Acrylic Acid γ-Ray Irradiation-Grafted Nylon 4 Membranes

J. Y. LAI,* M. H. CHEN, C. Y. SHIH, and K. Y. HSU

Department of Chemical Engineering, Chung Yuan University, Chung Li, Taiwan, Republic of China

SYNOPSIS

This study was to improve the performances of nylon 4 membranes for washing waste-water treatment of nuclear power plants, e.g., removal of detergent and salt by membranes. The effects of the degree of grafting and ionization on the reverse osmosis performances of acrylic acid (AA)-grafted nylon 4 membranes by γ-ray irradiation modification were investigated. The relationships of operating conditions, such as feed concentrations of salt and detergent, operating temperature, and pressure, and the performances of water flux and solute rejection of the prepared membranes were obtained. Water flux of the prepared membranes was highly sensitive with the operating temperature. It was found that an increase in the operating pressure could increase the water flux and the impaction effect directly. Water flux and salt rejection were significantly improved by both ionized and nonionized AA-grafted nylon 4 membranes compared to ungrafted nylon 4 membranes. Water flux increased rapidly and solute rejection dropped off slightly as the grafted membranes were ionized. The 100% detergent rejection could be obtained by the nonionized AA-grafted nylon 4 membranes with 38.6 and 69.6% degrees of grafting under various operating conditions. Results obtained showed that these modified nylon 4 membranes were usable for washing waste-water treatment of nuclear power plants. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The improved performance of nylon 4 membranes was reported by Huang et al.[1,2] using the improved polypyrrolidone synthesis and membrane preparation method. To improve the performance of nylon 4 membranes, Lai et al.[3] utilized γ-ray irradiation and Jong et al.[4] used the chemical initiation method to induce monomers to be grafted onto nylon 4 membranes. Plasma treatment was also utilized by our laboratory to improve the performance of nylon 4 membranes.[5] As a result, it was found that the modification of nylon 4 membranes is a useful method for improving their reverse osmosis performance.

Acrylic acid (AA) grafted onto nylon 6 membranes was used by Takigami et al.[6] to improve their reverse osmosis performance. Nylon 4 membranes were selected by us for this study because they possess higher hydrophilicity than that of nylon 6 membranes.

Sea water is used as a cooling water in some nuclear power plants. The washing waste water that contains low radioactive detergent is often drained away by mixing with the used cooling sea water. Thus, removing the detergent from the washing waste water was the main purpose of this study. However, the desalting effect was also investigated simultaneously.

In the present study, the nonionized AA-grafted nylon 4 membranes with various degrees of grafting and the ionized AA-grafted nylon 4 membranes were prepared and treated with the washing waste water of a nuclear power plant. Effects of the degree of grafting and ionization on the reverse osmosis performance of modified nylon 4 membranes were investigated. The relationships of the operating conditions, such as feed concentrations of salt and detergent, operating temperature and pressure, and

* To whom correspondence should be addressed.

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water flux and solute rejection of the prepared membranes, were also studied.

EXPERIMENTAL

Materials

Nylon 4 was synthesized by CO_2-initiated polymerization of 2-pyrrolidone using potassium 2-pyrrolidonate as a catalyst.[3] The molecular weights of the samples, measured by a Cannon-Fenske viscometer with *m*-cresol as the solvent at 25°C, were about 25,000. Normal propanol and formic acid supplied by Nihon Shiyaku Industries Co. were used as the medium solvent and the casting solvent, respectively. Acrylic acid (AA) supplied by Merck Co., Germany, was purified by vacuum distillation. The distilled monomer was filled in a brown glass bottle and stored in a refrigerator at 4°C until use. Distilled water was used as a solvent for extraction.

Membrane Preparation

Membrane was prepared from a casting solution of grafted copolymer in formic acid/*n*-propanol solvent. The detailed procedure for the membrane preparation was reported in our previous papers.[3-5]

Grafting Copolymerization

The nylon 4 membranes was dried in vacuum and weighed and then placed in a glass tube. The grafting monomer solution was poured onto the membrane and soaked the membrane completely. Graft copolymerization was carried out with 0.1 Mrad/h dose rate from 20 to 80 h. The membranes with 38.6 and 69.6% degrees of grafting could be obtained by a total dose of 2 and 8 Mrad, respectively. After the irradiation, the grafted membrane was washed with distilled water several times to remove all the homopolymer and then dried in vacuum. The degree of grafting was calculated from the weight increase of the grafted membrane.

