer (ca. 5 nm) was formed using an osmium coater (Neoc-STB; MEIWAFOSIS Co. Ltd., Tokyo, Japan). The surfaces and cross-sections of the membranes were observed using a field emission scanning electron microscope (JSF-7500F; JEOL Co. Ltd, Tokyo, Japan) with an accelerating voltage of 7 kV.

2.7. Fouling and polystyrene particle rejection experiment

Fouling experiments were conducted using a module containing a single hollow fiber membrane (approximately 110 mm long) [35]. First, deionized water was forced to permeate from the outside to the inside of the hollow fiber membrane at a flow rate of 16.6 mL/min and the flux was measured. Fouling experiments were carried out for 2 h using a 1,000 ppm BSA solution (pH 7.0) instead of deionized water, and water flux was measured over the filtration time. By adjusting the pressure at the outlet of the module for each membrane and then holding it constant during the experiment, the initial water flux was similar for all membranes and constant during each experiment. BSA concentrations of feed and permeate solutions were measured using an ultraviolet spectrometer (U-2000; Hitachi Co., Tokyo, Japan,) at a wavelength of 280 nm. Rejection of BSA was calculated using the following equation:

$$\text{Rejection } [\%] = (C_0 - C)/C_0 \times 100 \tag{2}$$

where C_0 and C are the concentrations of BSA in the feed and permeate solutions, respectively.

The solute rejection experiment was performed using the same apparatus as that used in the filtration experiment. The particle used was mono-dispersed polystyrene latex particles with 50 nm diameter. The feed solutions were prepared by adding the latex particles in an aqueous nonionic surfactant (0.1 wt% Triton X-100). The particle concentration in the filtrate and feed solution were measured with a UV spectrophotometer under the wavelength of 385 nm and rejection was calculated by using Eq. (2).

2.8. Water contact angle

Water contact angle of the membranes was measured using a contact angle goniometer (Drop Master 300, Kyowa interface science Co., Japan) at room temperature. Two micro liter droplet of water was dropped on the outer surface of membrane and the water contact angle was measured automatically. Each sample was measured 10 times at different positions and the average value was calculated.

3. Results and discussion

3.1. Characterization of the synthesized copolymer

ATR-FTIR spectroscopy was used to confirm that the reaction successfully produced the poly(MMA-MPDSAH) copolymer. The results are shown in Fig. 2. Infrared spectra of PMPDSAH, PMMA, and the poly (MMA-MPDSAH) copolymer were recorded (spectra (A), (B), and (C) in Fig. 2). In these spectra, a band at 1,729 cm^{-1} was observed for stretching of the carbonyl group in MMA, and a band at 1,036 cm^{-1} for stretching of the S=O group of MPDSAH. Spectrum (C) in Fig. 2 included both these bands and confirmed that the poly(MMA-MPDSAH) copolymer was synthesized successfully. The intensity of the S=O group transmittance for the synthesized copolymer was smaller than that for MPDSAH because there was less MPDSAH than MMA in the solution for the preparation of the copolymer (approximately 1:9 ratio).

Based on GPC results acquired using PMMA retention as a standard, the Mw and Mw/Mn of the synthesized poly(MMA-MPDSAH) were calculated as 120,000 and 1.4, respectively. Elemental analysis was performed to evaluate the actual monomer ratio. While the monomer feed composition suggested a theoretical C/N ratio of around 24.95, elemental analysis showed that this ratio was about 40. This indicates that the MMA/MPDSAH monomer ratio for the synthesized copolymer is 94:6, while the MMA/MPDSAH loading ratio was 9:1. This difference in the ratio suggests MMA is more reactive than MPDSAH in the polymerization reaction.

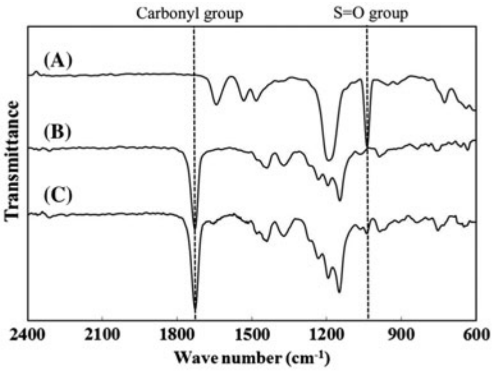

Fig. 2. ATR-FTIR spectra. (A) PMPDSAH (B) PMMA, (C) poly(MMA-MPDSAH).

