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Pervaporative dehydration of ethanol–water solution through asymmetric PC membrane surface modified via residual air plasma-induced graft polymerization of HEMA

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ABSTRACT

This study investigated on the surface modification of an asymmetric polycarbonate (PC) membrane by means of exposure to residual air plasma followed by graft polymerization with 2-hydroxyethyl methacrylate (HEMA) monomer. A tubular type of an evacuated reactor was used in the plasma-induced surface pretreatment. Surface grafting was conducted in a temperature-controlled shaking water bath. The degree of grafting was calculated by gravimetric means. Membrane characterizations were done with Fourier transform infrared spectroscopy, water contact angle measuring device, and scanning electron microscopy. The grafted PC membrane was tested for its pervaporation (PV) performance for dehydrating an aqueous ethyl alcohol solution by determining the permeation rate and the separation factor. We considered the monomer concentration, the plasma conditions, and the grafting time as the different parameters affecting the PV performance. In separating a 90 wt% ethanol in water at 25°C by PV, our findings showed that the PC membrane grafted with 30 wt% HEMA solution (PC-g-HEMA) attained the highest permeation flux of 380 g/m^2 h and separation factor of 410 (equivalent to 98 wt% water in the permeate). The conditions applied to produce such surface-modified PC film were 50 W and 90 s for the plasma treatment and 90 min and 80°C for the graft polymerization. The PV performance of the PC-g-HEMA membrane obtained from this study compared well with that of previously investigated flat-sheet membranes.

Keywords: Pervaporation; Asymmetric polycarbonate membrane; Residual air plasma; HEMA graft polymerization

1. Introduction

Polycarbonate (PC) exhibits toughness and resistance to abrasion. This characteristic mechanical integrity makes it suitable as a pervaporation (PV) membrane. However, as the PC membrane surface is intrinsically dense and hydrophobic, membrane modifications are necessary to improve its permeation flux and render it selective. Recent reviews [1–3] on PV membranes tested for their separation performance in dehydrating alcohols have listed several polymeric membranes. However, studies on PC-based PV membranes are not extensive.

The so-called wet-phase inversion method is a common technique to prepare an asymmetric membrane with a porous sublayer and a thin selective layer, which can be used as a support membrane for PV separation because of its lower mass transfer

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resistance. The permeation flux across the membrane should be as high as possible. For this purpose, several studies [4–6] have experimented on a number of different means to improve the bulk structure porosity of PC membranes. The most recent is by Iqbal et al. [7], who investigated on producing highly porous substructure of asymmetric PC membrane by varying solvent-nonsolvent pairs in casting solutions.

Some researchers [8–10] have reported great improvement in the wettability and adhesion of PC membrane after surface modification by plasma. A considerable increase in the surface energy and a corresponding decrease in the water contact angle occur with increasing discharge power and exposure time for a PC membrane surface modified by an RF plasma at a frequency of 13.36 MHz in air, O_2, or N_2.

In membrane surface modification, only the uppermost atomic layers are altered. The advantage is that the surface can be tailored to target selectivity without changing the makeup of the membrane below the surface. Moreover, the membrane bulk or support can be customized to desired structures that would offer good permeation rates. Different types of surface modification are available. Plasma treatment or plasma graft polymerization is a common main technique. A series of comprehensive investigations by Inagaki et al. [11–13] indicated the efficiency of plasma-induced surface treatment. Surface grafting techniques were reported to be effective in making hydrophobic surfaces hydrophilic by means of graft polymerization of monomers on plasma pretreated membranes [14,15]. To achieve high grafting degree, it is necessary to pretreat membranes by plasma. Various gases are used in plasma surface treatment; however, few studies have examined plasma-induced treatment in residual air. Lee et al. [16] modified the surface of PC membranes with plasma pretreatment using residual air, followed by dip-coating of the pretreated membranes in polyacrylic acid (PAA). Their resulting surface grafted PAA/PC membranes exhibited satisfactory PV separation performance.

