ELSEVIER

Characteristics of polyimide-based composite membranes fabricated by low-temperature plasma polymerization

Dung Thi Tran [a], Shinsuke Mori [b], Masaaki Suzuki [b],*

[a] *Department of Chemical Technology, Hanoi University of Science, VNU, Vietnam, 334-NguyenTrai, ThanhXuan, HaNoi, Vietnam*
[b] *Department of Chemical Engineering, Tokyo Institute of Technology, Japan, 2-12-1 O-okayama, Meguro-ku, Tokyo, 152-8552, Japan*

Abstract

Composite membranes were prepared by the deposition of plasma-polymerized allylamine films onto a porous polyimide substrate. The relationship between the plasma conditions and the membrane characteristics was described in terms of monomer flow rate, plasma discharge power, plasma polymerization time, and so on. Scanning electron microscope (SEM) images indicate that the thickness of the plasma polymer layer increased and the membrane skin pore size decreased gradually with the increasing of plasma polymerization time. Fourier transform infrared (FTIR) spectra demonstrate the appearance of amine groups in the plasma deposited polymer and the contact angle measurements indicate that the hydrophilicity of the membrane surfaces increased significantly after plasma polymerization. The composite membranes can reject salt from sodium chloride feed solution, and membrane separation performance depends strongly on the plasma conditions applied during the preparation of the plasma deposited polymer films.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Plasma polymerization; Deposition polymer; Composite membrane; Separation performance

1. Introduction

Plasma polymerization is a unique method of modifying polymers and other material surfaces by depositing a thin plasma polymer layer onto a substrate surface [1–5]. Plasma polymer films exhibit many properties different from those of films fabricated using conventional polymerization methods due to their special physical and chemical properties, such as a high degree of cross-linking, pinhole-free uniformity and extremely strong adherence to the substrate surface [6–10]. In the field of membranes, plasma polymerization techniques have been used to prepare highly selective composite membranes, especially for gas separation, nanofiltration and reverse osmosis processes. Urrutia, Schreiber and Wertheimer [11] have prepared plasma polymer films from monomer mixtures of hexamethyldisiloxane with methyl methacrylate and styrene with vinyl acetate, and these plasma polymer films were deposited on porous silicone rubber sheets substrates to form composite membranes for gas separation processes. Inagaki and Kawai [12] have used mixtures of perfluoromethylcyclohexane with methane as the monomer to prepare plasma polymer layers deposited onto Millipore porous substrates; the formed membranes can be used for the separation of oxygen and nitrogen mixtures. Nomura et al. [13] have prepared composite membranes by plasma polymerization using fluoro compound monomers, with and porous polysulfone hollow fibers as the substrate. Cho and Ekengren [14] have deposited plasma-polymerized acrylic acid films onto the surface of various porous support materials (cellulose acetate, polyethersulfone, polyvinylidene fluoride and polypropylene) to prepare composite membranes for the ultrafiltration of bleach effluent. Lai and Chao [15] have carried out the plasma polymerization of hydrophilic monomers such as 1-vinyl-2-pyrolidone, 2-hydroxyethyl methacrylate and acrylic acid to fabricate nylon 4-based composite membranes for desalination. Tsutsui, Takao and Murase [16] have prepared composite membranes via plasma polymerization using nitrogen-containing compound as the monomer and porous polyacrylonitrile as the sublayer. We have modified polyacrylonitrile ultrafiltration membranes by deposition of a plasma-polymerized acrylic acid

---

* Corresponding author.
E-mail address: masaaki@chemeng.titech.ac.jp (M. Suzuki).

layer onto a substrate membrane surface to form reverse osmosis composite membranes [17].

Reverse osmosis membranes have a dense skin polymer layer with no visible pores, in which the separation occurs. These membranes show different transport rates for permeated molecules as small as 2–5 Å in diameter. The transport is best described by the solution–diffusion model. The tiny spaces between the polymer chains in these membranes are less than 5 Å in diameter and so are within the normal range of thermal motion of the polymer chains that make up the membrane matrix [18]. The reverse osmosis process uses the large pressure difference across the membrane to separate water from salt solution. The permeated molecules will diffuse through the dense polymer layer of the membrane and fluctuate in the polymeric matrix before moving out of the membrane bulk. Therefore, the membranes have to have a dense enough skin polymer layer to reject salt and allow water molecules to pass through. In other words, the separation property of reverse osmosis membranes is greatly affected not only by the degree of cross-linking of the membrane skin polymer layer but also by the hydrophilicity of this polymer.