“Although” not shown here, degradation of the synthesized copolymer was measured using TGA was found to be around 270°C that is 40°C higher than the dope solution preparation and membrane preparation temperature. Thus, it can be concluded that the copolymer did not degrade during the membrane preparation.

3.2. Crystallization temperature and spherulite growth rate

To evaluate the effect of synthesized copolymer addition on the PVDF solution crystallization temperature and spherulite growth rate, the total copolymer concentration of the polymeric solution was constant at 30 wt% even in the case of copolymer addition. The crystallization temperature results for PVDF (30 wt%)/DEP (70 wt%) solution and PVDF (25 wt %)/poly(MMA-MPDSAH) (5 wt%) copolymer/DEP (70 wt%) solutions are summarized in Table 2. While the crystallization temperature for the 30 wt% PVDF solution was 113°C, with addition of 5 wt% of copolymer it sharply decreased to 87°C. From these results, we hypothesized that adding the copolymer to the PVDF retards the crystallization properties of the PVDF.

Fig. 3 shows the spherulite diameter growth over crystallization time for two different polymeric solutions [PVDF (30 wt%)/DEP(70 wt%) and PVDF (25 wt%)/poly(MMA-MPDSAH) (5 wt%) copolymer/DEP(70 wt%)] used to determine the crystallization temperature. To calculate the spherulite growth rate, the slope of each curve was calculated from the point spherulites were observed until the spherulite growth stopped. The spherulite growth rate for the PVDF/DEP solution was around 16 μm/min, and that for the PVDF/copolymer/DEP solution was around 8.4 μm/min. It is clear from these results that a 5 wt% copolymer addition approximately halves the spherulite growth rate. From Fig. 3, it can be observed that although the spherulite growth rate for the solution including the copolymer is half of that without copolymer, crystal growth time is longer for this solution. Longer crystal growth time for the solution including the synthesized copolymer is resulted in spherulites with larger diameter although the growth rate is slow. On the other hand, it is worth to mention here that by decreasing the crystalline polymer concentration, final spherulite diameter increases [36]. For the solution including the copolymer, PVDF concentration is 5 wt% lower than that the other solution whose PVDF concentration is 30 wt%. Thus, we expect that the spherulite size of the solution including the synthesized copolymer would be larger than that of the solution including only PVDF.

Table 2
Crystallization temperature of polymeric solution

Polymeric solution	Crystallization temperature (℃)
PVDF 30 wt% + DEP 70 wt%	113
PVDF 25 wt% + Copolymer 5 wt% + DEP 70 wt%	87

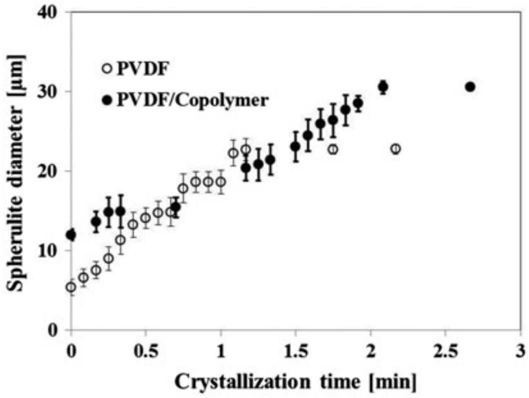

Fig. 3. Spherulite growth rates.

3.3. BSA adsorption on the polymer films

To evaluate the effect of the synthesized copolymer on BSA interactions, several polymeric films with different PVDF to synthesized copolymer ratios were used for QCM-D analysis. For coating the QCM sensor, the total polymer concentration was fixed at 1% and the PVDF to synthesized copolymer ratios were changed. The QCM-D results are shown in Fig. 4. Increasing the copolymer ratio in the film resulted in a sharp decrease in the amount of BSA adsorbed, from 3 mg/m^2 for the pure PVDF film to 1.7 mg/m^2 for a film containing 14.7% copolymer film. Thus, it can be concluded that the addition of the copolymer successfully reduces BSA adsorption.

3.4. Morphological study of PVDF hollow fibers

Enlarged cross-sections and outer surface SEM images of the prepared hollow fiber membranes are shown in Fig. 5. Cross-sections of all prepared membranes (images A1, B1, and C1) showed typical spherulite structures. Similar surface porosity was observed in the outer surface images of all the prepared membranes (images A2, B2, and C2). As described in section 3.4, the similar pore sizes on the hollow fiber membrane outer surfaces were confirmed by polystyrene particle rejection results.