To date, academic investigations have been searching for high performance PV membranes. In this study, an asymmetric PC membrane was fabricated by the wet-phase inversion method. A nonsolvent was added in the casting solution to increase the demixing rate for precipitating the membrane to the point that a macrovoid structure was formed near the membrane surface. In this way, a high permeation rate through the membrane could be ensured. To address the selectivity of the membrane, a highly hydrophilic monomer was surface grafted after subjecting the membrane to residual air plasma-induced surface pretreatment. This modification process was done as a function of the monomer concentration, the plasma power and exposure time, and the graft-polymerization time. The separation performance of the modified membrane was then assessed by conducting PV experiments.

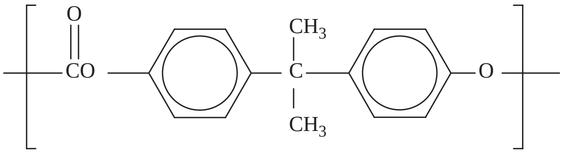

Fig. 1. PC structural formula.

2. Experimental

2.1. Materials

Polycarbonate PC in dichloromethane (DCM) as casting solvent, mixed with n-octanol as nonsolvent additive, was the polymer solution used to fabricate the membrane investigated in this study. PC (Upervaporation separation indexlon S-2000) (molecular weight = 28,000) was purchased from Mitsubishi Gas Chemical Company. Fig. 1 illustrates the PC structural formula.

The coagulant used was methanol. The monomer used was 2-hydroxyethyl methacrylate (HEMA) (see Fig. 2 for its structural formula).

Distilled water was used in preparing the HEMA solution. DCM, *n*-octanol, methanol, and HEMA were supplied by Merck Company and were all reagent grades.

2.2. Preparation of asymmetric PC membrane

The method of forming the PC membrane used for this study was by wet phase inversion (Fig. 3). A PC solution was hand cast onto an A4-size glass plate using a Gardner knife (300-μm gap). The composition of the PC solution without additive was 12 wt% PC and 88 wt% DCM, and that with the *n*-octanol additive was 10 wt% PC, 13 wt% *n*-octanol, and 77 wt% DCM. After casting the membrane, the glass plate was immediately

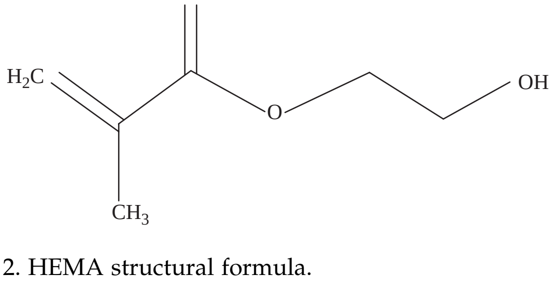

Fig. 2. HEMA structural formula.

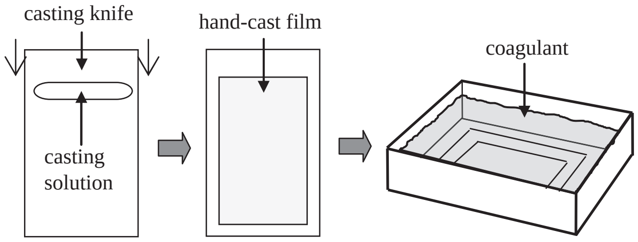

Fig. 3. PC membrane formation by means of wet-phase inversion method.

immersed in a coagulation bath containing methanol for 10 min. Within such time, the membrane peeled off the glass plate by itself. The membrane was then dried in a vacuum oven at room temperature for 24 h, after which it was characterized using SEM and FTIR-ATR.

2.3. Pretreatment of PC membrane by plasma

Degassing of the HEMA solution was first done before exposure of the asymmetric PC membrane surface to residual air plasma. A batch of degassing consisted of freezing the HEMA solution in liquid nitrogen for 20 min and successively thawing it in hot water. This processing of degassing was done thrice under a vacuum of less than 0.2 torr.

After the degassing process, RF power was applied on the electrodes wound around the reactor tube (Fig. 4), the range of which was from 5 to 75 W. The plasma exposure time was for a duration range of 30–120 s. Fig. 4 provides the details of the setup for the plasma pretreatment of the PC membrane.

