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Hydrophilic Modification of Polypropylene Hollow Fiber Membrane by Dip Coating, UV Irradiation and Plasma Treatment

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Abstract: PP hollow fiber membrane was hydrophilized by EVOH dip coating followed by low temperature plasma treatment and UV irradiation. EVOH coating attained high water flux without any prewetting but its stability did not guaranteed at high water permeation rate. At high water permeation rate, water flux declined gradually due to swelling and delamination of the EVOH coating layer causing pore blocking effect. However, plasma treatment reduces the swelling, which suppress delamination of the EVOH coating layer from PP support result in relieving the flux decline. Also, UV irradiation helped the crosslinking of the EVOH coating layer to enhance the performance at low water permeation rate. FT-IR and ESCA analyses reveal that EVOH dip coating performed homogeneously through not only membrane surface but also matrix. Thermogram of EVOH film modified plasma treatment and UV irradiation show that crosslinking density of EVOH layer increased. Chemical modification by plasma treatment and UV irradiation stabilized the hydrophilic coating layer to increase the critical flux of the submerged membrane.

Keywords: *polyethylene membranes, hydrophilic modification, dip coating, UV irradiation, plasma treatment*

1. Introduction

Industrial wastewaters are diversified with the developments of various industries and their treatments became big issues in the environmental processes. Membrane process has advantages over the conventional wastewater treatment process and is proposed as a promising one in the future[1]. Treatment of the industrial wastewater by membrane process requires thermally and chemically strong membranes for its operation under the coarse conditions of high temperature with various chemicals.

Polyolefin membranes such as polypropylene (PP) and polyethylene (PE) membrane are one of the most widely used one in this application. PP and PE hollow fiber membrane that have high porosity and controlled pore size can be prepared by thermally induced phase separation (TIPS) or melt spinning and cold stretching (MSCS) process. It has good thermal and chemical resistance and can retain its original performances under the coarse operating conditions[2-7]. However, due to the hydrophobicity of the polyolefin membrane, it has lower water flux and cause fouling during the operation. Surface modifications of the membrane with hydrophilic materials have been conducted by using several techniques to solve these problems. The primitive technique of the surface modification was physical coating of the hydrophilic agents, which is a simple technique. But its lasting effect is not guaranteed owing to stability of the coating layer. Kamo *et al.* hydrophilized PE hollow fiber membrane having a large pore diameter and high porosity by saponification of ethylene vinyl acetate copolymer[8]. The other hand, various chemical surface modification techniques were developed such as UV-grafting and plasma treatment. Ranby *et*

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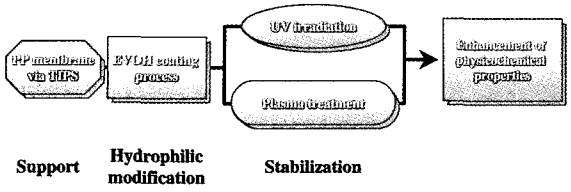


Fig. 1. Hydrophilic modification of PP hollow fiber membrane and stabilization of coating layer.

al. applied glycidyl acrylate, glycidyl methacrylate, and acrylic acid on the surfaces of polyethylene (PE), PP, and polystyrene (PS) film by UV-grafting technique[9-11]. Plasma treatment was initiated by Yasuda, who plasma coated nitrile type monomers on the silicone sheet to enhance the hydrogen/methane selectivity. He prepared the various composite membranes by applying the various plasmas to the metal, ceramic, and polymeric supports[12,13]. These chemical methods are complicated and cannot be applied to continuous process in spite of permanent surface modification. Also, temporary hydrophilization of membrane is needed at initial permeation stage. Among these hydrophilic modification processes as mentioned above, saponification is efficient methods of hydrophilic modification. However, this method has disadvantages, for example, delamination or swelling of coated layer resulting in pore blocking and flux reduction. Because Saponification product is physically adhered to PP hollow fiber membrane, its stability is poor so that the coating layer delaminates during water permeation. The physical coating layer need to crosslink for preventing delamination or swelling.

Irradiating polymers with ionization radiation can cause several chemical effects such as grafting, polymerization and degradation in the presence of a monomer as well as crosslinking. When exposed to an electron beam, some polymers will be degraded and others will be crosslinked, depending on their chemical structure. Although the processes take place simultaneously, cross linking was found to predominate in polymers that generally possess the structure, -(CH_2-CHR)- [14].

