

Plasma Modification of Aromatic Polyamide Reverse Osmosis Composite Membrane Surface

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ABSTRACT: The surface of aromatic polyamide reverse osmosis composite membrane was modified by oxygen and argon plasma. The water permeability of oxygen-plasma-modified membrane increases, and the chlorine resistance of argon-plasma-modified membrane increases. The spectra of the attenuated total reflection–Fourier transform infrared and X-ray photoelectron spectroscopy and the contact angle of the water were analyzed to explain the improvement of the two performances of the composite membrane. The carboxyl groups were introduced when modified by oxygen plasma, and cross-linking occurred when modified by argon plasma. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1923–1926, 1997

INTRODUCTION

Plasma treatment is a convenient technique for the surface modification of polymer materials for improving the surface properties, such as adhesion and wettability. These properties result from introducing functional groups or making cross-links in the molecule's surface.^{1–4}

Aromatic polyamide reverse osmosis membrane possesses high performance on seawater desalination and ultrapure water preparation, but its water permeability and chlorine resistance is not high enough and thus restricts its broad application.⁵ Surface modified by plasma was used in this article to improve these two performances. The effect of surface modified by plasma on the performance of the aromatic polyamide reverse osmosis composite membrane was studied and the surface was characterized by attenuated total reflectance–Fourier transform infrared

(ATR-FTIR) and X-ray photoelectron spectroscopy (XPS) and contact angle of the water.

EXPERIMENTAL

The poly(-1,3-phenylene terephthalamide) thin film was prepared on the surface of the polysulfone substrate by *in situ* interfacial condensation polymerization.⁶

The membrane was treated by oxygen plasma and argon plasma at a discharge power 100 w and 20 kHz frequency. The plasma pressure was 13.3 Pa.

ATR-FTIR spectra of the surface of the composite membrane were obtained by U.S. Digilab FTS-20E IR spectrometer, XPS spectra of the composite membrane were obtained by ESCA LAB MKII photoelectron spectrometer of Britain VG Company, and advanced contact angle of water was tested by G-II type of instrument of Japan Optical Ltd.

The performance of the composite membrane was tested by a homemade instrument. The method is described in Petersen.⁵

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Table I Effect of the Plasma Treatment on the Water Permeability of Polyamide Composite Membrane

Plasma Treatment Time (min)	Water Permeability (m ³ /m ² /d)	
	Oxygen	Argon
0	0.49	0.51
1	0.58	0.52
2	0.86	0.48
3	1.21	0.49

Test conditions: 1500 ppm NaCl(aq); 1.5MPa; 20°C.

RESULTS AND DISCUSSION

Effect of the Surface Plasma Treatment of the Polyamide on Water Permeability and Chlorine Resistance of Composite Membrane

Table I shows the effect of plasma treatment on water permeability. The water permeability of the composite membrane increased significantly with increasing time of plasma treatment with oxygen, but that with argon plasma treatment membrane decreased slightly. These phenomena could be explained by the structural changes of polyamide in the composite membrane. Carboxyl groups were introduced to the surface of the polyamide by oxygen plasma treatment, and the hydrophilicity increased⁷; but such hydrophilic groups were not introduced by argon plasma treatment.

Table II shows the effect of the surface plasma treatment on the chlorine resistance of the composite membrane. It was found that the chlorine

Table II Effect of the Argon Plasma Treatment on the Chlorine Resistance of Composite

Plasma Treatment Time (min)	Chlorine Resistance (ppm/h) ^a	
	Oxygen	Argon
0	500	500
2	1000	2500
4	3000	5000
6	4500	20,000

^a Chlorine resistance was determined by soaking the membrane in 100 ppm NaClO(aq) for a certain time (h) and then testing the salt rejection. When salt rejection decreased, 0.5%, the amount expressed by ppm/h, was the chlorine resistance of this membrane. Test conditions: 1500 ppm NaCl(aq); 1.5 MPa; 20°C.

Table III Effect of the Plasma Treatment on the Contact Angle of the Water of the Surface of the Composite Membrane

Plasma Treatment Time (min)	Contact Angle of the Water	
	Oxygen	Argon
0	77	78
2	70	76
4	59	77
6	44	69

resistance of the composite membrane increased with an increase in the time of plasma treatment when the surface was modified by argon plasma. The chlorine resistance with oxygen plasma also increased, but the changes were less than those with argon plasma. The cross-linking degree of the polyamide is the major reason for the improved chlorine resistance,⁸ so we could conclude that the cross-linking degree in the argon plasma is more than in the oxygen plasma. The possible cross-linking mechanism of polyamide cross-linked by argon plasma was examined by analysis of ATR-FTIR and XPS spectra.

