Macromolecular Research, Vol. 12, No. 6, pp 553-558 (2004)

Effects of Surface Modification of the Membrane in the Ultrafiltration of Waste Water

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Received April 26, 2004; Revised November 2, 2004

Abstract: An ultrafiltration membrane (polyethersulfone, PM10) was surface-modified by treating it with low-temperature plasmas of oxygen, acrylic acid (AA), acetylene, diaminocyclohexane (DACH), and hexamethyldisiloxane (HMDSO). The effects that these modifications have on the filtration efficiency of a membrane in waste water treatment were investigated. The oxygen, AA, and DACH plasma-treated membranes became more hydrophilic. The water contact angles ranged from $< 10^{o}$ to 55^{o} depending on the type of plasma and the treatment conditions. The oxygen plasma-treated membranes displayed a higher initial flux (312-429%), but lower rejection (6-91%), than did an untreated membrane. The AA plasma-treated membranes displayed lower or higher initial flux (42-156%), depending upon the treatment conditions, but higher rejection (224-295%) in all cases. The DACH plasma-treated membranes displayed lower initial flux. All of them, especially the AA plasma-treated membrane, displayed improved fouling resistance with either a slower or no flux decline. Acetylene and HMDSO plasma-treated membranes became more hydrophobic and displayed both lower initial flux and lower fouling resistance.

Keywords: flux, fouling resistance, plasma surface modification, rejection, ultrafiltration membrane.

Introduction

Ultrafiltration is recently considered as a quite promising process for waste water treatment because of its advantageous features such as wide range of application areas, compactness of the facilities, and low energy-cost. However, it needs further improvement, especially in the filtration efficiency of a membrane, to compete over the other conventional processes. The filtration efficiency of a membrane is determined by flux and rejection. Since the flux and the rejection are intrinsically inversely proportional to each other, however, it very difficult to improve both of them. The flux may increase as the thickness of a membrane decreases or the pore-size of a membrane increases but the rejection decreases and vice-versa. Therefore, most efforts are given to improve either of them without sacrificing the other through development of various composite membranes and surface modifications. Composite membranes which are composed of a thin dense film and a porous substrate can provide high rejection without a significant reduction of the flux due to its thin film thickness.[1] Higher flux can be obtained if the membrane becomes more hydrophilic due to improved wettability and decreased capillary pressure.[2-7]

The filtration efficiency of a membrane is also highly dependent on fouling resistance of the membrane. Fouling which occurs by the deposition of solid materials on the membrane surface from the feed stream causes continuous flux decline during the filtration resulting in the poor filtration efficiency and short service-life of the membrane. Therefore, high fouling resistance is an essential factor for high filtration efficiency. It has been reported that the fouling was closely related to the physico-chemical properties of a membrane surface and hydrophilic surfaces were more resistant to the fouling than hydrophobic surfaces.[2-7] As a consequence, large attention is paid on the hydrophilic surface-modification of a membrane. Commercial membranes are in general made of hydrophobic materials which have

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good thermal, physical, and chemical properties.

One of effective methods to improve the filtration efficiency of membranes may be plasma treatment. It was reported that O_2 plasma treatment or Ar plasma treatment followed by grafting of acrylic acid made the membrane hydrophilic and improved the flux, the fouling resistance, and/or the rejection.[8-10] In this study, a polyethersulfone membrane was surface-modified by the plasma treatment method and effects of the modification on the filtration efficiency of a membrane in waste water treatment were investigated. Polymer-forming plasmas[11] such as acrylic acid (AA), diaminocyclohexane (DACH), acetylene, and hexamethyldisiloxane (HMDSO) plasmas as well as a nonpolymer-forming plasma, O_2 plasma, were used for the modification. In former works, the plasma treatment for the modification of a membrane has mainly been focused on the nonpolymer-forming plasmas. Since an ultrathin film is deposited on the membrane surface in a polymer-forming plasma, improvement of the rejection without large sacrifice of the flux can be expected. Modifications were done mainly for hydrophilization of the membrane surface but hydrophobization was also tried for comparison.