In this work, PP hollow fiber membrane was hydrophilized by EVOH dip coating process. Also, low temperature plasma treatment and UV irradiation process were tested to enhance the stability of the EVOH coating layer by crosslinking or grafting of polymer chains. Hy drophilic modification and stabilization procedure was sum marized in Figure 1. Operational parameters of plasma treatment and UV irradiation were investigated in terms of performance properties and membrane structure.

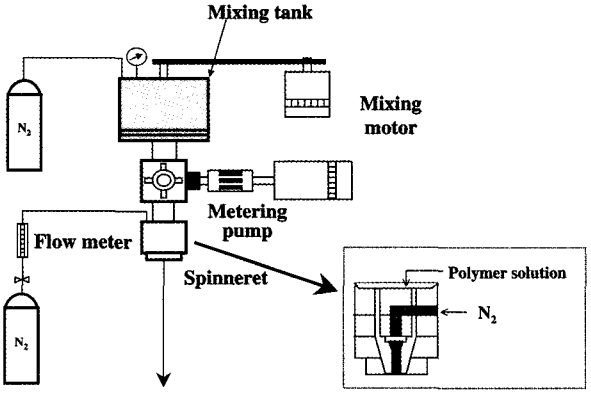


Fig. 2. A schematic diagram of preparation apparatus PP hollow fiber membrane.

2. Experimental

2.1. Preparation of PP Membrane

Hollow fiber membranes were prepared via thermally induced phase separation (TIPS) process followed by stretching process from isotactic PP/soybean oil/benzoic acid (BA) (45/55/1 wt%) system. PP (H715F) was supplied by Yukong Co. and soybean oil as diluent was purchased from Cheil Jedang Co. Figure 2 represents the schematic diagram of vessel-type melt spinning apparatus. After mechanically mixing polymer and diluent at 230°C vessel temperature, spinning was started at 172°C spineret temperature. The PP hollow fiber was drawn by take-up roller with appropriate take-up speed at room temperature. Freon (141B) was used as extractor of soybean oil from PP membrane after spinning. PP hollow fiber membrane have 500 μm outer diameter and average pore size 0.4 μm.

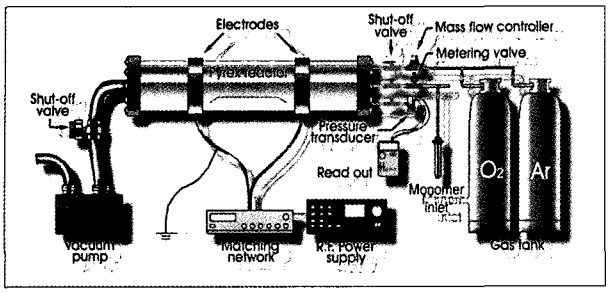


Fig. 3. A schematic diagram of plasma treatment apparatus.

2.2. Modification of Membrane

2.2.1. Hydrophilic Modification by EVOH Dip Coating

EVOH coating was performed by dipping PP membrane in EVOH/ethanol/water solution at 60°C. After coating, PP membrane was dried in room temperature for overnight. The pore size of PP membrane slightly decrease after coating but the pure water flux of EVOH coated PP membrane was retained its original water flux. Before further chemical treatment, EVOH coated PP membrane washed twice with distilled water.

2.2.2. Low Temperature Plasma Treatment

A schematic diagram of plasma reactor is shown in Figure 3. Tubular type pyrex reactor with a pair of external moving copper electrodes with 10 cm apart was assembled. The rf generator (model RFX-600, advanced energy) which operated at frequency of 13.56 MHz and matching network (Model ATX-600 advanced energy) were used to convert the complex impedance of plasma to 50 Ω resistance. A rotary vacuum pump (E2M8, Edwards) was used to evacuate the reactor for the proper glow discharge. After PP hollow fiber membrane sample was placed on center of the electrodes, reactor was evacuated below 30 mTorr. Then, carrier gas was introduced into the reactor by adjusting mass flow controller. At steady state, power was switched on for arbitrary reaction time. After plasma treatment, the sample was exposed to air.