Ionization of the Membrane

The AA-grafted nylon 4 membrane was ionized by a 0.5*N* NaOH solution at room temperature for 20 min and, afterward, washed with distilled water. The mechanical strength of the treated membranes was lower than that of the untreated membranes. Unfortunately, the mechanical strength of the ionized membrane with a 69.6% degree of grafting was too low to test.

Reverse Osmosis Properties

The reverse osmosis (R.O.) experiments were carried out in R.O. high-pressure testing equipment (Purification Water Co. Type MS-002). The apparatus, which consists of six testing cells, can test six membranes at the same time. The permeate flowing down from the cell was collected and measured. The water flux (W.F.), the salt rejection (S.R.), and the detergent rejection were determined by the following equations:

$$\text{W.F.} = \frac{V \times \rho}{A \times t} \ (\text{g/cm}^2\ \text{s}) \quad (1)$$

$$\text{S.R. (or D.R.)} = \frac{C_{f0} - C_f}{C_{f0}} \times 100\% \quad (2)$$

where V is the permeate volume; ρ, the density of permeate solution; A, the effective membrane area; t, the operation time, and C_{f0} and C_f, the feed and permeate concentrations, respectively. The salt (sodium chloride) concentration was determined by a conductivity meter, and the detergent concentration, by a UV spectrophotometer.

RESULTS AND DISCUSSION

Effect of Total Dose on the Degree of Grafting

As shown in Figure 1, the degree of grafting (D.G.) increased sharply with the total dose at the beginning of irradiation and increased slowly after about 4 Mrad of total dose. The active sites formed by irradiation were increased with the total dose. Consequently, the possibilities of grafting was enhanced and the degree of grafting was increased. The reason for the slow increase of the degree of grafting at

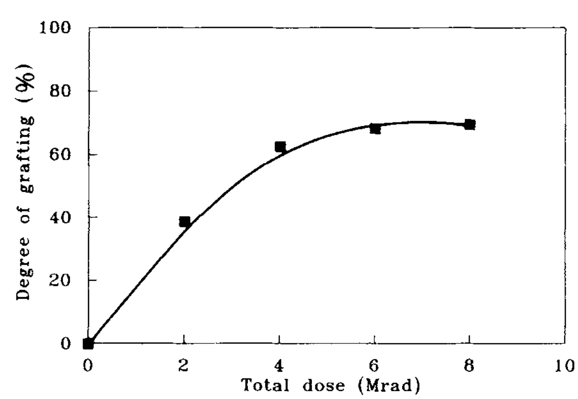

Figure 1 Effect of total dose on the degree of grafting of nylon 4 membranes.

higher total dose was due to the slowed down diffusion rate of the AA monomer into nylon 4 membranes as more and more AA monomer was grafted onto the nylon 4 membranes. Similar results were also obtained by Hegazy et al.[7] and Lai and Chen.[8]

Effect of Operating Conditions on Reverse Osmosis Desalination Performances of Membranes

Before the study of the detergent removal, the desalination performances test was conducted first in order to characterize the membranes.

Effect of Feed Concentration of Salt

The effect of salt feed concentration on water flux and salt rejection was examined first. There were no appreciable differences by changing salt concentrations from 0.1 to 10 g/L. This was probably due to that the osmotic pressure difference was not changed significantly between both sides of the membrane with increasing salt feed concentration.