Experimental

Membrane and Surface Modification. The ultrafiltration membrane used in this study was a polyethersulfone flat-sheet membrane with a diameter of 43 mm, which was purchased from Amicon (PM10, 10,000 MWCO). The membrane was surface-modified in a home-made cylindrical R.F. plasma reactor shown in Figure 1. The plasmas used for the modification were oxygen (99.99%, Daesung Gas), AA (Junsei Chemical), acetylene (Daesung Gas), DACH (Aldrich Chemical), and HMDSO (Aldrich Chemical) plasmas.

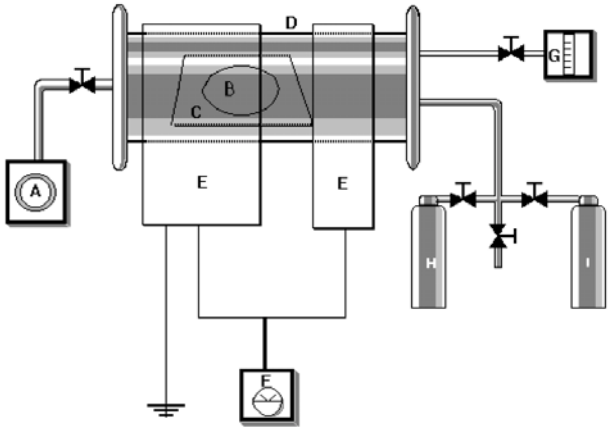


Figure 1. Schematic diagram of a plasma reactor for surface modification.

A: vacuum pump
B: sample
C: sample holder
D : reaction chamber
E : electrodes
F : RF generator
G : pressure gauge
H : monomer reservoir (liquid)
I : monomer reservoir (gas)

Table I. Composition of Synthetic Waste Water

Component	Amount/L
KH_2PO_4	0.200
K_2HPO_4	0.350
$MgSO_4 \cdot 7H_2O$	0.292
$CaCl_2 \cdot 2H_2O$	0.180
$FeSO_4 \cdot 5H_2O$	0.040
NaCl	2.000
$C_6H_{12}O_6$	0.188
NH_4Cl	0.382
KNO_3	0.181

Test and Analysis. Chemical structure and morphology of the modified membrane surfaces were characterized with FTIR/ATR (Jasco, Model FT/IR-430) and SEM (Hitachi, Model S-4700). Filtration efficiency of the membrane was evaluated by dead-end filtration of synthetic waste water in a batch stirred cell apparatus (Amicon). Composition of the synthetic waste water is in Table I. The cell was filled with 50 mL of the synthetic waste water and pressurized with nitrogen gas to 5.0 bars. The flux was determined by measuring the time for the filtration of 20 mL. The rejection was evaluated by comparing BOD_5 of the feed solution and the permeate. The fouling resistance was evaluated based on the flux decline when the filtration was repeated to 30 times with the same membrane.

Results and Discussion

The membrane was modified first by treating the surface with oxygen and AA plasmas. The modifications resulted in the formation of hydrophilic groups on the surface. Figure 2 shows FTIR/ATR spectra of membrane surfaces treated with oxygen plasma for 1, 3, and 5 min at the pressure of 120 mtorr and the discharge power of 20 W. After the treatments, an absorption peak by OH groups appears newly near 3200 cm^{-1} while absorption peaks by sulfones near 1300-1375 cm^{-1} and aromatic carbons near 1600 cm^{-1} decrease. Figure 3 shows FTIR/ATR spectra of membrane surfaces treated with AA plasma for 1, 3, and 5 min at the pressure of 70 mtorr and the discharge power of 20 W. After the treatments, absorption peaks by COOH groups appear newly near 3200 and 1700 cm^{-1} while absorption peaks by sulfones and aromatic carbons decrease.

As a result, hydrophilicity of the membrane surface increased. Water contact angles of the O_2 and AA plasma treated surfaces before and after the modifications are in Table II. As shown in the table, water contact angle decreased down to less than 10° depending on the treatment condition.