In this study, reverse osmosis composite membranes were prepared by radio frequency (RF) plasma polymerization using allylamine (AlAm) as the monomer and microporous polyimide (PI) film as the substrate. Microporous PI films are widely used commercially as separation membranes, and PI is a very useful material due to its thermal stability (up to 300 °C) as well as its high chemical resistance. AlAm is an advantageous non-saturated monomer for plasma polymerization because it requires relatively little energy for polymerization and a large amount of primary amine groups can be retained in the formed plasma polymer. The aim of this paper is to describe how plasma polymerization conditions affect the characteristics of PI-based composite membranes; also, the influence of plasma operational parameters on membrane separation performance is described in terms of the desalination property.

2. Experimental

2.1. Materials

Microporous polyimide films supplied by UBE Co. (Japan) were used as substrates for the plasma polymerization processes. Scanning electron microscope (SEM) images (Fig. 1) indicate that virgin porous PI film has an asymmetric structure with a very high porous sublayer and an average top-layer pore size of 0.2 μm. Allylamine, purchased from Wako Industrial Chemicals Co. (Japan), was used as the monomer with no further purification.

2.2. Preparation of the composite membranes

Composite membranes were prepared by the plasma polymerization of allylamine vapor to form plasma polymer films deposited on a porous PI substrate. A 13.65-MHz radio frequency (RF) plasma generator combined with a matching unit was used to establish the plasma in the reactor. Details of
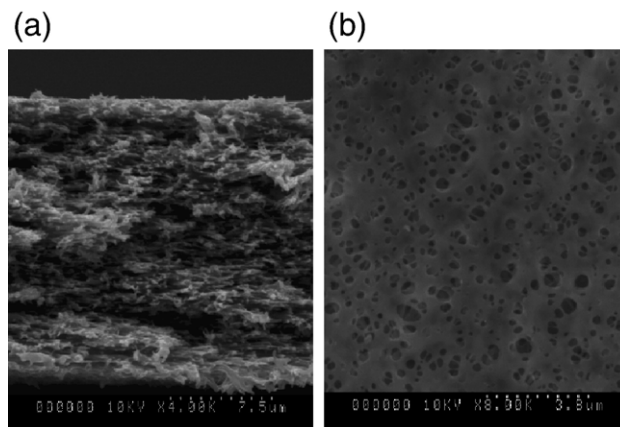

Fig. 1. SEM images of virgin porous PI film: (a) cross-section and (b) top surface.

the experimental setup are given elsewhere [17]. The plasma polymerization system consisted of a tubular reaction chamber (diameter 30 mm, length 400 mm) with two external electrodes (8 mm wide and 100 mm apart) connected with a cold trap, a monomer reservoir with a mass flow meter and connecting tubes made from glass, a radio frequency power supply with a matching network; the system also had a pressure gauge and a vacuum pump.

Porous PI film substrate was placed in the reactor before evacuating; monomer vapor (allylamine) was introduced into the reactor at a determined flow rate when the vacuum inside the reactor reached a pressure below 3 Pa. Then, the RF power supply was switched on to initiate the glow discharge for plasma polymerization. In this work, the effects of the monomer flow rate, polymerization time, power input and deposition pressure on the formed composite membrane characteristics were investigated.

2.3. Membrane characteristics

2.3.1. Contact angle measurements

The contact angles of water droplets were measured using a goniometer equipped with a camera which captured images of drops of room-temperature pure water on the membrane surfaces. For each sample, three drops were placed at different locations and the average value of these measurements was calculated.