Effect of Operating Pressure

Water flux was increased with increasing the operating pressure for four series of membranes because raising the operating pressure resulted in a significant acceleration in the rate of the water molecule passing through the membrane, as shown in Figure 2. The effect of operating pressure on salt rejection is shown in Figure 3. As the operating

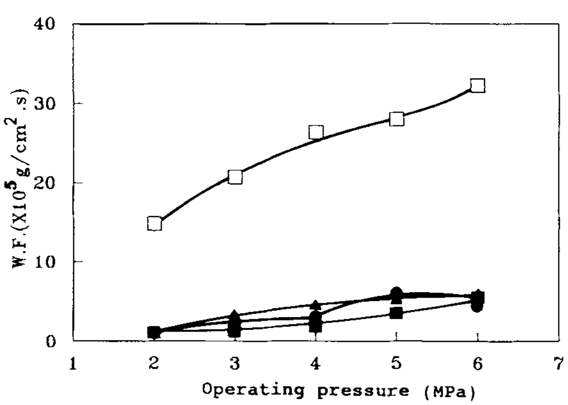

Figure 2 Effect of the operating pressure on W.F. of membranes: operating temperature, 30°C; feed concentration, 10 g NaCl/L; (●) ungrafted nylon 4; (■) nonionized PAA-*g*-nylon 4, D.G. = 38.6%; (▲) nonionized PAA-*g*-nylon 4, D.G. = 69.6%, (□) ionized PAA-*g*-nylon 4, D.G. = 38.6%.

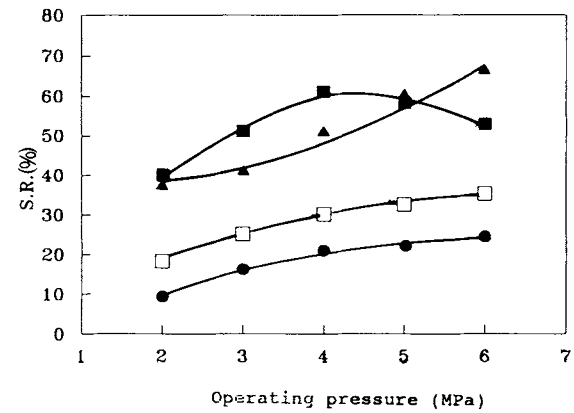

Figure 3 Effect of the operating pressure on S.R. of membranes: operating temperature, 30°C; feed concentration, 10 g NaCl/L; (●) ungrafted nylon 4; (■) nonionized PAA-*g*-nylon 4, D.G. = 38.6%; (▲) nonionized PAA-*g*-nylon 4, D.G. = 69.6%; (□) ionized PAA-*g*-nylon 4 D.G. = 38.6%.

pressure was increased, the salt rejection also increased. Additionally, increasing the operating pressure would compress the amorphous regions of the membrane, which is called the impaction effect. Thus, it would be difficult for salt and water molecules to pass through the membrane. This led to an increase in the salt rejection and a decrease in the water flux. Summarizing the above-mentioned phenomena, water flux of the membrane was influenced by the occurrence of acceleration and impaction simultaneously. Thus, the water flux was not proportional to the operating pressure.

Effect of Operating Temperature

The effect of raising operating temperature on water flux and salt rejection is shown in Figures 4 and 5, respectively. Water flux increased with increasing operating temperature from 30 to 60°C due to the higher diffusion rate through the membrane and the greater swelling of the membrane by water solvation. On the other hand, salt rejection dropped off as the operating temperature increased. This was attributed to the increasing of the water swelling effect on the membrane structure and the solubility of salt in the membrane. A similar observation was also reported by Petersen.[9]

Effect of AA-grafted Membrane

The water molecule would be favorable to pass through the hydrophilic monomer-grafted mem-

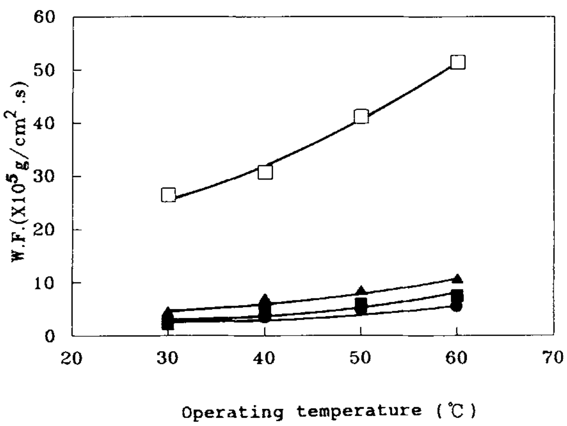

Figure 4 Effect of the operating temperature on W.F. of membranes: operating pressure, 4 MPa; feed concentration, 10 g NaCl/L; (●) ungrafted nylon 4; (■) nonionized PAA-*g*-nylon 4, D.G. = 38.6%; (▲) nonionized PAA-*g*-nylon 4, D.G. = 69.6%; (□) ionized PAA-*g*-nylon 4, D.G. = 38.6%.

brane. On the contrary, a barrier was also formed gradually that would resist the water molecule passing through the membrane. This was because the grafted polymer chains masked the partial pores of the membrane, which is called the mask effect. A competition between hydrophilicity and the mask effect of the membrane would cause the various results.