2.4. Graft-polymerization reaction

Following the plasma pretreatment, HEMA solution was introduced into the reactor tube that held the plasma-pretreated membrane. The reaction between the HEMA solution and the pretreated membrane was allowed to take place for a duration range of 30–120 min in a shaking water bath maintained at 80°C.

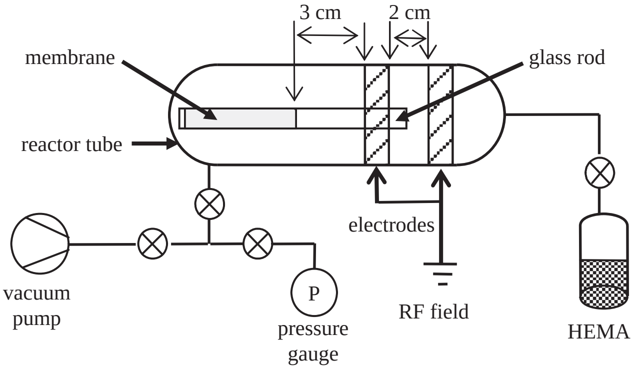

Fig. 4. Plasma pretreatment in residual air.

The grafted membrane was removed from the reactor tube and was transferred to a bottle containing distilled water. This was to wash off any unreacted monomer and homopolymer adhering on the grafted membrane. The washing was done for a total of 24 h, changing the distilled wash water several times within such period of washing time. After washing the grafted membrane, it was vacuum dried at room temperature for 24 h.

The degree of grafting was evaluated based on the weight of the dry membrane before and after the plasma graft-polymerization.

$$DG = \frac{W_{m,f} - W_{m,i}}{W_{m,i}} \times 100\% \qquad (1)$$

where DG means degree of grafting, $W_{m,f}$ refers to the final weight of the dry modified membrane, and $W_{m,i}$ the initial weight of the dry unmodified membrane.

SEM and FTIR-ATR were used to characterize the grafted PC membrane.

2.5 PV separation of ethanol–water solution

A conventional PV apparatus was used in this study, the description of which can be found in [17]. The effective membrane area (A) was about 5 cm^2. A vacuum pump maintained the downstream pressure at 3–5 mmHg. The permeation rate was determined by measuring the weight of the permeate (W_p) collected over a period of time (t). This permeation rate ($= W_p.t$) divided by the effective membrane area gives the permeation flux, as follows:

$$J = \frac{W_p}{tA}. \qquad (2)$$

The separation factor ($\alpha_{H_2O/EtOH}$) was calculated from the following equation:

$$\alpha_{H_2O/EtOH} = \frac{Y_{H_2O}/Y_{EtOH}}{X_{H_2O}/X_{EtOH}}, \qquad (3)$$

where Y denotes the concentration of the permeate and X the concentration of the feed.

The PV separation index (PSI) was determined from the product of the permeation flux and the separation factor.