2.3.2. Fourier transform infrared spectroscopy (FTIR)

Qualitative information of the characteristics of the plasma polymer was gathered using FTIR spectra. In order to determine the functionality of the polymer layer deposited on the membrane surface as a result of due to plasma polymerization, FTIR spectra were recorded by the attenuated total reflection (ATR) technique, using a Jeol-SPX 200 spectrometer with a horizontal ATR device at an incidence angle of 30°. One hundred scans were taken at a resolution of 4 cm^{-1}.

2.3.3. Scanning electron microscopy (SEM)

The morphological characteristics of the membrane surface and membrane cross-section were determined by studying
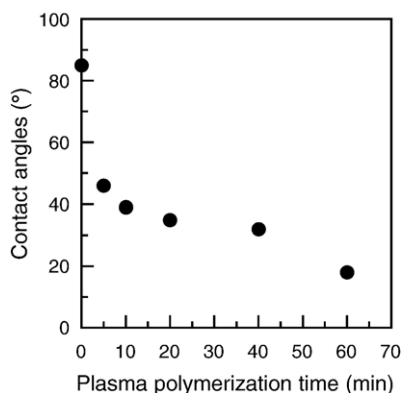
Fig. 2. Influence of the plasma polymerization time on the contact angles to the membrane surface (plasma discharge of 10 W).

through scanning electron microscope (SEM, Hitachi, S-800) images. To prevent surface charging, a thin film (5 nm) of Pt was sputtered onto all samples by means of ion sputter unit (E-1030, Hitachi) prior to imaging.

2.3.4. Separation performance

The separation performance of the reverse osmosis membranes was determined based on the water flux, J, and the salt rejection coefficient, R, which are defined by the equations: $J = [V/(S\,t)]\ [\mathrm{l/m^2\ h}]$ and $R = \{[(C_0 - C)/C_0] \times 100\}[\%]$, where V, S and t are the filtrate volume, the membrane area and the separation time, respectively; C_0 and C are the concentrations of salt in the feed solution and filtrate, respectively. The separation performance of reverse osmosis membranes depends strongly not only on membrane characteristics such as the membrane skin pore size, the degree of cross-linking and the thickness of the skin polymer layer but also on the relative transport rates of components, such as their solubility and diffusivity in the membrane.

In this study, the separation performance of a PI-based composite membrane was evaluated in a desalination experiment using a 3000-ppm sodium chloride (NaCl) feed solution. Desalination experiments were carried out in Membrane Cell (Osmonic, USA) under a pressure driving force of 3.5 MPa;
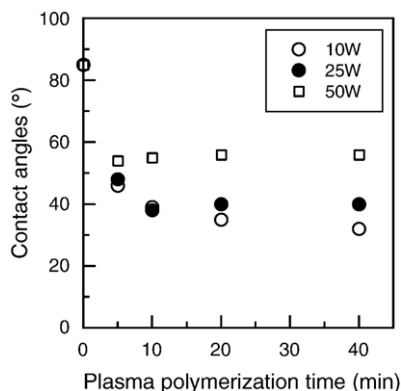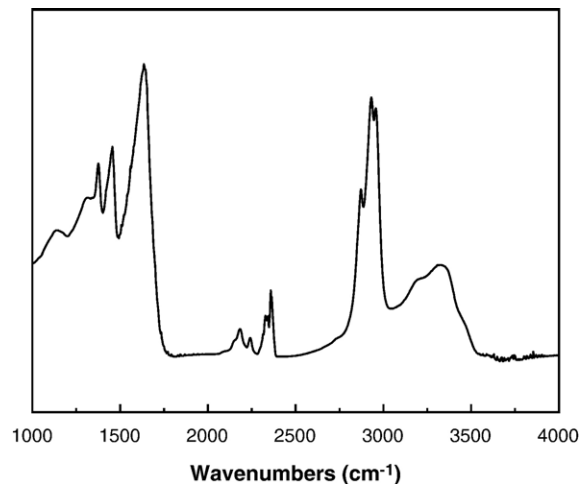

Fig. 4. FTIR spectrum of plasma-polymerized allylamine polymer.

the concentrations of salt in the feed solution and filtrate were determined by conductivity measurements.