The salt rejection of nonionized AA grafted onto nylon 4 membranes with two different degrees of grafting were higher than that of ungrafted nylon 4 membrane, as shown in Figures 3 and 5, respectively. This was due to the slightly charged effect by grafted PAA chains and to the mask effect on the membrane structure. Both effects would resist the large particle salts passing through the membrane and lead to a higher salt rejection.

The water flux of nonionized AA grafted onto nylon 4 membranes with a 38.6% degree of grafting was lower than that of ungrafted nylon 4 membranes, except for several with higher operating temperatures, as shown in Figures 2 and 4, respectively. This was because the mask effect of the membrane overcame the increase of membrane hydrophilicity. The membrane hydrophilicity was increased gradually with increasing degree of grafting. It was proved that the water flux of nonionized AA-grafted nylon 4 membranes with a 69.6% degree of grafting was higher than that of nonionized AA-grafted nylon 4 membranes with a 38.6% degree of grafting and of ungrafted nylon 4 membranes.

Effect of Ionized AA-grafted Membrane

As the nonionized AA-grafted nylon 4 membranes were immersed in a 0.5*N* NaOH solution for 20 min, the functional group "—COOH" would be transformed into the more hydrophilic ionic form functional group "—COO^-Na^+." After the nonionized AA-grafted nylon 4 membranes were ionized, a remarkable increase in water flux and a decrease in salt rejection were obtained, as shown in Figures 2–5. This was because these ionized membranes were easily swollen by water. Thus, both the water molecule and the salt would pass through these membranes easily.

The water flux of ionized AA-grafted nylon 4 membranes with a 38.6% degree of grafting was larger than that of nonionized AA-grafted nylon 4 membranes with a 38.6% degree of grafting and of ungrafted nylon 4 membranes. For example, the water flux of three series of membranes, which were tested under 4 MPa operating pressure and 30°C operating temperature, were 26.38, 2.25, and 3.12 $\times 10^{-5}$ g/cm^2 s, respectively, as shown in Figure 2. The salt rejection of ionized membranes with a 38.6% degree of grafting was 30.1%, which was higher yet than that of ungrafted nylon 4 membranes (20.9%). These values remarkably revealed that the reverse osmosis performances of ungrafted nylon 4 membranes had been improved.

Effect of Detergent Feed Solution

The effect of the detergent feed concentration on the water flux of the membranes is shown in Figure

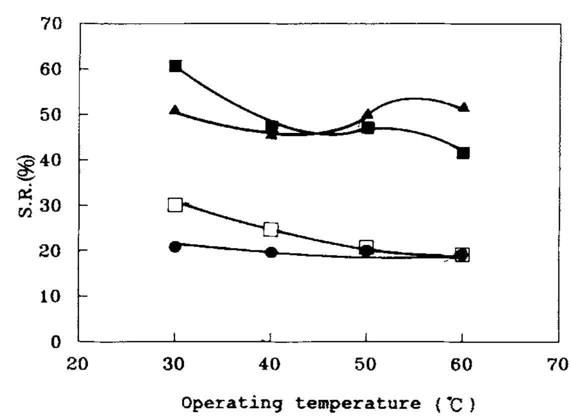

Figure 5 Effect of the operating temperature on S.R. of membranes: operating pressure, 4 MPa; feed concentration, 10 g NaCl/L; (●) ungrafted nylon 4; (■) nonionized PAA-*g*-nylon 4, D.G. = 38.6%; (▲) nonionized PAA-*g*-nylon 4, D.G. = 69.6%; (□) ionized PAA-*g*-nylon 4, D.G. = 38.6%.