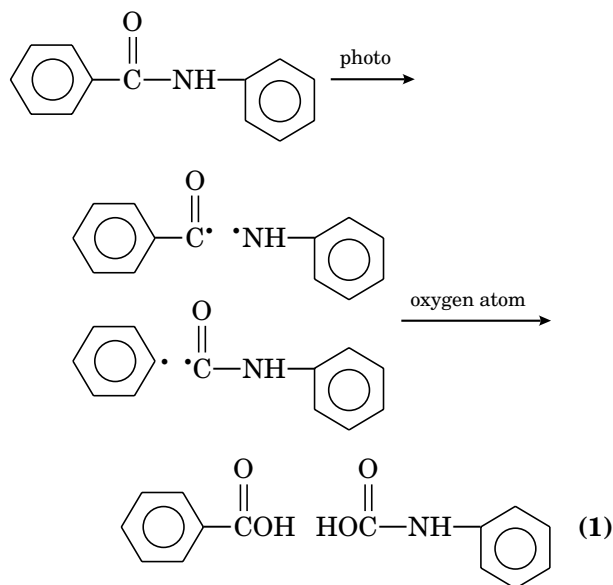
Contact Angle of Water on Plasma-treated Polyamide Surface of the Composite Membrane

Table III shows the effect of the plasma treatment on the contact angle of water of the surface of the composite membrane. The contact angle of the water decreased with an increase in plasma treatment time, from 77 to 44 degrees in oxygen plasma treatment; but the contact angle changed very little in argon plasma treatment. This means the hydrophilicity increased with an increase in the oxygen plasma treatment time. Although the hydrophilicity increases in the argon plasma, it is not as high as that of oxygen plasma. These results could be explained by the introduced carboxyl groups in the oxygen plasma, which make the hydrophilicity higher.

Analysis of ATR-FTIR of the Surface Modified by the Plasma

Figure 1 shows the ATR-FTIR spectra of the surface of the unmodified, modified by oxygen plasma, and modified by argon plasma polyamide composite membrane. Since the polyamide layers are quite thin (less than a micrometer), the poly-

sulfone substrate also contributed to the spectra and made the spectra complicated.⁹ We chose several typical bands to explain the changes in structure of the polyamide. 1657 cm^{-1} is the C=O stretching vibration wave in CONH, 1540 cm^{-1} is the amide II, and 1413 cm^{-1} is the aromatic C—N stretching vibration. Figure 1(c) shows that 1771 cm^{-1} , which is attributed to COOH, appears after oxygen plasma treatment; and 1540 and 1413 cm^{-1} become stronger. These means that the polyamide chain cleaves. The possible cleavage mechanism is as follows.⁷



Comparing the spectra of argon plasma modified with unmodified polyamide surface, we found that 1540 and 1413 cm^{-1} became weak; this possibly results from the environmental changes of C—N in polyamide. With spectra of N-substituted polyamide, the 1540 and 1413 cm^{-1} bands are absent.¹⁰ It was concluded that the H in CONH was substituted by other atoms, or cross-linking occurred at this site. This could explain why the hydrophilicity increased a little but the permeability of the composite membrane decreased compared with unmodified composite membrane, and it could explain the increasing chlorine resistance of the polyamide composite membrane with the argon-plasma-modified surface.

Chemical Composition of Surface of Polyamide Modified by Plasma

From the results of the contact angle measurement and analysis of ATR-FTIR spectra, we ex-