$$PSI = J \times \alpha_{H_2O/EtOH}. \qquad (4)$$

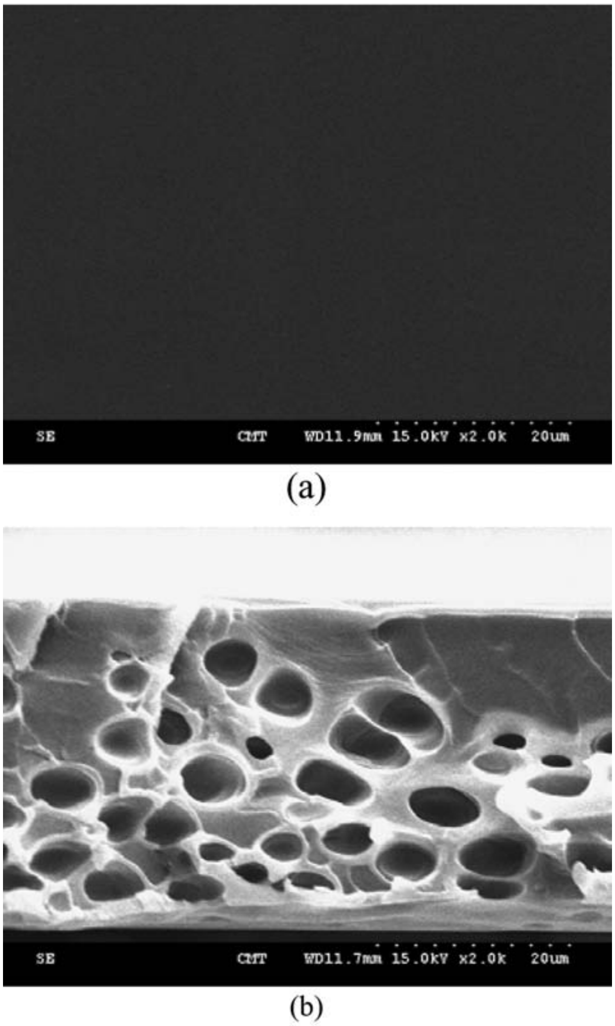

Fig. 5. SEM images of PC membrane cast from solution without additive (12 wt% PC, 88 wt% DCM).

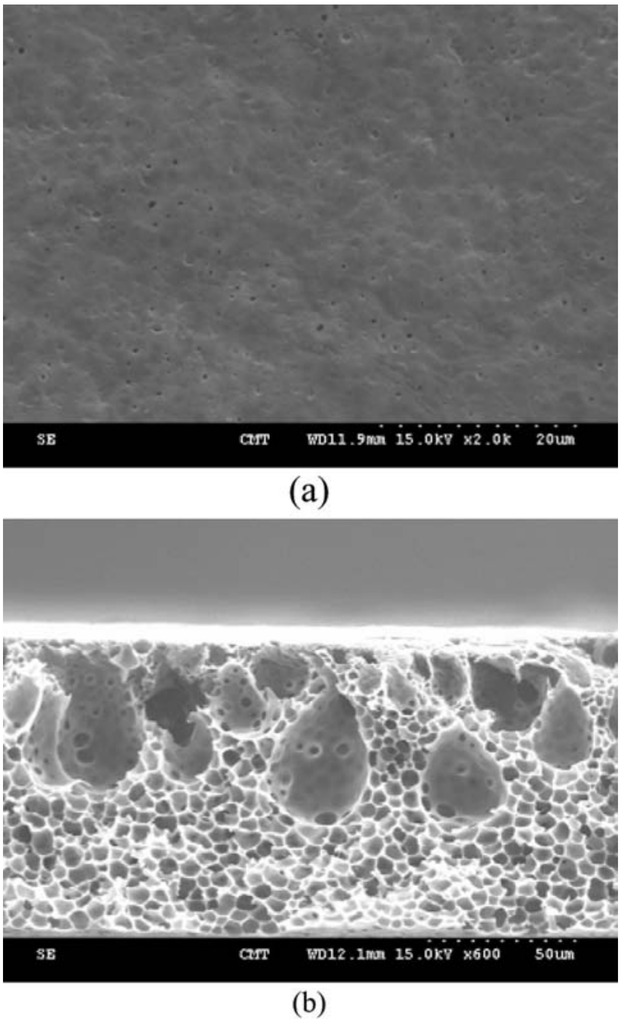

Fig. 6. SEM images of PC membrane cast from solution with *n*-octanol additive (10 wt% PC, 13 wt% *n*-octanol, and 77 wt% DCM).

3. Results and discussion

3.1. Asymmetric PC membrane formation

Fig. 5 displays SEM micrographs of a PC membrane cast from a solution without a nonsolvent additive, whereas Fig. 6 presents those of the membrane formed from a solution with *n*-octanol as an additive. A comparison of these two SEM images reveals that the former micrographs illustrate a dense surface (Fig. 5a) and a thick dense upper layer shown by the cross-sectional image in Fig. 5b, as opposed to the latter micrographs that depict a surface with holes distributed over it (Fig. 6a) and a porous structure with macrovoids near the surface (see cross-sectional picture in Fig. 6b). This latter result is similar to the findings by Lee et al. [16], who reported that the rate of demixing between a casting solvent and a coagulant is increased with the presence of an alcohol as a nonsolvent additive in a PC/DCM casting solution. They concluded that the higher the number of the carbon atoms in the alcohol, the higher is the demixing rate, and therefore, the more porous the PC membrane structure becomes.