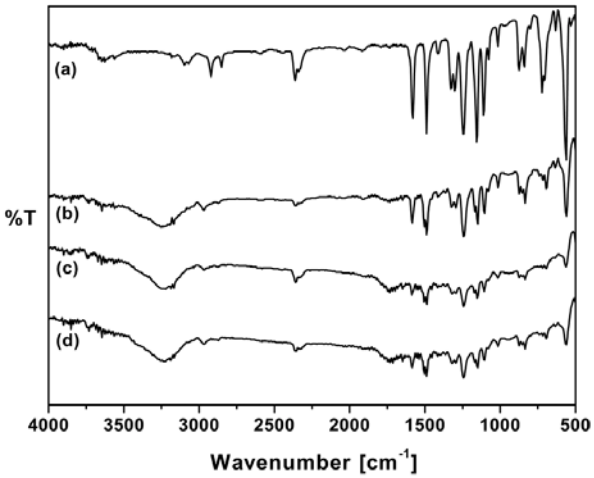


Figure 2. FTIR/ATR spectra of untreated and oxygen plasma treated (120 mtorr, 20 W) membrane surfaces; (a) untreated, (b) 1 min, (c) 3 min, and (d) 5 min.

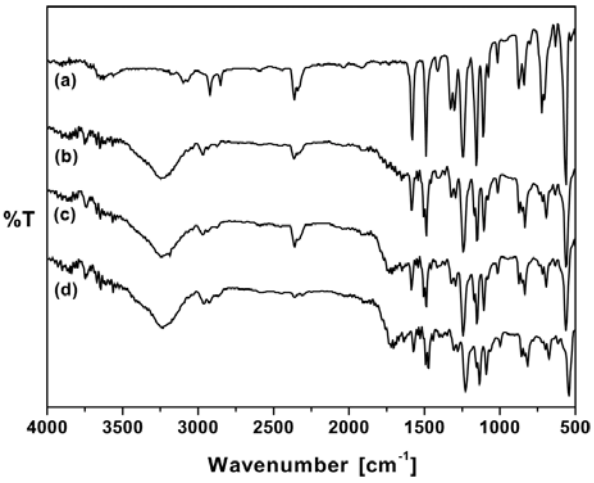


Figure 3. FTIR/ATR spectra of untreated and AA plasma treated (70 mtorr, 20 W) membranes; (a) untreated, (b) 1 min, (c) 3 min, and (d) 5 min.

In the case of O_2 plasma treatment, water contact angle decreased as the treatment time increased, possibly due to increased degree of oxidation with time. Note that intensity of OH peak increases as the treatment time increases in Figure 2. In the case of AA plasma treatment, water contact angle was more dependent on the discharge power than the treatment time and increased as the discharge power increased. More COOH groups in AA monomers can be fragmented as discharge power increases and converted to less polar groups.[12]

The modifications influenced the filtration efficiency of the membrane in ultrafiltration of waste water. The oxygen plasma treatment gave a positive effect on the flux and the fouling resistance but a negative effect on the rejection. Figure 4 shows the water flux as a function of repeated

Table II. Water Contact Angles of Plasma Treated Membranes

Type of Treatment	Treatment Condition	Contact Angle (°)
Untreated	-	70-80
Oxygen Plasma	120 mtorr, 20 W, 1 min	35-40
	120 mtorr, 20 W, 3 min	30-35
	120 mtorr, 20 W, 5 min	10
AA Plasma	70 mtorr, 10 W, 3 min	10
	70 mtorr, 20 W, 1 min	40-45
	70 mtorr, 20 W, 3 min	35-40
	70 mtorr, 20 W, 5 min	35-40
	70 mtorr, 30 W, 3 min	50-55
DACH Plasma	70 mtorr, 20 W, 3 min	40-45
Acetylene Plasma	70 mtorr, 20 W, 3 min	80-85
HMDSO Plasma	70 mtorr, 20 W, 3 min	95-100

