Effect of Low-Frequency Oxygen Plasma on Polysulfone Membranes for CO_2/CH_4 Separation

Siamak Modarresi,[1] Mohammad Soltanieh,[1] Seyyed Abbas Mousavi,[1] Iman Shabani[2]

[1]Membrane Research Laboratory, Department of Chemical and Petroleum Engineering,
Sharif University of Technology, Tehran, Iran
[2]Nanotechnology and Tissue Engineering Department, Stem Cell Technology Research Center, Tehran, Iran

ABSTRACT: Low-frequency O_2 plasma was used to modify the surface of polysulfone gas-separation membranes. The effects of the treatment time and plasma power input on the membranes were also investigated. Pure CO_2 and CH_4 gas-permeation measurements were performed before and after plasma treatment. The results show the increase of permeability of the treated membranes due to surface ablation and surface polarization up to 5.63 and 68.80 gas-permeation units for CH_4 and CO_2, respectively, whereas, the CO_2/CH_4 selectivity of the treated membranes varied from 7.7 to 45.3, depending on the treatment conditions. Attenuated total reflection–Fourier transform infrared spectroscopy determined the introduction of oxygen-containing polar groups on the surface of the membranes following treatment. Water contact angle measurements also showed a significant increase in the wettability of the membranes after plasma treatment. Furthermore, the morphology of the surface of the membranes was studied by scanning electron microscopy. The images displayed a gradual smoothness of the surface under mild treatment conditions. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 124: E199–E204, 2012

Key words: gas permeation; membranes; modification

INTRODUCTION

Gas separation has become a major industrial application of membrane technology during recent decades.[1] Among various membrane-based, gas-separation processes, CO_2 separation from natural gas is of great importance, and polymeric materials are still the most widely used membranes for this application.[2,3] However, despite dozens of new polymers developed during the last 3 decades, only a few polymeric membranes are commercially available.[4] Thus, besides the development of new materials for membrane preparation, the postformation modification of available membranes has gained much attention, and various modification techniques have been reported, including UV or plasma graft polymerization,[5,6] surface fluorination,[7] crosslinking via chemical reaction or UV irradiation,[8,9] and plasma treatment.[10,11] Among these, low-temperature plasma treatment has been broadly studied as a simple, versatile, and relatively cheap means for modifying the surface properties of polymer membranes.[12–14]

Polysulfone (PSf) is a typical commercial membrane polymer. Relatively sufficient separation properties, mechanical, thermal, and chemical stability, and also excellent film-forming properties have turned this polymer to one of the most important polymers for gas-separation membranes.[4,15] Therefore, much effort has been made to improve the separation properties of PSf membranes.[16–19]

In this study, the effect of low-frequency (LF) plasma on the modification of asymmetric PSf gas-separation membranes was investigated. Oxygen was chosen as the plasma gas, and the effect of the plasma parameters on the membrane surface properties was studied by the variation of the plasma exposure time and discharge power. CO_2/CH_4 separation of membranes before and after plasma treatment were measured, and attenuated total reflection (ATR)–Fourier transform infrared (FTIR) spectroscopy, contact angle measurement, and scanning electron microscopy (SEM) were used to characterize the surface properties of the treated membranes. Furthermore, it is worth mentioning that to the best of our knowledge, the use of LF plasma for the modification of gas-separation membranes has not been reported in literature.

EXPERIMENTAL

Materials

PSf (granules, ULTRASON S6010) was supplied from BASF (Ludwigshafen, Germany). *N*-methyl-2-pyrrolidone, tetrahydrofuran (THF), ethanol, and methanol were obtained from Merck (Darmstadt, Germany); all were analytical grade and were used as received.

TABLE I
Permeation Properties of the Untreated PSf Membranes

Membrane ID	$(P/l)_{O2}$[a]	$(P/l)_{N2}$[a]	$(P/l)_{CO2}$[a]	$(P/l)_{CH4}$[a]	$\alpha_{O2/N2}$	$\alpha_{CO2/CH4}$
A	6.39	1.06	29.81	1.01	6.01	29.37
B	6.27	0.99	30.07	0.92	6.31	32.64
C	5.87	0.95	26.90	0.87	6.15	30.88
D	7.99	1.48	33.97	1.48	5.40	22.95
E	6.78	0.97	30.35	0.88	7.01	34.28
F	6.62	0.97	29.97	0.90	6.79	33.13
G	7.63	1.40	32.84	1.38	5.46	23.75
H	6.94	1.22	29.65	1.19	5.67	24.80
I	7.18	1.46	33.01	1.59	4.92	20.74

[a] 1 GPU = 10^{-6} cm^3 (STP) cm^{-2} s^{-1} cmHg^{-1}.

Distilled water at 17°C was used as the coagulation medium. The polymer was oven-dried at 70°C overnight before use.