2.2.3. UV Irradiation

The PP hollow fiber membrane was placed at a distance of 18 cm from UV light source and irradiated in nitrogen environment. 350 W high-pressure mercury UV lamp (Oriel Co.) having mixed wavelengths of 303, 313, 348 and 363 nm was used for irradiation. Benzophenone (B.P.) having optimum absorption wavelength about a range of 240~350 nm was added as a photoinitiator to promote radical formation on the PP hollow fiber membrane. After UV irradiation, the membrane was stored in atmosphere before to test.

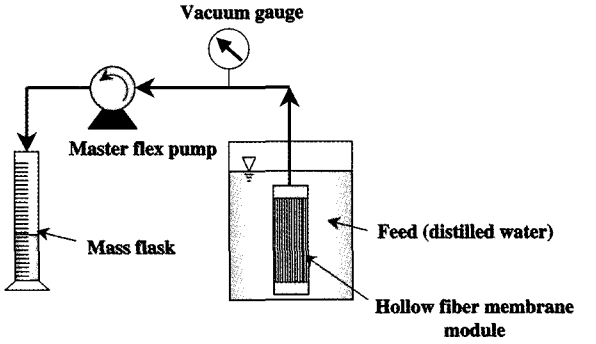


Fig. 4. A schematic diagram of membrane testing apparatus (submerged module type).

2.3. Characterization of Membrane

Morphological analyses of membrane surface were performed by using a scanning electron microscope (SEM, Leica, Stereoscan 440). The sample was gold coated prior to scan. Chemical analysis of the membrane composition was performed by using FT-IR (Perkin-Elmer, System 2000). The sample was analyzed by grinding into powder with KBr. Also, ESCA (ESCA 2000, VG MicroTech.) analysis was characterized the membrane surface chemical composition.

Figure 4 shows a schematic diagram of water flux measurement apparatus. Membrane module was potted with 100 piece of PP hollow fiber membrane in acryl tube. The water flux was measured using master flex rotary pump without further wetting process. The performance data was collected at intervals of 60 min by checking the pressure gage with constant permeation rate. The permeation rate was varied with a range of 7~380 LMH. Flux variation after drying the membrane was investigated to test the stability of EVOH coating

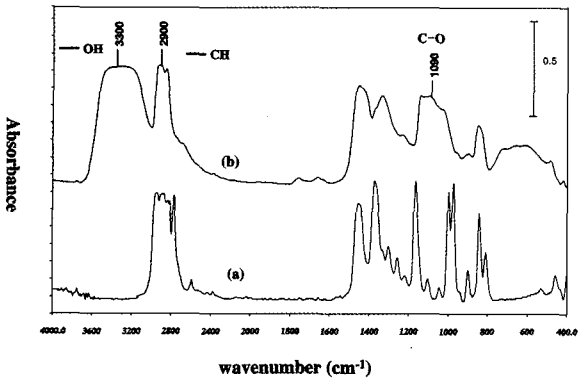


Fig. 5. FT-IR spectra of original (a) PP and (b) EVOH coated PP membrane.

layer. After permeation test, PP hollow fiber membrane was dried for 24 hr and the water flux was measured again with same procedure.

3. Results and Discussion

3.1. FTIR Analysis

EVOH dip coated layer on PP hollow fiber membrane was confirmed by FTIR analyses as shown in Figure 5. The sample was analyzed by grinding EVOH coated PP hollow fiber membrane into powder with KBr. The characteristic peaks at 3300 cm^{-1} (-OH) and 1090 cm^{-1} (C-O) for alcohol functional group were observed to reveal the EVOH coating layer formation on the PP hollow fiber membrane. Several sample showed same results indicating homogeneous coating was performed.

3.2. ESCA Analysis

XPS spectra of PP and EVOH coated PP hollow fiber membrane were presented in Figure 6. XPS analysis indicates the chemical changes that occur in PP membrane as a result of EVOH dip coating. As shown Figure 6(a), PP membrane has a single peak at 285 eV indicating C-C bond. This peak shifts to 286 eV so that the shoulder peak appears indicating C-O bond, which is included in EVOH molecules. The peak ratio of C-O/C-C was 34% approximately. EVOH coating layer was considerably deposited on not only PP hollow fiber membrane surface but also membrane matrix.