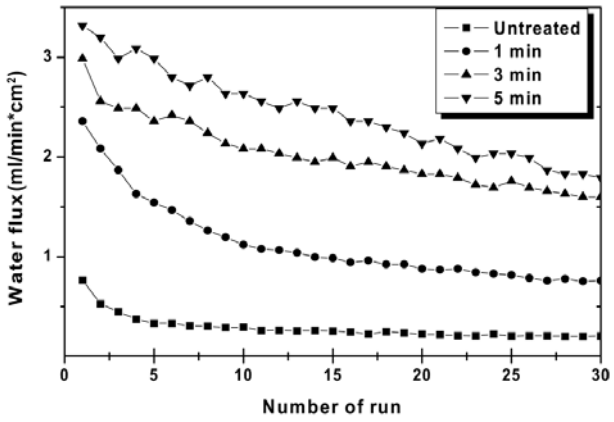
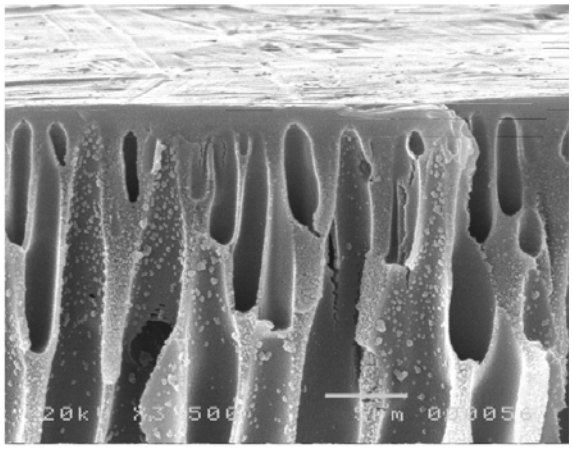


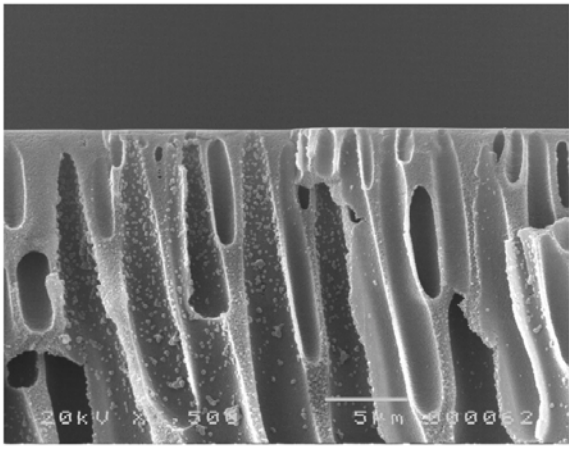
Figure 4. Water flux of untreated and oxygen plasma treated (120 mtorr, 20 W) membranes as a function of repeated filtration for various treatment times.

number of filtration for untreated and oxygen plasma treated membranes. Treated membranes show 34 times higher initial flux with slower flux decline than an untreated membrane and the effect is more pronounced as the treatment time increases. Considering that water contact angle in Table II decreases as the treatment time increases, it is clear that the water flux and the fouling resistance are closely related to the hydrophilicity of a membrane.

There seems to be another factor for the increased flux although not for the increased fouling resistance, etching effect of oxygen plasma. Oxygen plasma is known to be able to etch the organic material through ashing reaction. If etching occurs, the membrane will be getting thinner increasing the flux. Figure 5 shows SEM pictures of the membrane cross-section before and after oxygen plasma treatment. It is observed that some part of a dense skin layer in the mem-



(a)



(b)

Figure 5. SEM pictures (× 3,500) of (a) an untreated and (b) an oxygen plasma treated (120 mtorr, 20 W, 5 min) membrane.

Table III. BOD of Permeate after Filtration of BOD_{50} Synthetic Waste Water with Plasma Treated Membranes

Type of Treatment	Treatment Condition	BOD
Untreated	-	35.2
Oxygen Plasma	120 mtorr, 20 W, 1 min	36.5
	120 mtorr, 20 W, 3 min	48.8
	120 mtorr, 20 W, 5 min	49.1
AA Plasma	70 mtorr, 20 W, 1 min	16.9
	70 mtorr, 20 W, 3 min	9.52
	70 mtorr, 20 W, 5 min	6.27

brane is cut away after the treatment. The negative effect of the oxygen plasma treatment on the rejection seems to be due to the etching effect. Table III shows BOD of the permeate for untreated and oxygen plasma treated membranes. BOD increases as the treatment time increases.