3.2. Effect of HEMA concentration

Fig. 7 indicates the changes in the degree of grafting and the water contact angle as a function of the concentration of HEMA solution. The degree of grafting increased with the HEMA concentration increasing from 10 to 40 wt%, resulting in greater amount of HEMA grafted on the PC membrane surface, which was made reactive by the plasma pretreatment. This result was expected as more HEMA is available for surface grafting. The same trend of increasing degree of

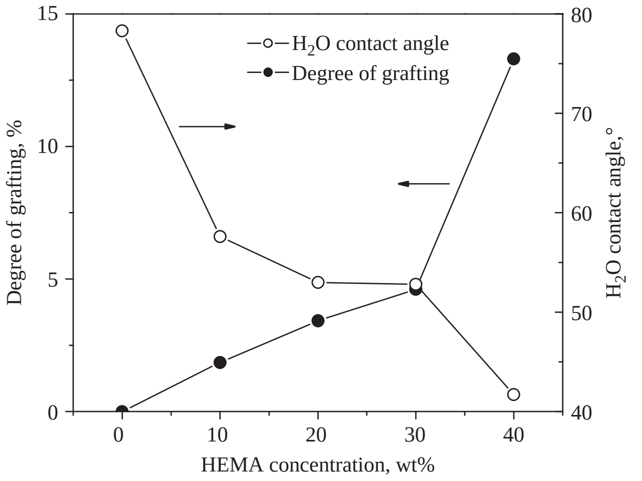

Fig. 7. Effect of HEMA concentration on degree of grafting and water contact angle (plasma conditions: 50 W and 90 s; grafting conditions: 90 min and 80°C).

grafting with monomer concentration was observed by other studies [16,18,19].

With increased HEMA graft on the surface of the plasma-pretreated PC membrane as a function of the increasing HEMA concentration, it would follow that the water contact angle would decrease (Fig. 7), indicating that the membrane surface becomes more hydrophilic due to the greater amount of HEMA grafted. This effect of HEMA concentration on the water contact angle was also reported by a number of research work [5,20,21].

Fig. 8 shows the FTIR-ATR spectra for the PC membranes grafted with different concentrations of the HEMA solution (10–40 wt%), as well as those for the pristine and plasma-treated membranes. By contrasting these spectra, it becomes evident that the changes in the spectra of the grafted membranes are due to surface grafting, since the spectra for the membranes before grafting show practically no difference.

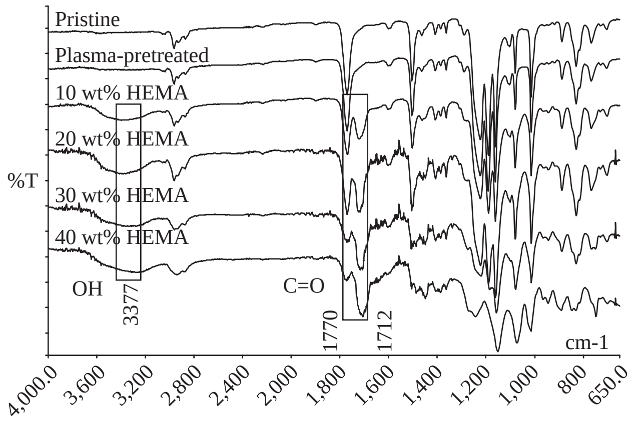

Fig. 8. FTIR-ATR spectra showing effect of HEMA concentration (plasma conditions: 50 W and 90 s; grafting conditions: 90 min and 80°C).