Preparation of the PSf membranes

Asymmetric, flat-sheet PSf membranes were prepared with a dry–wet phase-inversion technique reported by Pesek and Koros.[20] A dope solution with about 26 wt % PSf, 27.51 wt % N-methyl-2-pyrrolidone, 27.51 wt % THF, and 18.98 wt % ethanol was made. The solution was cast on a glass plate with a thickness of 170 μm at room temperature. Before the membrane was submerged in the coagulation bath of distilled water at 17°C for 10 min, the solution on the plate remained in the air for 2 min to let the selective layer of the membrane form by convective evaporation of the volatile solvent (THF).

The membrane was then moved to a methanol bath for solvent exchange for 2 h and subsequently air-dried for 12 h at room temperature; this was followed by drying *in vacuum* at 65°C for 3 h before testing.

The permeances and ideal selectivities of the membranes before plasma treatment are presented in Table I. The membranes used were considered to be defect free because they had O_2/N_2 permselectivities over 87% of the bulk polymer ($\alpha_{O2/N2}$ = 5.6).[20] The main purpose of this research was to study the effect of plasma modification on the enhancement of CO_2/CH_4 separation, and the presentation of the results for O_2 and N_2 permeation through untreated membranes is just for the purpose of the initial screening of the membranes to ensure that the untreated membranes were defect free and had the minimum requirement for gas separation, as described by Pesek and Koros.[20] For this reason, the results for O_2 and N_2 separation after plasma treatment are not presented in this work.

Plasma treatment

An LF plasma generator with a frequency of 40 kHz and a cylindrical quartz reactor (LFG 40, Diener Electronic, Ebhausen, Germany) was used. Pure O_2 was used as the process gas. The reaction chamber was evacuated to 0.4 mbar. After the membrane was placed in the reactor, before ignition of the generator, the process gas was allowed to pass through the reactor for 10 min so that there were no impurities remaining in the plasma chamber. Also, the O_2 gas was allowed to pass through the chamber for 30 min after treatment and before the sample was taken out. This was to prevent the reaction of the free radicals still remaining on the surface with outside air. After this time, the reaction of free radicals with outside air was almost negligible. Plasma power was varied from 6 to 20 W, and the treatment time was changed from 30 to 150 s. In the first trial, we used 20, 30, and 40 Watts as plasma power inputs, and we observed that 30 and 40 W of power resulted in decreased selectivities of the samples. Therefore, we repeated the experiments with 6, 12, and 20 W. The results for the samples treated with 20 W in both tests were reproducible within acceptable agreement.

Membrane characterization

Gas-permeation measurement

The pressure-normalized fluxes, the so-called permeances, of the membranes before and after treatment were determined for pure CO_2 and CH_4 with a constant-pressure test cell at ambient temperature, 25°C. All of the permeation tests before and after treatment were performed at least three times.

Circular membrane discs with a diameter of 5.5 cm and an effective permeation area of 8.04 cm^2 were used. The upstream pressures of pure O_2, N_2, CO_2, and CH_4 were adjusted to 7, 15, 4, and 15 bar, respectively, whereas the downstream pressure was atmospheric. The permeances were evaluated from the volumetric gas-permeation rate measurements of a bubble flow meter by the following equation:

$$\text{Permeance} = \left(\frac{P}{l}\right)_i = \frac{Q_i}{\Delta P_i A} \qquad (1)$$

<div align="center">

TABLE II
Permeation Properties of the Plasma-Treated PSf Membranes

</div>

Membrane ID	Plasma parameter		$(P/l)_{CO2}$[a]	$(P/l)_{CH4}$[a]	$\alpha_{CO2/CH4}$
	Time (s)	Power (W)			
A	30	6	36.45	1.14	31.92
B	60	6	41.08	1.02	40.23
C	150	6	47.70	1.05	45.34
D	30	12	41.86	5.03	8.33
E	60	12	39.71	2.53	15.67
F	150	12	46.17	1.14	40.41
G	30	20	43.09	5.63	7.70
H	60	20	43.38	1.37	31.69
I	150	20	68.80	2.71	25.37

[a] 1 GPU $= 10^{-6}$ cm^3 cm^3 (STP) cm^{-2} s^{-1} cmHg^{-1}.

where P_i is the permeability of the gas i, l is the thickness of the selective layer, Q_i is the volumetric flow rate of gas i at standard temperature and pressure (STP), ΔP_i is the pressure difference across the membrane, and A is the effective surface area of the membrane. The common unit for representing pressure normalized flux is gas-permeation units (GPUs), where

$$1GPU = 1 \times 10^{-6} \frac{cm^3(STP)}{cm^2s\ cmHg} \qquad (2)$$

Through the determination of the permeances of components i and j, the ideal selectivity or separation factor (α) of a membrane can be calculated, as follows:

$$\alpha_{i/j} = \frac{\left(\frac{P}{l}\right)_i}{\left(\frac{P}{l}\right)_j} \qquad (3)$$

FTIR spectroscopy

The FTIR spectra of the unmodified and plasma-modified membranes were obtained by the ATR technique with a Vertex 80 IR spectrometer (Bruker Optics, Ettlingen, Germany) with a Pike MIRacle ATR device (Madison, Wisconsin). Thirty-two scans were performed at a resolution of 4 cm^{-1} with a diamond crystal at an incident of 45°. The IR penetration depth for this incident angle was 2 μm.[21]

Contact angle measurements

Contact angle measurements of a di-ionized water drop on the surface of the both modified and unmodified membranes were performed by the sessile drop method. Droplets of water (5 μL) were formed on the sample surface with a microsyringe, and measurements were carried out with a G10-Krüss contact angle measurement device (Hamburg, Germany). The reported values are the average of at least five readings from different positions on the sample surface.