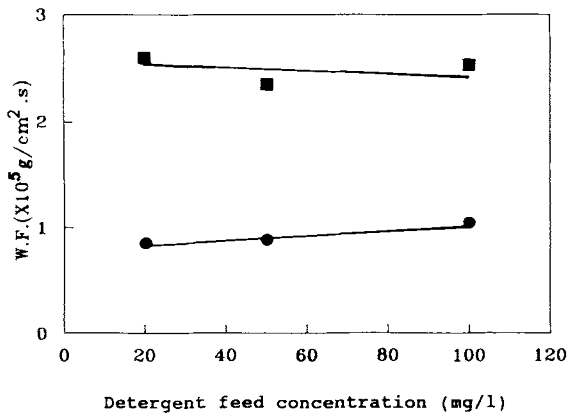

Figure 6 Effect of the detergent feed concentration on W.F. of membranes: operating pressure, 4 MPa; operating temperature, 30°C; (●) nonionized PAA-*g*-nylon 4, D.G. = 38.6%; (■) nonionized PAA-*g*-nylon 4, D.G. = 69.6%.

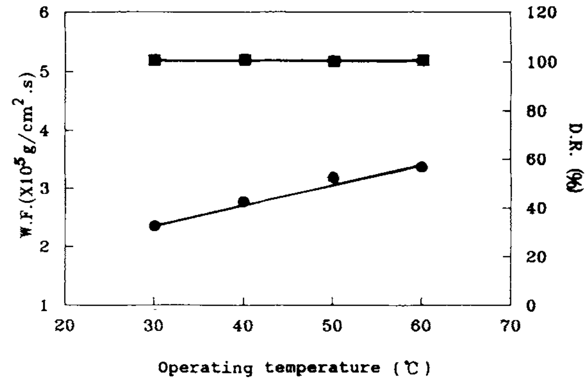

Figure 8 Effect of the operating temperature on performance of membranes with detergent feed solution: operating temperature, 30°C; feed concentration, 50 mg/L; D.G., 69.6%; nonionized; (●) W.F.; (■) D.R.

6. As the feed concentration increased from 20 to 100 mg/L, the water flux changed only slightly for both nonionized AA-grafted nylon 4 membranes with 38.6 and 69.6% degrees of grafting. This was because an increase in detergent feed concentration merely increased the amount of detergent and not appreciably increased the osmotic pressure difference between both sides of the membrane. On the other hand, detergent rejection of nonionized AA-grafted nylon 4 membranes with 38.6 and 69.6% degrees of grafting were all 100% in this study. The detergent is an organic substance, which could not exist as an ionic electrolyte form. Salt rejection was influenced by the charge and morphology of the membrane. Rejection of the detergent by the membrane depended on the molecular weight and molecular structure of the detergent and on the morphology of the membrane.

The effect of operating pressure on the water flux and detergent rejection is shown in Figure 7. Water flux was increased with increasing operating pressure. Detergent rejection did not depend on the operating pressure. However, all the detergent rejection was 100% within the operating pressure range of 2–6 MPa. This revealed that the morphology of the membrane was dense enough to reject all of the detergent.

When the feed was the detergent solution, these water flux values were lower than those of the salt feed solution. This was probably due to the parts of

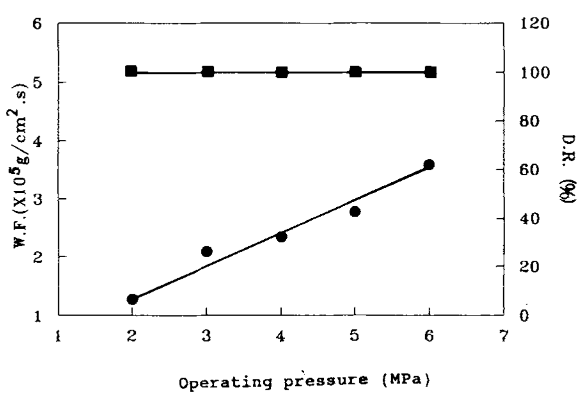

Figure 7 Effect of the operating pressure on performance of membranes with detergent feed solution: operating temperature, 30°C; feed concentration, 50 mg/L; D.G., 69.6%; nonionized; (●) W.F.; (■) D.R.