3. Results and discussion

3.1. Membrane surface characteristics

3.1.1. Contact angles

Contact angle measurement is one of the simplest methods of determining the changes in hydrophilicity that take place in the outermost layer of materials during or after a modification process. We also used this method to evaluate the changes in the wettability of the composite membrane surfaces prepared by plasma polymerization. In this experiment, the plasma processes were carried out at a fixed monomer flow rate of 2.5 sccm and a plasma discharge pressure of 18 Pa; the polymerization time and plasma power input were varied. The correlation between the contact angles to the membrane surface and the polymerization time and discharge power is shown in Figs. 2 and 3. The obtained

Fig. 3. Influence of the plasma duration and power input on the contact angles to the membrane surfaces.
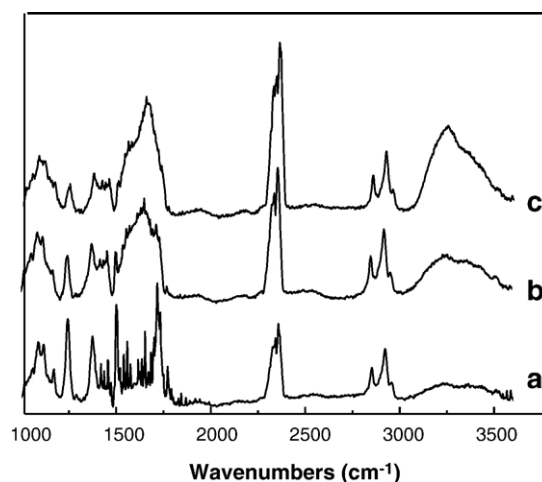

Fig. 5. FTIR-ATR spectra of virgin PI film and composite membrane surfaces prepared with different plasma polymerization times: (a) virgin PI film, (b) 10 min and (c) 20 min.
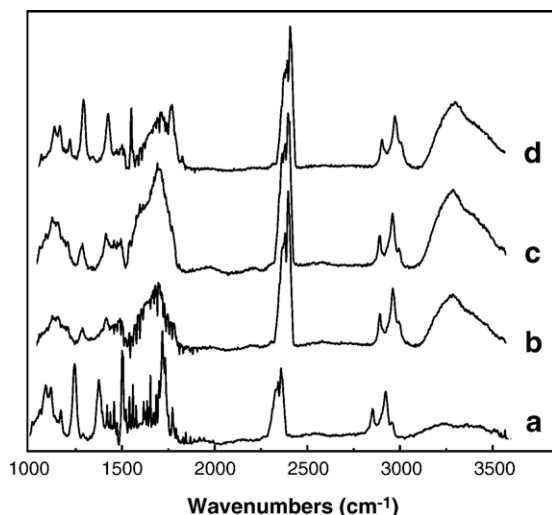
Fig. 6. FTIR-ATR spectra of virgin PI film and PI-based composite membrane surfaces prepared at different power inputs: (a) virgin PI film, (b) 10 W, (c) 25 W and (d) 50 W.

3.1.2. FTIR spectra

Fig. 4 shows the FTIR spectrum of a plasma-polymerized allylamine layer deposited onto a CaF_2 plate at a power input of 20 W, a monomer flow rate of 2.5 sccm, and a plasma discharge pressure of 18 Pa for 20 min. The obtained results indicate that the plasma polymer contains highly dense primary amine groups. The main peaks are a broad NH_2, NH stretching absorption band between 3500 cm^{-1} and 3000 cm^{-1}, and a strong NH_2, NH vibration absorption band between 1600 cm^{-1} and 1500 cm^{-1}. In addition, there are also some absorption peaks of the CH_2 stretching band between 3000 cm^{-1} and 2900 cm^{-1}, and CH_2 and CH vibration bands between 1450 cm^{-1} and 1380 cm^{-1}. Next, the FTIR-ATR spectra of the PI-based composite membranes surfaces were recorded. Fig. 5 shows the spectra of virgin porous PI film and PI-based composite membrane surfaces formed with different plasma polymerization times (at a fixed power input of 10 W, a monomer flow rate of 2.5 sccm and a plasma discharge pressure of 18 Pa). The results also demonstrate the appearance of amine groups in the composite membrane surface as evidenced by the absorption bands between 3500 cm^{-1} and 3000 cm^{-1}, and between 1600 cm^{-1} and 1500 cm^{-1}. Furthermore, the intensity of these absorption peaks increased with increasing polymerization time. It is well known that the power input also influences the plasma polymerization process significantly [19]. Fig. 6 shows the spectra of virgin porous PI film substrate and PI-based composite membrane surfaces prepared at different plasma discharge powers. The obtained results indicate that the intensity of the absorption bands due to NH_2 and NH vibration between 1600 cm^{-1} and 1500 cm^{-1} in the polymer prepared at 50 W is lower than those in the polymers formed at 10 W and 25 W. It is reported [20] that plasma polymerization can take place by either an opening of the monomer double bonds or a formation of reactive species through the fragmentation of monomer molecules. Opening the double bonds requires less energy than the dissociation of single bonds or fragmentation. Therefore, at low discharge powers, plasma polymerization takes place mainly through the opening of the double bonds. The energy transferred to the monomer molecules increases with increasing discharge power, and fragmentation effects become more important at high discharge powers. Hence,