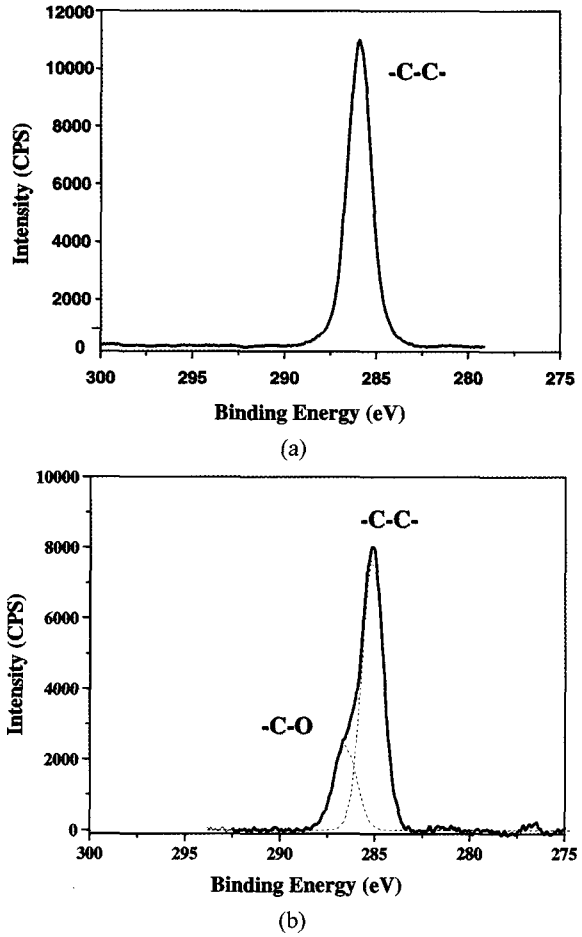


Fig. 6. XPS analyses of (a) PP and (b) EVOH coated PP membrane (C1s).

3.3. Effect of Permeation Rate on Performance of Membrane

Effect of permeation rate on flux of EVOH coated membrane was tested. Figure 7 shows the water flux variation while permeation rate increase from 3 mL/min to 66 mL/min. The initial water permeation could be achieved without more prewetting, dramatically. It appeared stable performance without no water flux decline until the permeation rate about 10 mL/min. However, the water flux of EVOH coated PP hollow fiber membrane decreased when the permeation rate is higher than 10 mL/min depending on permeation rate. The rate of water flux decline rate was remarkable when the permeation rate was increased. For higher permeation rate, the last water flux was lower than those of lower permeation rate. It was presumed that

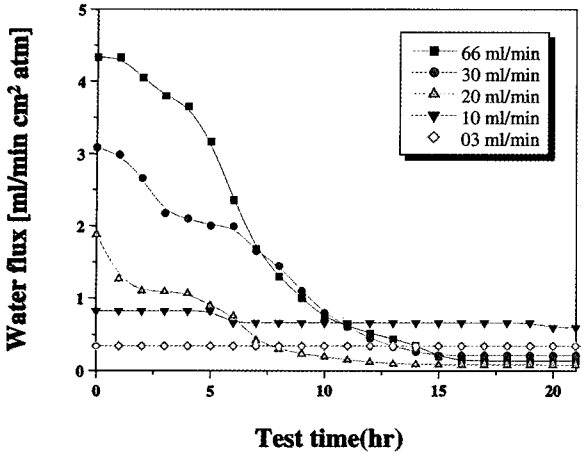


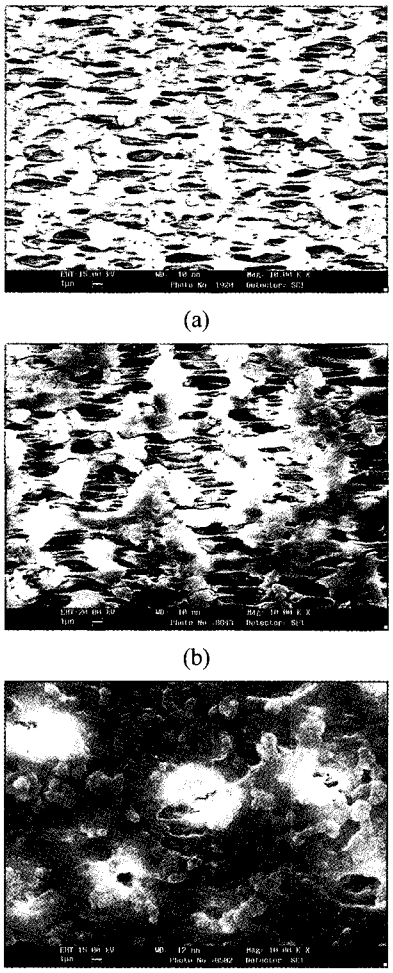
Fig. 7. Effect of permeation rate on flux of EVOH coated membrane (Effective membrane area=100 cm^2).