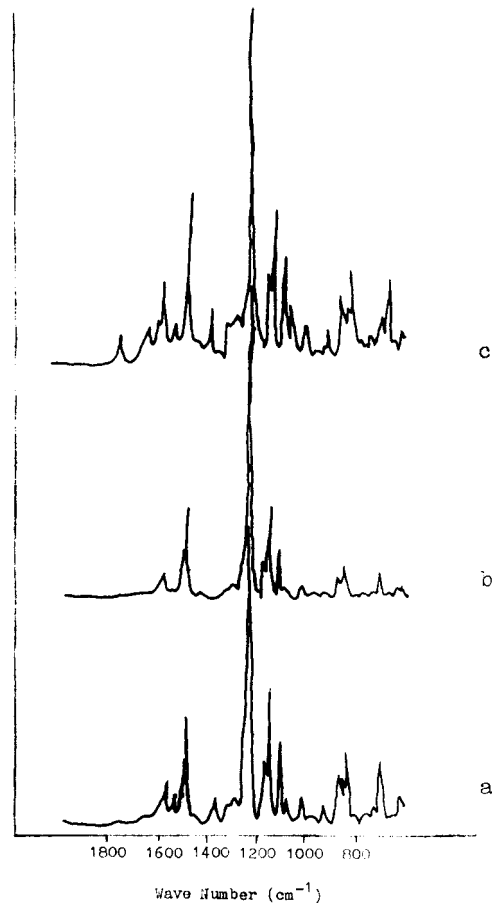


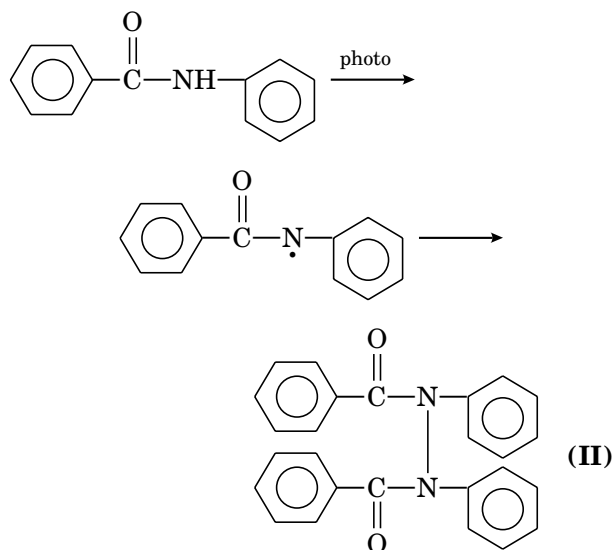
Figure 1 Spectra of the ATR-FTIR of surface of the composite membranes: (a) unmodified membrane; (b) modified by argon plasma membrane; (c) modified by oxygen plasma membrane.

pect the introduction of —COOH and cross-linking in the modified surface of the polyamide by oxygen and argon plasma, respectively. Table IV shows the atom composition (O/C atom ratio) of the oxygen and argon plasma treatment of polyamide surface. The O/C ratio increases from 0.14

Table IV Effect of Plasma Treatment on the O/C Atom Ratio

Plasma Treatment Time (min)	O/C Atom Ratio	
	Oxygen Plasma	Argon Plasma
0	0.15	0.14
2	0.24	0.15
4	0.48	0.18
6	0.68	0.20

to 0.62. This means that more oxygen introduced, the longer the oxygen plasma treatment; but the O/C atom ratio changes little in the argon plasma treatment. In order to illustrate the cross-linking mechanism of the polyamide surface of the composite membrane, we must examine the change of the XPS spectra of unmodified surface and that modified by argon plasma. Figure 2 shows these spectra. From the spectra, we found the N_{1s} binding energy increases from 400.5 to 401.4 eV, which means the environment of the N changes. The most possible change is that the H in $-\text{CONH}$ was substituted by other atoms or groups. Through examining the changes of the spectra of ATR-FTIR, the water permeability, as well as the changes of chlorine resistance of the composite membrane, we conclude that cross-linking at the nitrogen occurs. The possible cross-linking mechanism is as follows.



CONCLUSIONS

- 1) Carboxyl was introduced in the surface of a polyamide composite membrane by oxygen

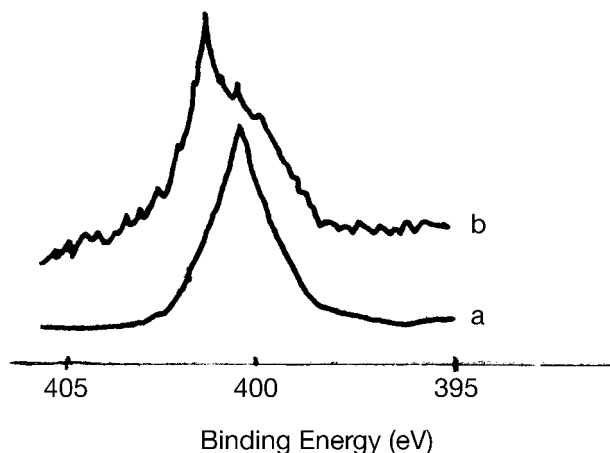


Figure 2 XPS(N_{1s}) spectra of composite membranes: (a) unmodified; (b) modified by argon plasma.

plasma modification and made the permeability increase.

- 2) Cross-linking occurred at the nitrogen site in the surface of a polyamide composite membrane by argon plasma and made the chlorine resistance of the membrane increase.

REFERENCES

1. J. Y. Lai and Y. C. Chao, *J. Appl. Polym. Sci.*, **39**, 2293 (1990).
2. M. Takayanagi and T. Katayose, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1133 (1981).
3. M. R. Wertheimer and H. P. Schreiber, *J. Appl. Polym. Sci.*, **26**, 2087 (1981).
4. K. Kupper and P. Schwartz, *J. Adhes. Sci. Tech.*, **5**, 165 (1991).
5. R. J. Petersen, *J. Membr. Sci.*, **81**, 83 (1993).
6. J. E. Cadotte, U.S. Pat. 4,259,183 (Mar. 31, 1981).
7. N. Inagaki, S. Tasaka, and H. Kawai, *J. Polym. Sci. A, Polym. Chem.*, **33**, 2001 (1995).
8. M. Kurihara, *Polymer J.*, **23**, 513 (1991).
9. S. D. Arthur, *J. Membr. Sci.*, **46**, 243 (1989).
10. Shaoyu Wu, M.S. Thesis, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, People's Republic of China, 1994.