results indicate that the membrane surface became more hydrophilic and that a sharp decrease of the water contact angles (from 85.1° on virgin PI substrate to 46.5° on plasma-polymerized film) took place during the first 5 min of plasma polymerization. After that, the contact angles decreased more slowly with plasma polymerization time at the fixed plasma discharge power of 10 W (Fig. 2). Apart from that, at the same monomer flow rate, the contact angles to the membrane surfaces prepared at 50 W were more acute than those to the surfaces formed at 10 W and 25 W (Fig. 3). The decrease of the contact angles could be due to the presence of hydrophilic groups in the plasma polymer layer deposited on the membrane surface after plasma polymerization. Since allylamine ($CH_2=CH-CH_2-NH_2$) vapor was used as the monomer, it is plausible to assume that the hydrophilic groups are primary amine groups. Furthermore, the amount of these groups in the polymer depends on the plasma conditions. Qualitative information on the chemical composition of the membrane surface was given by the FTIR spectra, as described below.
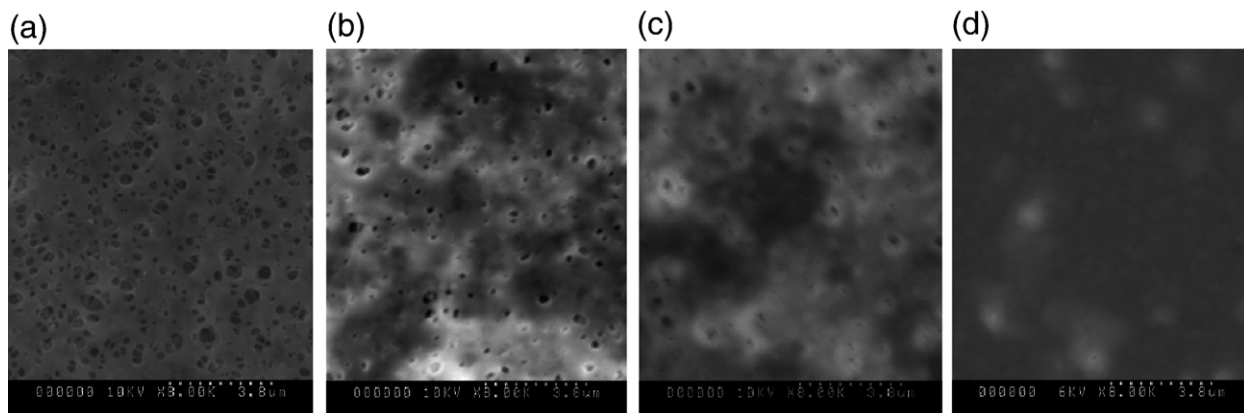