the water flux decline is caused by delamination and swelling resulting in pore blocking phenomenon. Also, the shear force at the membrane surface was influenced on swelled EVOH coating layer during permeation. Figure 8 presents surface image change of PP membrane and EVOH coated PP membrane before and after performance test. The pore size of PP hollow fiber membrane fabricated in our laboratory is 0.5 μm approximately. The pore size was decreased slightly by EVOH dip coating to 0.4 μm approximately. But, the water fluxes through PP and EVOH coated PP membrane were similar. After performance test for 10 hr with 66 mL/min of permeation rate, the pore at the membrane surface was disappeared entirely by pore blocking as shown in Figure 8(c). So, the water flux of this case was lower. As a result, delamination and swelling of EVOH coating layer at higher permeation rate cause the pore blocking so that the water flux decreased. The stability of EVOH coated layer must be improved for higher permeation rate.

3.4. Stability Enhancement of EVOH Coating Layer

3.4.1. Effect of Plasma Treatment on Performance of EVOH Coated PP Hollow Fiber Membrane

The stability of physically adhered coating layer



(a)

(b)

(c)

Fig. 8. Surface image change of EVOH coated PP membrane after performance test (a) Untreated PP membrane (b) EVOH coated PP membrane (c) After performance test (Permeation rate=66 mL/min, test time=10 hr).

could be improved by crosslinking of coating layer. Plasma treatment, which forms a free radical on the polymer surface, can be applied to enhance the stability of the EVOH coating layer by intermolecular crosslinking. The delamination and swelling of EVOH coating layer would be suppressed so that the water flux performance of PP hollow fiber membrane could be retained its initial water flux without pore plugging by delaminated or swelled EVOH. Various plasma gases were tested for plasma treatment and the time depending water flux variation was investigated as shown in Figure 9. The flux of EVOH coated PP hollow fiber

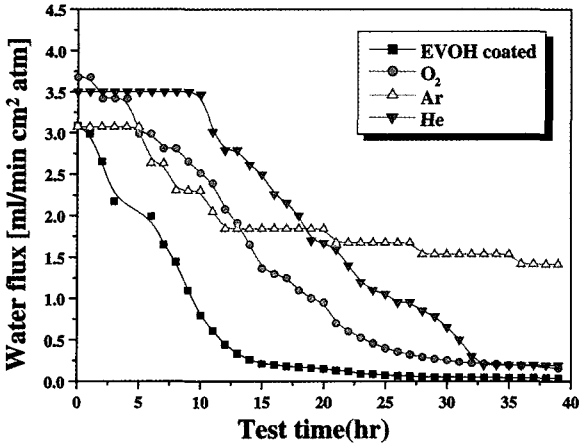


Fig. 9. Effect of plasma treatment on water flux of EVOH coated PP membrane (Plasma treatment conditions: power = 10 W, treatment time = 30 min Performance test conditions: permeation rate = 30 mL/min).

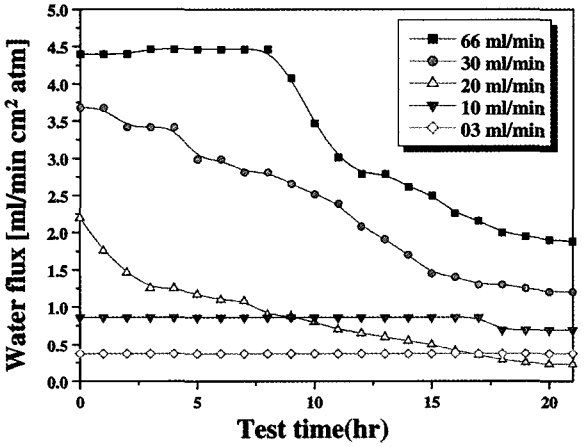


Fig. 10. Effect of permeation rate on flux of EVOH coated membrane followed by plasma treatment (Plasma treatment conditions: power = 10 W, treatment time = 30 min, gas = Ar).