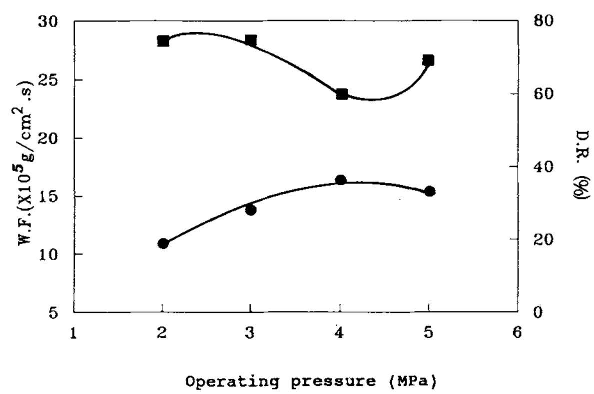

Figure 9 Effect of the operating pressure on performance of ionized membranes with detergent feed solution: operating temperature, 30°C; feed concentration, 50 mg/L; (●) W.F.; (■) D.R.

the pores of the membrane that were filled with detergent, which was caused by the detergent precipitating easily in water. Thus, water flux would drop off. The effect of the detergent precipitating easily could be improved by increasing the turbulence of the feed.[10]

The effect of operating temperature on water flux and detergent rejection for detergent feed solution is shown in Figure 8. Water flux increased slowly with increasing operating temperature, and these water flux values were lower than those of the feed salt solution, which could be explained by the similar reasons above. However, the values of 100% detergent rejection were still constant.

Figure 9 shows the effect of operating pressure on the water flux and detergent rejection of ionized