Fig. 7. SEM images of virgin PI film and PI-based composite membrane surfaces: (a) virgin PI film, (b) 5 min, (c) 10 min and (d) 30 min plasma polymerization.
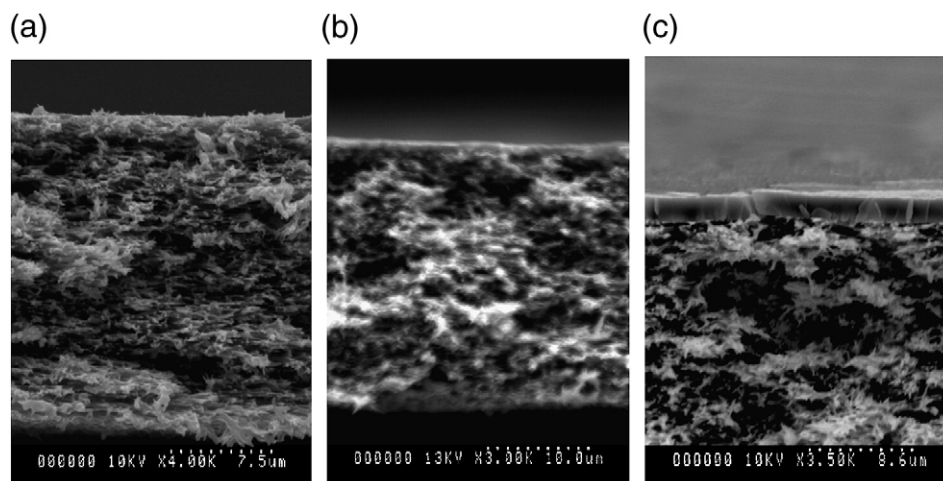
Fig. 8. SEM images of virgin PI film and PI-based composite membrane cross-sections: (a) virgin PI film, (b) 30 min and (c) 60 min plasma polymerization.

the amount of amine groups in the plasma-polymerized allylamine film formed at the power input of 50 W may be smaller than that in the polymers formed at 10 W and 25 W.

3.1.3. SEM studies

The structural characteristics of the membranes were studied by SEM; images of the top membrane surfaces and the membrane cross-sections are given in Figs. 7 and 8, respectively. These figures show morphological images of composite membranes prepared at a fixed monomer flow rate of 2.5 sccm, a plasma discharge pressure of 18 Pa and a power input of 10 W, with different polymerization times. The pictures show that the membrane skin pore size decreased gradually during plasma polymerization (Fig. 7). Also, the thickness of the deposited plasma polymer layer increased with increasing plasma duration (Fig. 8). The results indicate that the deposition of plasma polymer takes place not only in the surface but also in the skin pores of the substrate membrane.

3.2. Membrane separation performance

3.2.1. Influence of the plasma polymerization time

In this experiment, plasma polymerization was carried out at a fixed power input of 10 W, a monomer flow rate of 1.5 sccm

and a plasma discharge pressure of 18 Pa. The influence of the polymerization time on the separation property of the composite membranes is illustrated in Fig. 9. The experimental results indicate that membrane salt rejection (R) increased and water flux (J) decreased quickly within the first 20 min of polymerization. This altering of the membrane separation property could be the result of changes in membrane morphology which occurred during plasma polymerization, in which the membrane skin pore size decreased and the thickness of the top layer increased due to the deposition of the plasma polymer layer onto the substrate membrane surface.

3.2.2. Influence of the monomer flow rate

In this experiment, the monomer flow rate range was varied from 1.5 to 6.0 sccm, the plasma discharge power was maintained at 10 W, the polymerization time was fixed at 20 min and the plasma discharge pressure was 20 Pa. The experimental result (Fig. 10) shows that there is an optimum range of monomer flow rate (from 2.0 to 3.0 sccm) in which the obtained membranes have a higher selectivity. At insufficiently high monomer flow rates (below 1.5 sccm), it is plausible to assume that the separation property of the membranes is poor because of the extremely low salt rejection coefficient, R. However, when
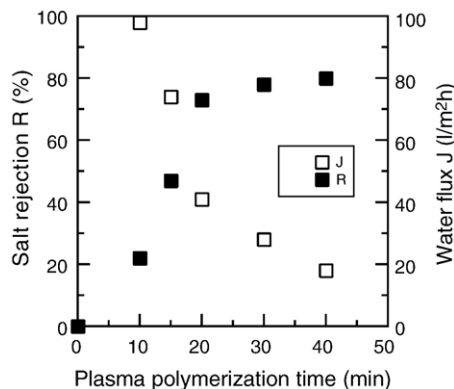