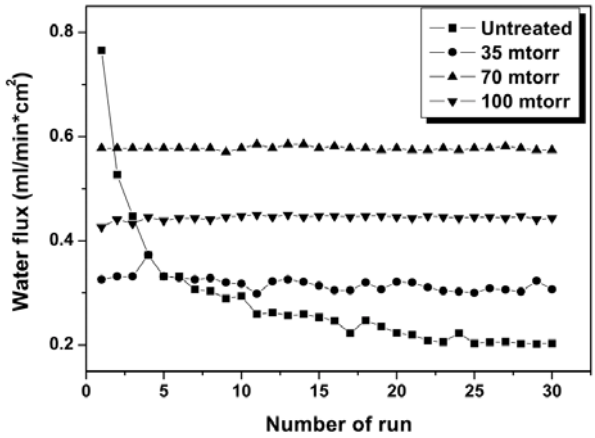


Figure 6. Water flux of untreated and AA plasma treated (20 W, 2 min) membranes as a function of repeated number of filtration for various pressures.

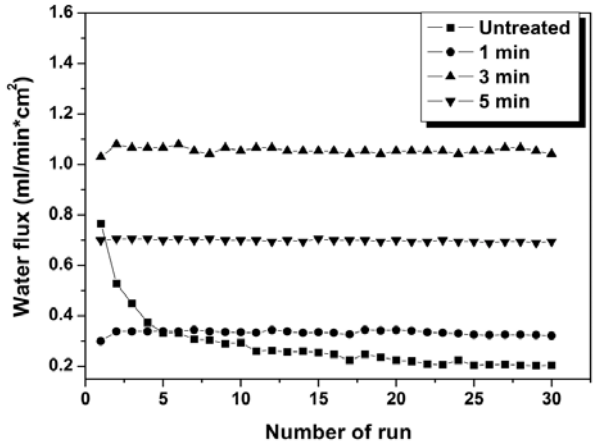


Figure 7. Water flux of untreated and AA plasma treated (70 mtorr, 20 W) membranes as a function of repeated number of filtration for various treatment times.

On the contrary to the oxygen plasma treatment, the AA plasma treatment gave a positive effect not only on the flux and the fouling resistance but also on the rejection. Figures 6, 7, and 8 show the water flux as a function of repeated number of filtration for untreated and AA plasma treated membranes at various conditions. Some treated membranes show higher initial flux than an untreated membrane while the others show lower initial flux, which indicates that the flux is highly dependent on the treatment condition and the treatment gives a positive effect on the flux only when the treatment condition is optimized. However, the fouling resistance does not seem to be much dependent on the treatment condition. All the treated membranes show almost no flux decline indicating the greatly improved fouling resistance. Figure 9 shows SEM pictures of untreated and AA plasma treated membrane surface used in the filtration for 30 times. Little amount of fouled deposit is observed on the treated