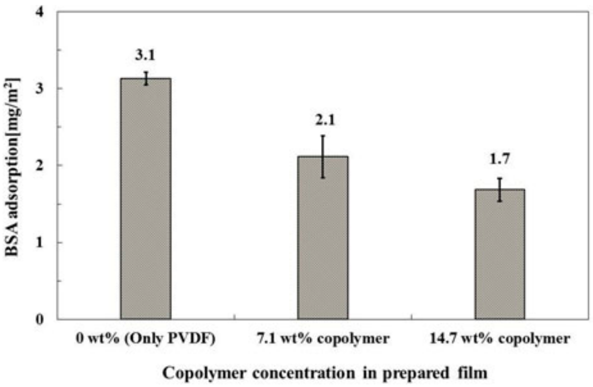

Fig. 4. Amount of the adsorbed BSA on the different prepared films.

3.5. Water permeability and solute rejection

Because we were investigating the effect of the copolymer on fouling properties, and since fouling is affected by pore size, we attempted to correct the effect of pore size by adjusting the temperature of the quenching bath and the air gap during membrane preparation to produce membranes with similar pore sizes. Detailed explanation about the membrane preparation and effect of each parameter on prepared hollow fiber membrane properties were investigated in our previous published papers [28,29,33]. The success of this was investigated by water permeability and rejection of 50-nm polystyrene nanoparticles studies (Fig. 6). Regardless of the copolymer concentration, all the prepared membranes showed similar water permeabilities and polystyrene rejections. Thus, it can be concluded that the adjustments during membrane preparation were successful, and the pore sizes of all of the prepared membranes were approximately the same.

3.6. Fouling experiment

The water flux and rejection results for a 1,000 ppm BSA solution with the different prepared membranes are shown in Fig. 7(a) and (b), respectively. The initial water fluxes for all membranes were almost the same

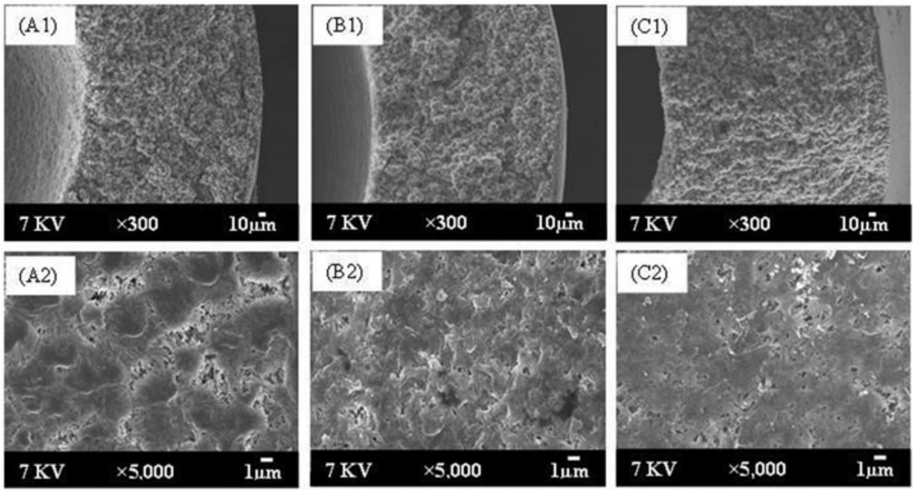

Fig. 5. SEM images of membrane A, B and C. (1) Cross section and (2) outer surface. Membrane A: only PVDF, Membrane B: 7.1 wt% copolymer, Membrane C: 14.7 wt% copolymer.

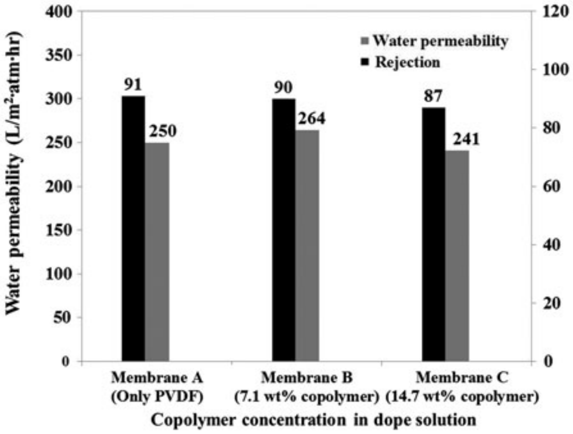

Fig. 6. Water permeabilities and rejections of the prepared membranes.