Fig. 9. Influence of the plasma duration on the separation performance of PI-based composite membranes.
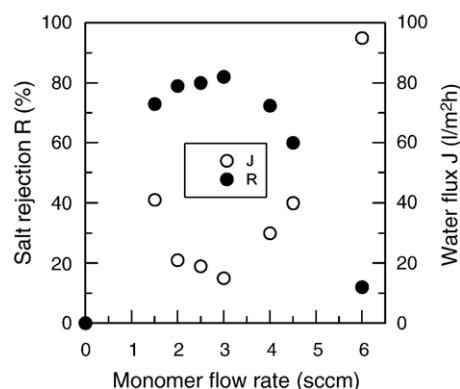

Fig. 10. Influence of the monomer flow rate on the separation performance of PI-based composite membranes.

the monomer flow rate exceeds the optimum range (higher than 4.0 sccm), the selectivity of the membranes worsens again. The changes in the selectivity of the membranes relate to the changes in the characteristics of the plasma polymer layer formed at different monomer flow rates. The following presumptions are considered: at insufficiently high monomer flow rates, the deposition rate of the polymer is very slow, and after 20 min of polymerization the formed deposition layer is not thick enough to create a selective barrier layer which can reject the salt from the feed solution. In the optimum monomer flow rate range, the deposited polymer film can work as an active barrier layer to reject the salt. At excessive monomer flow rates, deposited polymers with lower cross-linking are formed because the resident time of the monomer in the reactor decreases and the plasma energy transferred to the monomer is reduced when the monomer flow rate increases, thereby reducing the salt rejection capability of the barrier layer. This effect should be investigated in more detail in future studies.

3.2.3. Influence of the plasma discharge power

Plasma polymerization was carried out at a fixed monomer flow rate of 2.5 sccm, a plasma discharge pressure of 18 Pa and a polymerization time of 20 min; the power input range was varied from 10 W to 40 W. Fig. 11 shows the influence of the plasma power input on the separation property of the composite membranes. The results indicate that the membrane salt rejection increased and the water flux decreased with increasing plasma power. Because the fragmentation effect of the monomer molecules becomes more dominant when the plasma power increases [19], a plasma polymer with higher cross-linking would be formed at high discharge powers, whereas a little branched polymer would be formed at low discharge powers; this may be why membranes prepared at low discharge powers have smaller selectivity.

3.2.4. Influence of the deposition pressure

In this experiment, plasma polymerization was carried out under the fixed conditions with a monomer flow rate of 2.5 sccm, a power input of 10 W and a polymerization time of 20 min. The influence of the deposition pressure on the membrane separation property is shown in Fig. 12. It is well known
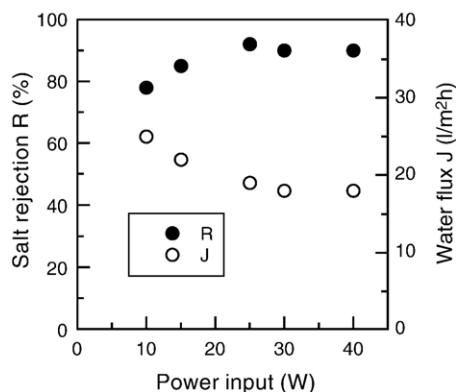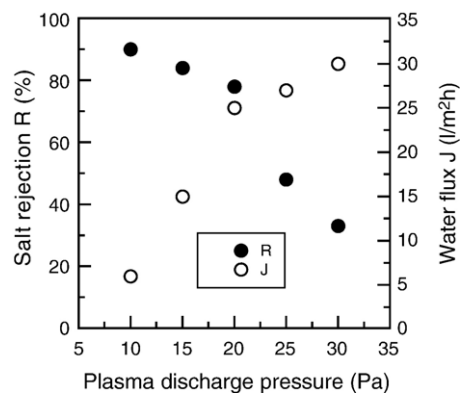
Fig. 12. Influence of the plasma discharge pressure on the separation performance of PI-based composite membranes.