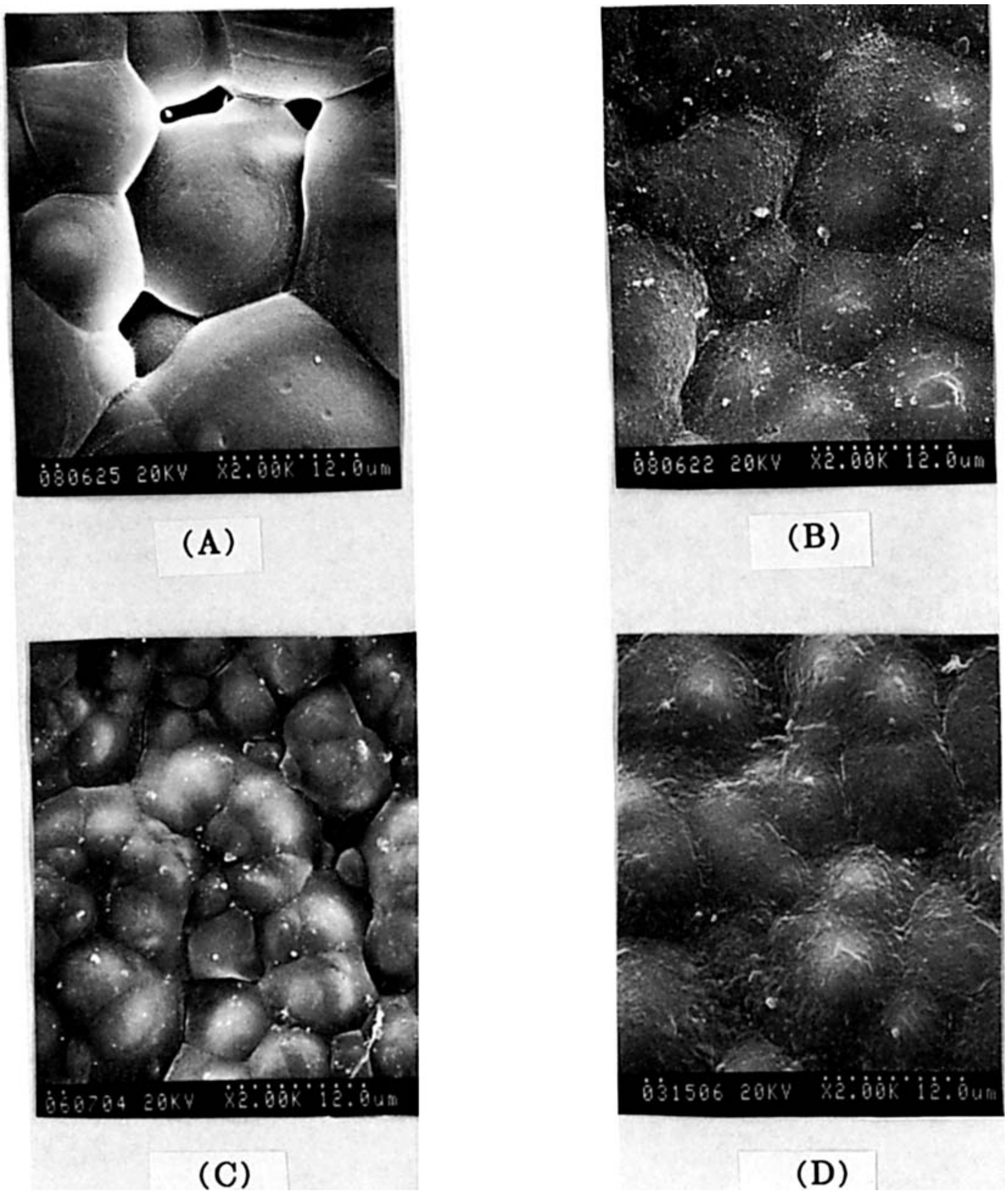

Figure 10 Scanning electron micrographs of the membrane surface structure: (A) ungrafted nylon 4; (B) nonionized PAA-*g*-nylon 4, D.G. = 38.6%; (C) nonionized PAA-*g*-nylon 4, D.G. = 69.6%; (D) ionized PAA-*g*-nylon 4, D.G. = 38.6%.

membranes. Water flux was increased and detergent rejection was decreased with increase of the operating pressure. Similar results had been observed in salt rejection. These membranes would be swollen remarkably when the nonionized AA-grafted nylon 4 membranes were ionized. The high water flux of ionized membrane could be understood and explained, but it is regrettable that detergent in the waste water could not be rejected completely.

Morphology of the Membrane

Figure 10 shows the SEM of four kinds of membrane surface structure. The denseness of the membrane surface structure was increased with increasing degree of grafting from 0 to 69.6%. A crease was formed during drying of the swollen ionized membrane. An increase of the denseness of the membrane surface structure pointed out that the mask effect would increase and the water flux would decrease. Water fluxes of three series of membranes with various degrees of grafting from 0 to 69.6% under 4 MPa operating pressure and 30°C operating temperature were 3.12, 2.25, and 4.57×10^{-5} g/cm^2 s, respectively, as shown in Figure 2. From the SEM of membrane surface structure and the reverse osmosis performance of membranes, both the mask effect and hydrophilicity of the hydrophilic AA monomer grafted onto the nylon 4 membrane were observed. A competition between the mask effect and the hydrophility of the membranes would remarkably affect the water flux of the membranes. Thus, we could conclude that the mask effect could overcome the hydrophilic effect for a lower degree of grafting and the hydrophilic effect could overcome the mask effect for a higher degree of grafting.

CONCLUSION

The ionized and nonionized AA-grafted nylon 4 membranes with various degrees of grafting were successfully prepared and examined. Water flux and solute rejection of these prepared membranes were influenced by the operating conditions, such as feed concentration, operating temperature, and operating pressure. In this study, water flux and salt rejection were improved by grafted AA monomer onto nylon 4 membranes. Water flux was enlarged remarkably because the grafted membranes were ionized. When the feed solution contained detergent, the detergent rejections of nonionized AA-grafted nylon 4 membranes with 38.6 and 69.6% degrees of grafting were all 100% under various operating conditions. For example, the water flux of 3.60×10^{-5} g/cm^2 s and 100% detergent rejection could be obtained under 6 MPa operating pressure and 30°C operating temperature by these nonionized AA-grafted nylon 4 membranes with a 69.6% degree of grafting. From these results, it is feasible to apply grafted AA monomer onto nylon 4 membranes by the irradiation-grafting method to improve the performances for washing waste-water treatment of a nuclear power plant.

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