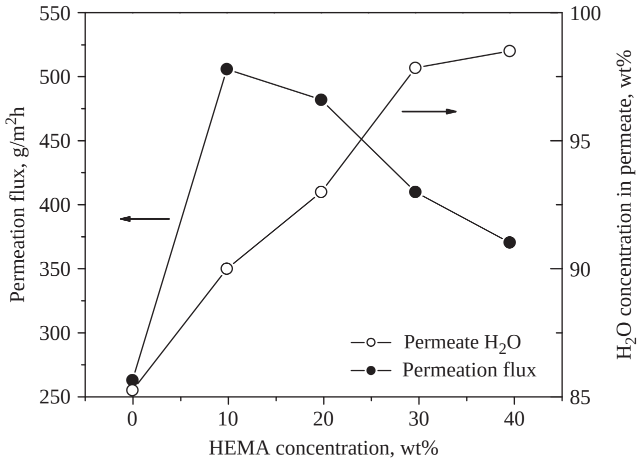

Fig. 9. Effect of HEMA concentration on permeation flux and permeate water concentration (plasma conditions: 50 W and 90 s; grafting conditions: 90 min and 80°C; PV conditions: 90 wt% ethanol-water solution and 25°C).

The spectra for the grafted membranes reveal that the graft on the surface of the PC membrane was due to the presence of HEMA, as the spectra exhibit new peaks at about 1,712 and 3,377 cm^{-1}, corresponding to the C=O and OH functional groups, respectively. These functional groups are characteristic of the vinyl HEMA (see Fig. 2 for the structural formula). FTIR-ATR data reported by previous researchers [22–24] indicate similar peaks identifying the presence of HEMA grafted on a substrate.

From analyzing the spectra for the grafted membranes in Fig. 8, we may realize the effect of HEMA concentration on the degree of grafting. This qualitative analysis is based on the changes in the peaks at about 1,770, 1,712, and 3,377 cm^{-1}, attributable to the pristine PC C=O functional group (see Fig. 1) and to the HEMA C=O and OH functional groups (see Fig. 2), respectively. We might observe that the intensity of the C=O peak at about 1,770 cm^{-1} decreases as that at 1,712 cm^{-1} increases and that the intensity of the OH peak at about 3,377 cm^{-1} seems to increase in terms of the peak's length and breadth. This would be the case of HEMA graft gradually covering the PC membrane surface as the concentration of the HEMA solution used in the graft-polymerization reaction increases. Such observation seems to provide evidence for the increasing amount of HEMA grafted on the PC membrane surface as a function of the increasing HEMA solution concentration.

The PC membrane grafted with HEMA was tested for its PV performance, and Fig. 9 plots the variation in the permeation flux and the concentration of water