that the deposition rate of a plasma polymer in a flow system is a function of the working gas pressure, and that the working gas pressure strongly influences the plasma polymer's characteristics [1]. In this experiment, the working gas pressure was varied from 10 Pa to 30 Pa, and the results obtained from the separation experiment show that the salt rejection decreased and the water flux increased as the when working gas pressure increased. We consider that increasing the working gas pressure can induce the increase of the deposition rate of the plasma polymer, the reduction of the cross-linking degree of the deposited polymer and consequently the reduction of the selectivity of the composite membrane.

4. Conclusion

The preparation of reverse osmosis composite membranes using plasma polymerization was carried out by deposition of plasma-polymerized allylamine films onto a porous polyimide sublayer. The influences of the preparation conditions on the membrane properties was determined by investigating the membrane surface characteristics and the membrane separation performance. The results of this work indicate that the thickness of the plasma deposited films increases and the membrane skin pore size decreases gradually with polymerization time. Membrane surfaces become more hydrophilic due to the appearance of amine groups in the plasma deposited polymer layers. The characteristics of plasma deposited polymer films and the separation performance of PI-based reverse osmosis composite membranes depend strongly on the plasma polymerization conditions, such as the monomer flow rate, the plasma discharge power and the deposition pressure. The experimental results suggest the existence of an optimum monomer flow rate range and a critical discharge power, as well as a proper deposition pressure region in which the formed composite membranes have a high selectivity and a good water flux.

Fig. 11. Influence of the power input on the separation performance of PI-based composite membranes.

References

[1] H. Yasuda, Plasma Polymerization, Academic Press, Orlando, 1985.
[2] H. Biederman, Y. Osada, Plasma Polymerization Processes, Elsevier Science Publishing Inc., New York, 1992.
[3] C.M. Chan, T.M. Ko, H. Hiraoka, Surf. Sci. Rep. 24 (1996) 1.
[4] H. Aizawa, et al., Mater. Sci. Eng., C, Biomim. Mater., Sens. Syst. 12 (2000) 49.
[5] V. Sciarratta, U. Vohrer, D. Hegemann, M. Muller, C. Oehr, Surf. Coat. Technol. 174-175 (2003) 805.
[6] N. Suzuki, Y. Ogushi, K. Imai, N. Ohta, S. Ueno, U.S. Patent No. 4639285 (1987).
[7] S. Ueno, H. Nomura, K. Imada, U.S. Patent No. 4429024 (1984).
[8] J.D. Masso, W.D. Brennan, D.H. Rotenberg, U.S. Patent No. 4478873 (1984).
[9] S. Ueno, H. Nomura, K. Imada, U.S. Patent No. 4548867 (1985).
[10] T. Akagi, I. Sakamoto, S. Yamaguchi, U.S. Patent No. 4728564 (1988).
[11] M.S. Urrutia, H.P. Schreiber, M.R. Wertheimer, J. Appl. Polym. Sci., Appl. Polym. Symp. 42 (1988).
[12] N. Inagaki, H. Kawai, J. Polym. Sci., Part A, Polym. Chem. 24 (1986) 3381.
[13] H. Nomura, P.W. Kramer, H. Yasuda, Thin Solid Films 118 (1984) 187.
[14] D.L. Cho, O. Ekengren, J. Appl. Polym. Sci. 47 (1993) 2125.
[15] J.Y. Lai, Y.C. Chao, J. Appl. Polym. Sci. 39 (1990) 2293.
[16] N. Tsutsui, S. Takao, I. Murase, U.S. Patent No. 4283359 (1981).
[17] T.D. Tran, S. Mori, M. Suzuki, Thin Solid Films 515 (2007) 4148.
[18] R.W. Baker, Membrane Technology and Applications, John Wiley & Sons Ltd, 2004.
[19] H.K. Yasuda, Plasma Process. Polym. 2 (2005) 293.
[20] D.L. Cho, M. Claesson, C. Golander, K. Johansson, J. Appl. Polym. Sci. 41 (1990) 1373.