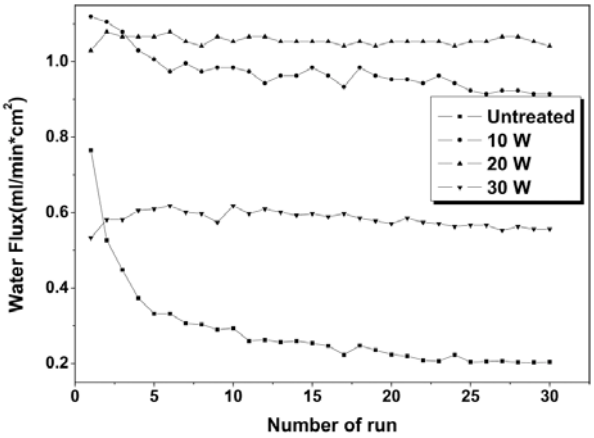
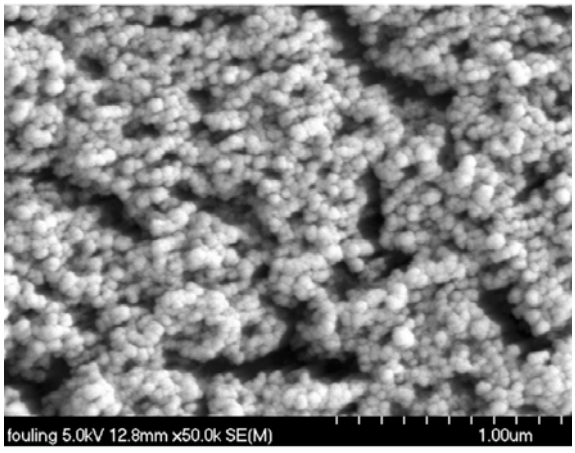
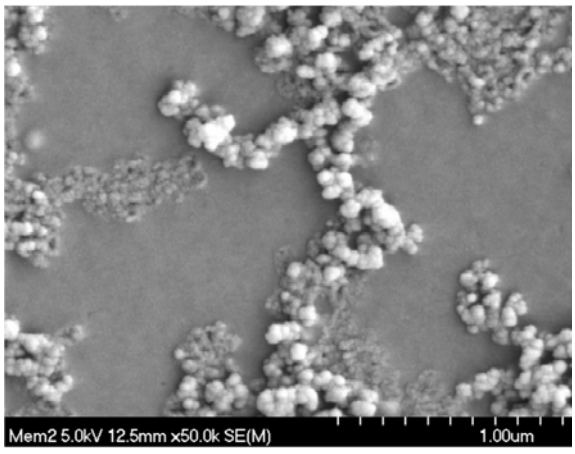


Figure 8. Water flux of untreated and AA plasma treated (70 mtorr, 3 min) membranes as a function of repeated number of filtration for various discharge powers.

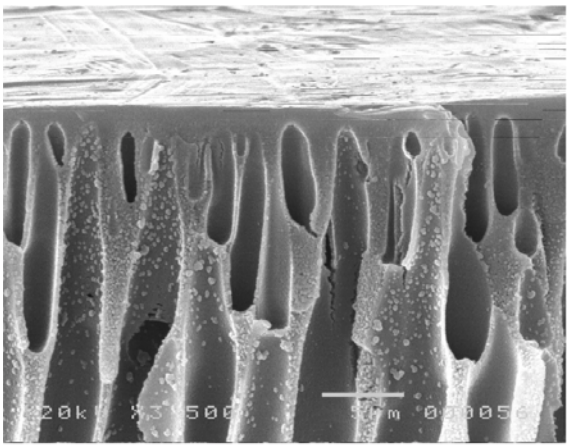


(a)

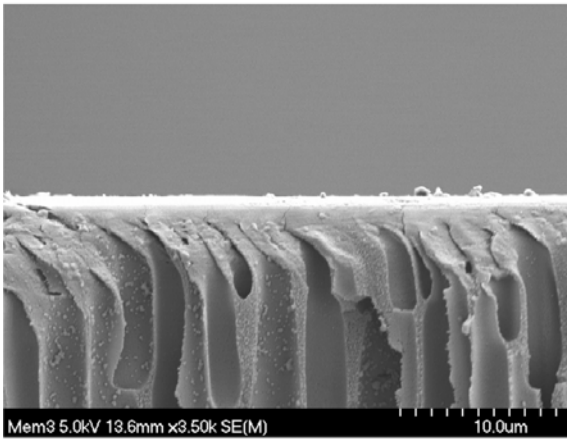


(b)

Figure 9. SEM pictures (× 50,000) of (a) an untreated and (b) an AA plasma treated (70 mtorr, 20 W, 3 min) membrane surface after filtrations for 30 times.



(a)



(b)

Figure 10. SEM pictures (× 3,500) of (a) an untreated and (b) an AA plasma treated (70 mtorr, 20 W, 5 min) membrane.

surface while large amount is observed on the untreated surface. Table III shows BOD of the permeate for untreated and AA plasma treated membranes. BOD decreases as the treatment time increases.

The conflicting effects of the AA plasma treatment with the oxygen plasma treatment may attribute to their different modification characteristics. While the oxygen plasma treatment modifies just the physico-chemical structure of the membrane surface itself, the AA plasma treatment results in the deposition of a thin film on the membrane surface through plasma polymerization which is getting thicker as the treatment time increases. Figure 10 shows SEM pictures of the membrane cross-section before and after AA plasma treatment. A thin film is shown on the top of the treated membrane. This is the reason why the AA plasma treated membranes show lower flux but higher rejection than oxygen plasma treated membranes although they have similar hydrophilicity.