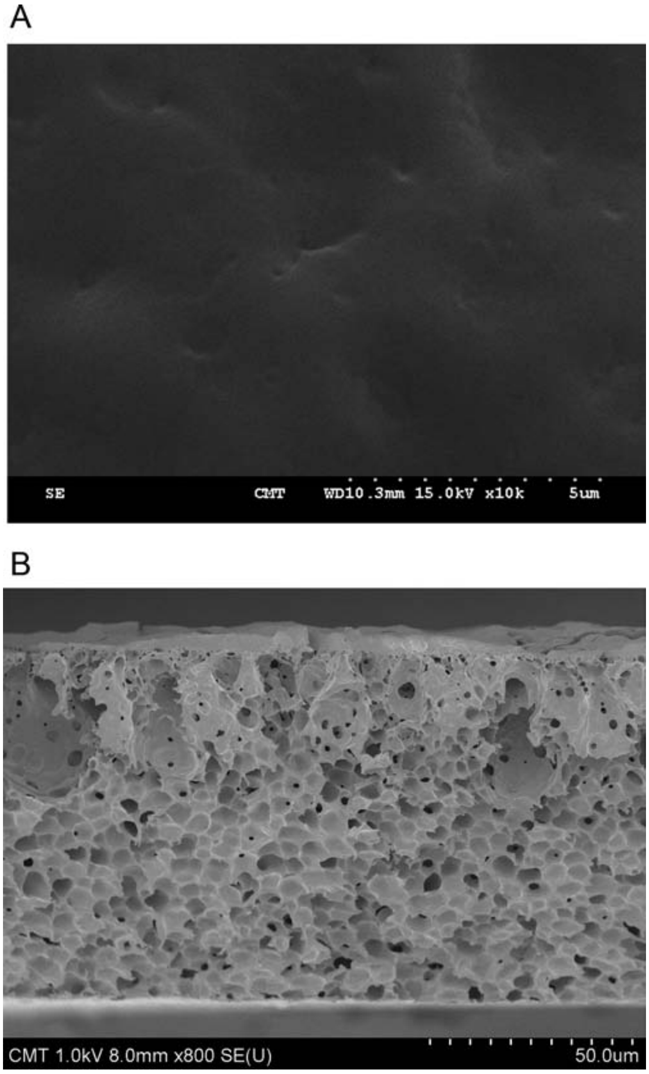

Fig. 10. SEM images of grafted PC membrane (30 wt% HEMA solution, plasma power at 50 W and exposure time of 90 s, and grafting for 90 min and at 80°C).

in the permeate vs. the HEMA concentration. On one hand, the flux decreases within the range of HEMA concentration increase from 10 to 40 wt%. This decrease may be ascribed to the intensifying crosslinking effect of the HEMA graft on the membrane surface with the increasing concentration of HEMA [16]. On the other hand, the selectivity of the PC membrane improves, as evidenced by increasing concentration of water in the permeate due to the increased hydrophilicity of the membrane surface.

Based on the data in Fig. 9, the 30 wt% HEMA concentration would give the highest PV separation index of 1.6×10^5. In other words, the plasma-induced graft polymerization with 30 wt% HEMA solution produced a modified PC PV membrane with a permeation flux of 380 g/m^2 h and a separation factor of 410 (equivalent to 98 wt% water in the permeate).

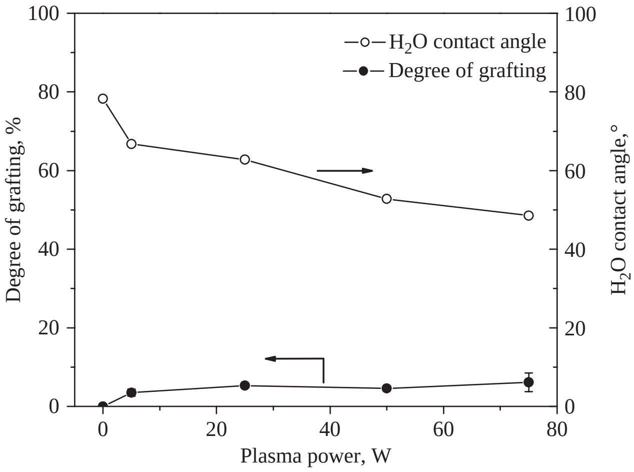

Fig. 11. Effect of plasma power on degree of grafting and water contact angle (30 wt% HEMA solution and 90 s plasma exposure time).

Fig. 10 shows the SEM surface morphology of the modified PC membrane as a result of grafting a plasma-treated membrane with 30 wt% HEMA solution. In contrast to the surface micrograph of the unmodified membrane in Fig. 6a, a now HEMA graft covered surface can be observed in Fig. 10a, whereas compared to the cross-sectional image in Fig. 6b, and a graft layer can be seen in Fig. 10b. This layer makes the modified PV membrane selective, resulting in a high concentration of water (98 wt%) in the permeate.

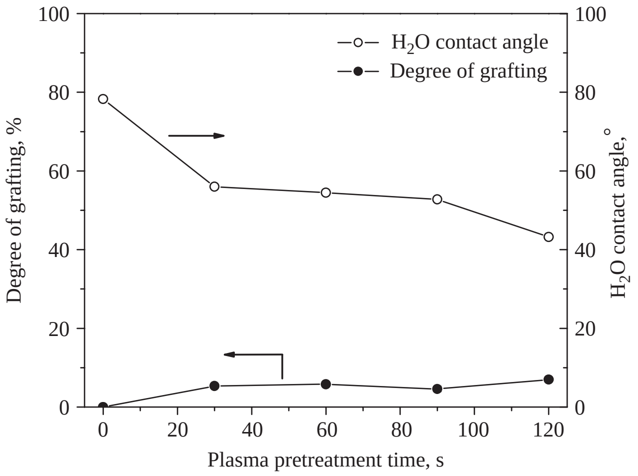

Fig. 12. Effect of plasma exposure time on degree of grafting and water contact angle (30 wt% HEMA solution and 90 W plasma).