membrane decreased rapidly depending on test time with 30 mL/min of permeation rate. With higher permeation rate, shear stress between EVOH coating layer and water flow should be increase so that delamination of coating layer should be accelerated. After 15hr test time, its water flux nearly zero because of pore blocking by delamination of EVOH coating layer as shown Figure 15(a). Surface pore was almost disappeared after performance test. However, plasma treated PP hollow fiber membrane show better performance than untreated one. Ar plasma treated PP hollow fiber membrane

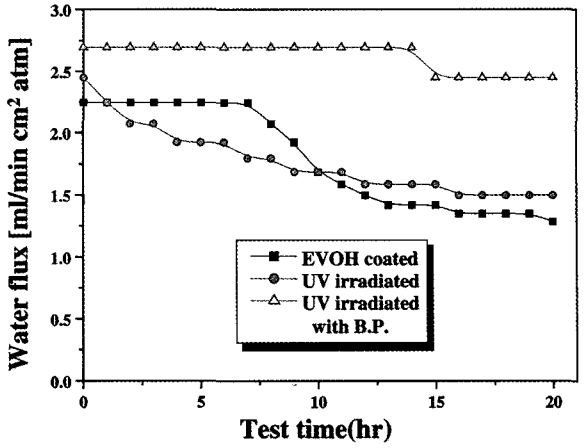


Fig. 11. Effect of UV irradiation on flux of EVOH coated PP membrane (UV irradiation conditions: power = 700 W, irradiation time = 30 min, photoinitiator = B.P. Performance test conditions: permeation rate = 20 mL/min).

show particularly superior performance. Surface images of plasma treated PP hollow fiber membrane was shown in Figure 14(b). Surface pore was maintained its initial morphology after performance. In case of Oxygen plasma treated PP hollow fiber membrane, the water flux was relatively lower because of degradation of coating layer. Ar plasma treated PP hollow fiber membrane, which has superior water flux, was tested for various permeation rates as shown in Figure 10. As permeation rate increase the water flux decline was remarkable. But latter water flux of Ar plasma treated PP hollow fiber membrane was higher than those of only EVOH coated one. Also, it shows stable water flux performance even higher permeation rate. The critical flux, the maximum water flux without water flux decline, became higher than EVOH coated one. As a result, plasma treatment crosslinked the coating layer to reduce the swelling, which relieved the flux decline at high permeation rate.

3.4.2. Effect of UV Irradiation on Performance of EVOH Coated PP Membrane

Polymer surface could be activated to form radicals by UV irradiation. Crosslinking of EVOH coating layer by UV irradiation was investigated. Effect of benzophenone (B.P.) as a photoinitiator on UV irradiation was tested because C-C and C-H bonds were able to

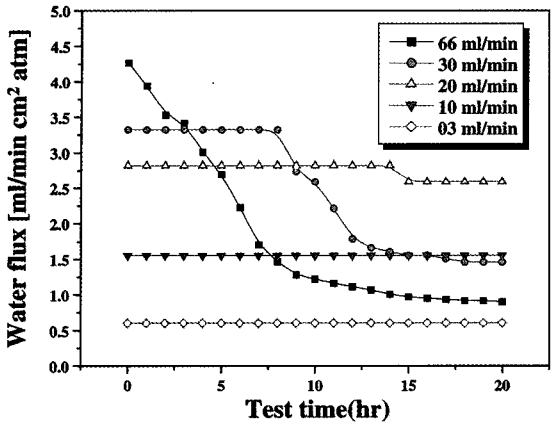


Fig. 12. Effect of permeation rate on flux of UV irradiated membrane (UV irradiation conditions: power = 700 W, irradiation time = 30 min).

decompose into radical uniformly at 250~360 nm wavelength. The water flux of UV irradiated PP hollow fiber membrane without B.P. was similar to EVOH coated one indicating UV irradiation has no effect. When the B.P. was loaded to the surface of PP hollow fiber membrane, it shows stable performance for long test time (over 20 hr). The effect of permeation rate on water flux of UV irradiated PP hollow fiber membrane was investigated. As shown in Figure 12, the water flux stability was enhanced compared with EVOH coated one. The critical flux of UV irradiated PP hollow fiber membrane enhanced although the water flux decline as permeation rate increase. UV irradiation with photoinitiator helped the grafting and crosslinking of the coating layer to enhance the performance at low permeation rate.