Dependence of the flux on the treatment condition seems to be related to the degree of modification and the chemical

structure and properties of the deposited film. 1 min treatment may not be enough to fully modify the surface. Note that 1 min treated membrane shows higher water contact angle and lower flux than 3 and 5 min treated ones. Lower flux of membranes treated at relatively higher discharge power (30 W) and lower pressure (35 mtorr) seems to be due to higher crosslinking of the deposited film. Chemical structure and properties of the film is known to be highly dependent on the treatment condition.[12]

The membrane was modified with DACH, acetylene, and HMDSO plasmas at the pressure of 70 mtorr and the discharge power of 20 W for 3 min to figure out the factors which cause the dramatically improved fouling resistance after the AA plasma treatment. DACH plasma treatment[13] results in the deposition of a hydrophilic thin film similar to the AA plasma treatment. However, the DACH treated surface is positively charged in aqueous solution while the AA plasma treated surface is negatively charged. Acetylene and HMDSO plasma treatments result in the deposition of hydrophobic thin films. Contact angles of the modified surfaces are in Table II. Figure 11 shows the flux of the treated membranes as a function of repeated number of filtration. All the treated membranes show lower initial flux than an untreated one and only the DACH plasma treated membrane shows a little bit slower flux decline. Therefore, it is clear that the dramatically improved fouling resistance of the AA plasma treated membrane attributes not only to the hydrophilic surface but also to the negatively charged surface. Although it is not quite clear, better fouling resistance of the negatively charged surface than the positively charged seems to be related to the ions in waste water. Positive ions such as K^+, Mg^{++}, and Ca^{++} will stay on the negatively charged surface while negative ions such as H_2PO_4, HPO_4, and SO_4 will stay on the positively charged surface, which will promote the fouling resistance because of better hydration of positive ions.

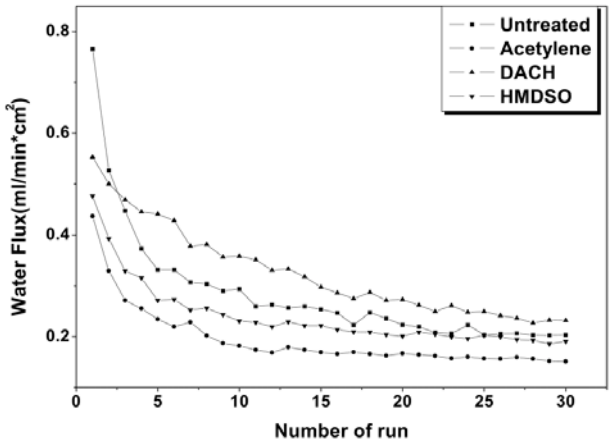


Figure 11. Water flux of untreated, DACH, acetylene, and HMDSO plasma treated (70 mtorr, 20 W, 3 min) membranes as a function of repeated number of filtration.

Conclusions

From the results of this study, followings are concluded:

1. Flux, rejection, and fouling resistance which determine the filtration efficiency of a membrane in ultrafiltration of waste water are closely related to the surface characteristics of the membrane and thus influenced by the surface modification.

2. All of them, especially the fouling resistance, can be greatly improved by AA plasma treatment which modifies the membrane surface by depositing a thin negatively charged hydrophilic film.

3. Oxygen plasma treatment also modifies the membrane surface to be hydrophilic and improves the flux and the fouling resistance but reduces the rejection due to its etching effect.

4. DACH plasma treatment also modifies the membrane surface to be hydrophilic by depositing a thin hydrophilic film but decreases the initial flux and increases the fouling resistance only a little bit due to the positively charged characteristic of the deposited film.

5. Hydrophobic modifications, acetylene and HMDSO plasma treatments, give a negative effect on the flux and fouling resistance.

Acknowledgments. A Korean Research Foundation Grant (KRF-Y00-290 and KRF-Y00-316) supported this research.

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