Table 1. Comparison of PV performance of different flat-sheet membranes

Membrane	Flux, $g/m^2 \cdot h$	Permeate H_2O wt%	Separation factor (α)	PSI $\times 10^{-5}$	Reference
PAA/PC	133	100	–	1.20	[16]
$Co(acac)_3$/PC	162	98	366	0.60	[25]
AAm/PSf	718	53	10	0.07	[19]
HEMA/PC	380	98	410	1.60	This study

3.3. Effect of plasma power and treatment time

Fig. 11 indicates the change in the plasma power, whereas Fig. 12 presents the variation in the plasma pretreatment time, as a function of the degree of grafting and the water contact angle for a PC membrane modified by grafting with 30 wt% HEMA solution. The effect of both plasma parameters may be considered minimal up to 50 W of plasma power applied or up to 90 s of plasma pretreatment time. Fig. 11 suggests that the degree of grafting and the water contact angle become apparently dependent on the plasma power above 50 W. In Fig. 12, the dependency on the plasma pretreatment time seems to be at times longer that 90 s.

As the plasma power applied is increased and the pretreatment time longer, more reactive sites for surface grafting are generated. As such, the degree of grafting would consequently be improved. Experiments on plasma pretreatment of PC membranes above 75 W and longer than 120 s were also conducted in this study, and the resulting membranes were singed. This outcome signifies that etching reactions begin to dominate over surface treatment reactions; these are the two reactions occurring during the process of plasma treatment [11–13].

Based from the experimental data obtained from this study, the PC membrane grafted with the 30 wt% HEMA solution (PC-g-HEMA) gave the highest permeation flux of 380 $g/m^2 \cdot h$ and separation factor of 410 (PV separation index = 1.6×10^5) for plasma conditions of 50 W power and 90 s pretreatment time and grafting conditions of 90 min graft-polymerization time and 80°C reaction temperature in dehydrating a 90 wt% aqueous ethanol solution at 25°C by PV. Table 1 indicates that the PV performance of such grafted PC membrane compares well with that of previously investigated flat-sheet membranes for separating a 90 wt% ethanol–water solution at 25°C.

To explain such PV performance, the SEM images (see Fig. 10) of the modified membrane plasma-treated at 50 W and for 90 s and grafted with 30 wt% HEMA solution for 90 min and at 80°C were examined in terms of the layer of HEMA graft on the membrane surface. This layer is responsible for the selectivity of the grafted PC membrane. The high permeation flux of 380 g/m^2 h can be attributed to the porous substructure of the modified PV membrane, which is characterized by a number of macrovoids near the surface and some pores in the membrane substructure.

4. Conclusions

This study was able to fabricate a porous structure of PC membrane with macrovoids near the surface and to modify it using the technique of plasma-induced graft polymerization. Surface grafting with HEMA made the plasma-pretreated membranes hydrophilic. The extent of grafting or the decrease in the water contact angle was a function of the increasing concentration of HEMA solution. On assessing PC membranes grafted with HEMA (PC-g-HEMA) through PV experiments, the highest permeation flux of 380 g/m^2 h and separation factor of 410 (equivalent to 98 wt% water in the permeate) were obtained with a plasma-pretreated PC membrane grafted with 30 wt% HEMA solution. For this PV performance, the conditions applied for separating a 90 wt% ethanol–water solution at 25°C were 50 W and 90 s plasma and 90 min and 80°C grafting. Such PC-g-HEMA PV performance compared well with previously investigated flat-sheet membranes.

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Symbols

A	effective membrane area, m^2
DG	degree of grafting, %
J	permeation flux, g/m^2 h
PSI	PV separation index, $g/m^2 \cdot h$
t	time, h
W_p	weight of permeate, g
$W_{m,f}$	weight of modified membrane, g

$W_{m,I}$	weight of unmodified membrane, g
X_{EtOH}	weight fraction of ethanol in feed
X_{H_2O}	weight fraction of water in feed
Y_{EtOH}	weight fraction of ethanol in permeate
Y_{H_2O}	weight fraction of water in permeate
$\alpha_{H_2O/EtOH}$	separation factor

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