3.4.3. Comparison Surface Modification Process

The performance of PP hollow fiber membrane fabricated by hybrid process of EVOH coating process followed by UV irradiation and plasma treatment was compared with EVOH coating process only. As shown in Figure 13, the water flux performance could be enhanced by stabilization of coating layer by both UV irradiation and plasma treatment. In lower permeation rate, it came out that the effect of UV irradiation on stability of coating layer was notable (Figure 13(a)). Also, the stability of the EVOH coating layer modified by plasma

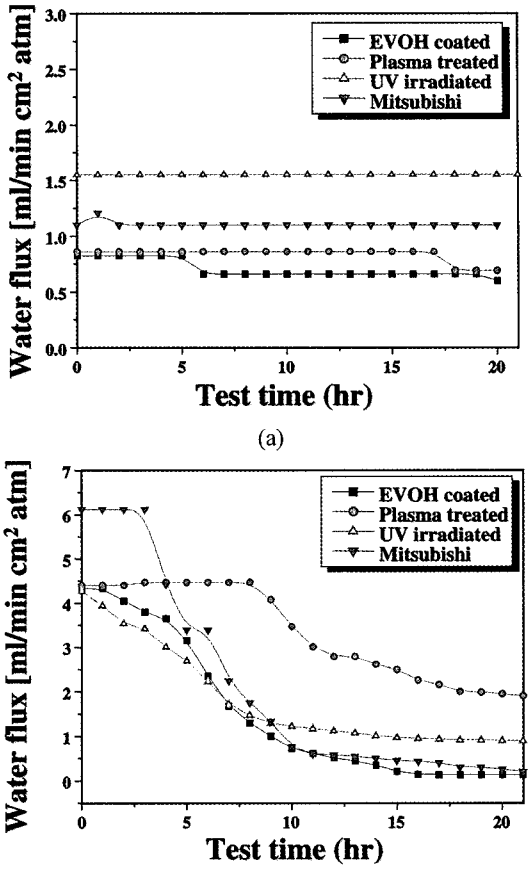


Fig. 13. Comparison of each hydrophilic modification method (a) low permeation rate: 10 mL/min (b) high permeation rate: 66 mL/min.

treatment was enhanced considerably in higher permeation rate (Figure 13(b)). Commercial PP hollow fiber membrane (Mitsubishe Co.) show stable performance in lower permeation rate, but the water flux decreased at once.

3.5. Thermal Stability EVOH Film

Figure 15 shows thermogram of EVOH film and its modified film by UV irradiation and plasma treatment. EVOH film was casted on a glass plate with a thickness about 200 μm. Then, UV irradiation and plasma treatment of EVOH film were performed in a similar way of PP hollow fiber membrane. If the degree of crosslinking of EVOH coating layer, the thermal degradation temperature was elevated to higher temperature. As shown in Figure 15, the plasma treated EVOH film disclosed higher thermal degradation tem-

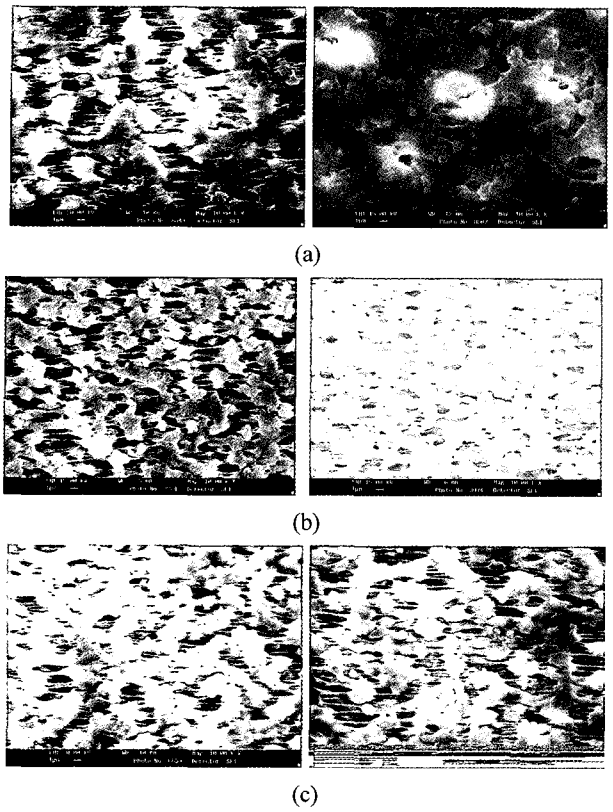


Fig. 14. Surface images of EVOH coated PP hollow fiber membrane before and after performance test (a) EVOH coated PP (b) Plasma treatment (c) UV irradiation.