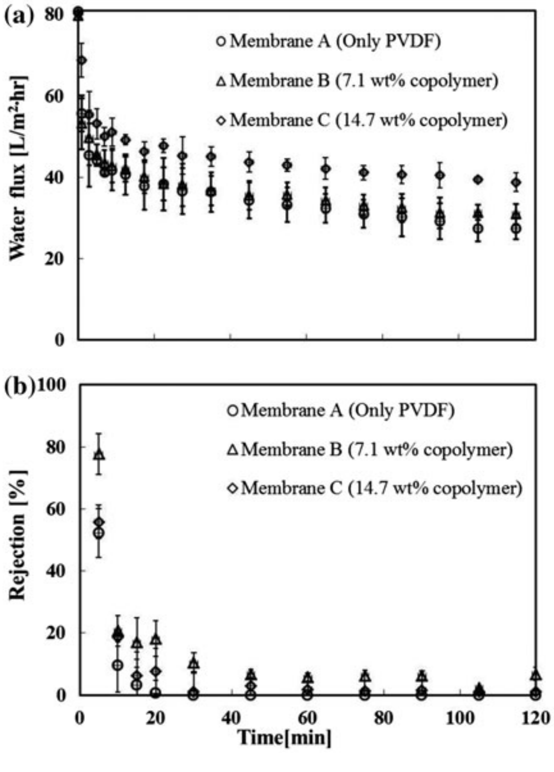

Fig. 7. Water flux (a) and rejection (b) as a function of filtration time for three membranes.

(80 L/(m^2h)). When a blended membrane containing 7.1 wt% copolymer was used for BSA filtration, the water flux trend over the filtration time was similar to that for the pure PVDF membrane. From these results, it can be concluded that a 7.1 wt% content of the copolymer in the blended membrane is not sufficient to obtain a membrane with good antifouling properties. When the copolymer was increased to 14.7 wt%, membrane fouling decreased (membrane C, Fig. 7). These results agree with QCM-D analysis results of Fig. 4 that shows by adding 14.7 wt% copolymer, BSA interaction with prepared film decreased. As another evaluation of the change in membrane properties by blending with copolymer, hydrophilicities of the prepared membranes were evaluated by measuring the water contact angle. While for PVDF membrane contact angle was 79±3˚, by blending 7.1 wt% copolymer it reached to 72±2˚ and with the further addition of copolymer to 14.7 wt% contact angle reached to 65±3˚. Thus, by increasing the copolymer content in prepared

membrane, water contact angle results decreased because of the increase in membrane hydrophilicity. Contact angle results also agree with our fouling results that adding synthesized copolymer improve the membrane material's antifouling properties. Thus, it can be concluded that this level of copolymer improved the membrane antifouling properties. The BSA rejection results were almost the same for all membranes. If we consider the pore size at the membrane outer surface was around 50 nm, it can be concluded that BSA cannot be filtrated by these membranes. The initial BSA rejection results were high because of adsorption of the BSA on the fresh membrane surface. However, after 30 min, the membrane surface was saturated with adsorbed BSA and the BSA rejection sharply decreased to less than 10%. Another point that can be understood from Fig. 7 is that as far as BSA adsorbed on the prepared hollow fiber membranes, error bar of the results was actually high and it is difficult to judge about the trend of the results within 20–30 min of filtration time. However, after BSA adsorption on the membrane finished, error bar decreases considerably and clearly it can be observed that the blend membrane with 14.7 wt% copolymer had better antifouling properties. Further studies on fouling process with backflushing are helpful to have a clear understanding of the membrane material's effect on fouling phenomena.

4. Conclusion

Poly(MMA-MPDSAH) copolymer was successfully synthesized by free radical polymerization of MMA with MPDSAH. The effect of adding this copolymer to a PVDF hollow fiber membrane was studied. Adding 5 wt% of the synthesized copolymer to PVDF sharply decreased the crystallization temperature from 113 to 87℃, and spherulite growth rate to half. QCM-D results showed addition of the copolymer to the blended film decreased BSA adsorbed amount almost to half which means BSA interaction decreased with the blend film. In order to evaluate the net effect of membrane material on the fouling tendency, PVDF membranes and blended membranes with similar water permeability, pore size, solute rejection, and membrane structure were prepared by changing the membrane composition and preparation conditions, and studied in BSA fouling experiments. Blending PVDF with the copolymer improved the antifouling properties.

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