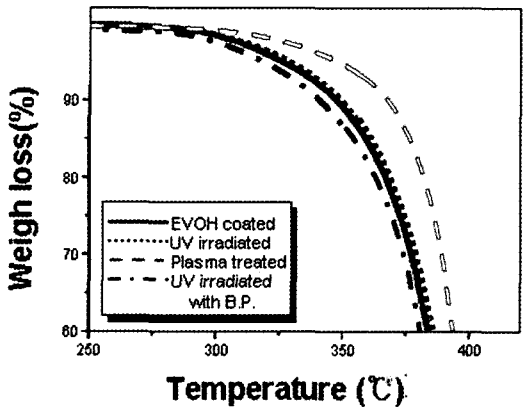


Fig. 15. Thermogram of EVOH film modified by UV irradiation and plasma treatment (Plasma treatment conditions: power = 10 W; treatment time = 30 min, gas = Ar; UV irradiation conditions: power = 700 W with B.P., treatment time = 30 min; Scanning rate = 20°C/min).

perature indicating better degree of crosslinking. Also, UV irradiated EVOH film showed the higher degradation temperature slightly.

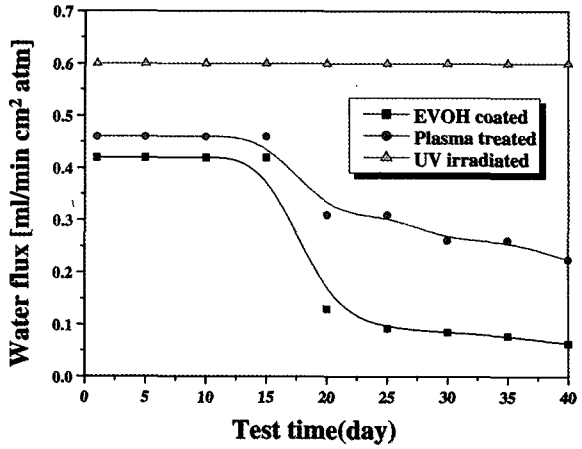


Fig. 16. Flux variation of EVOH coated PP hollow fiber membrane after drying (Plasma treatment conditions: power = 10 W, treatment time = 30 min. gas = Ar UV irradiation conditions: power = 700 W, irradiation time = 30 min, photoinitiator = B.P. Performance test conditions: permeation rate = 3 mL/min).

3.6. Performance Variation by Drying the Membrane

Figure 16 shows the water flux decline by drying the membrane every 5 days. After drying for 12 hr in vacuum oven, the water flux was measured again. The water flux of EVOH coated PP hollow fiber membrane decreased after 15 days and became low about 0.05 mL/min-cm^2-atm. This behavior was caused by converting of hydrophilic membrane surface into hydrophobic surface resulting from delamination of EVOH coating layer during permeation and drying. Also, migration of hydrophobic groups could be occurs at the air-polymer interface. However, the water flux of UV irradiated PP hollow fiber membrane was maintained its initial value after 40 days. It indicated that UV irradiation enhanced the stability of EVOH coating layer by crosslinking so that delamination of EVOH coating layer and migration of hydrophobic groups to the surface was prevented effectively. Also, plasma treatment could be effort to improve the stability of the EVOH coating layer.

4. Conclusion

Melt spinning and stretching process produced PP hol-

low fiber membranes with interconnected pore structure.

EVOH coating could physically hydrophilize the PP hollow fiber membrane to retain the stable performance at low permeation rate. At high permeation rate, water flux declined due to delamination and swelling of the EVOH coating layer causing pore blocking. However, plasma treatment crosslinked the EVOH coating layer to reduce the delamination and swelling, which relieved the flux decline at high permeation rate. Also, UV irradiation with photoinitiator helped the grafting and crosslinking of the coating layer to enhance the performance at low permeation rate. Chemical modifications by plasma treatment and UV irradiation stabilized the hydrophilic coating layer to increase the critical flux of the submerged membrane.

Acknowledgements

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