SEM

The surfaces of the virgin and treated PSf membranes were analyzed with a Hitachi S4160 electron microscope (Tokyo, Japan) at an accelerated voltage of 15 kV. The samples were coated with a thin layer of gold before analysis.

RESULTS AND DISCUSSION

Gas permeation

Two phenomena are effective on the gas-transport properties of membranes during O_2 plasma irradiation. One is the introduction of oxygen-containing functional groups on the membrane surface. The interaction between these polar groups and the lone-pair electrons of the CO_2 molecule will lead to augmentation of the affinity between the membrane surface and CO_2 and enhance the solubility selectivity of CO_2 over CH_4, which eventually will cause an increase in the CO_2/CH_4 selectivity.[22] However, it has been reported in the literature that the depth of plasma modification is about 50–60 nm.[23,24] Thus, considering the selective layer thickness of the samples used in this research, which was estimated to be about 60 nm,[20] we concluded that almost the entire thickness of the membranes' selective layer was modified by plasma irradiation.

The other phenomenon is the competing process of ablation of the surface due to surface etching and redeposition of degraded fragments.[25] The former will cause an increase in the permeability and reduction of selectivity by attenuation of the membrane selective layer, and the latter will thicken the selective layer, decrease the permeability, and improve the selectivity.

The pure CO_2 and CH_4 permeances and permselectivities of the membranes after plasma treatment were measured and are reported in Table II. The effects of the plasma exposure time and power were investigated by the application of three different
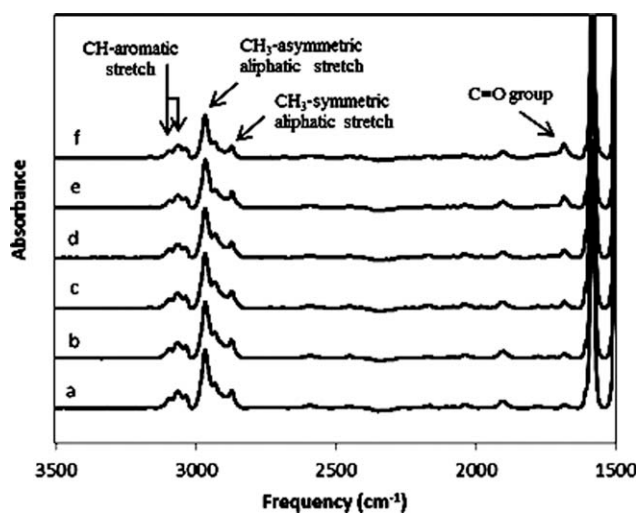
Figure 1 ATR–FTIR spectra of the PSf membranes: (a) untreated membrane and O_2 plasma-treated membranes: (b) D (12 W, 30 s), (c) E (12 W, 60 s), (d) C (6 W, 150 s), (e) F (12 W, 150 s), and (f) I (20 W, 150 s).

treatment times (30, 60, and 150 s) and treatment powers (6, 12, and 20 W).

The CO_2 permeances of the membranes treated with a low treatment power of 6 W (samples A, B, and C) increased with increasing treatment time, whereas the increase in the CH_4 permeance was insignificant. Because the increase in the CH_4 permeance was slight ($\leq$14% for sample C), we construed that surface etching was inconsiderable, whereas the increase of CO_2 permeance due to surface polarization was prominent. This led to an enhancement of the CO_2/CH_4 selectivity up to 45.3 with increasing treatment time for sample C.

The results of the membranes treated with a treatment power of 12 W (samples D, E, and F) show a different trend. For the lower treatment time (30-s plasma exposure), the CH_4 permeance increased drastically; this was followed by a sharp decrease in the CO_2/CH_4 selectivity. This severe increase in CH_4 permeability was probably the result of the formation of pinholes on the membrane surface due to surface etching. However, for membranes treated at a longer duration of plasma irradiation, the selectivity was rehabilitated by the reduction in the CH_4 permeance. This suggests that ablation was dominant and possessed the higher ratio at the beginning of the plasma process.[26] Gradually, with the elapse of time, the deposition process arose and began to recover the etched areas.

The results for the membranes treated with 20 W of plasma power (samples G, H, and I) are similar to those of the membranes treated with 12 W. Except for the long treatment time of 150 s (sample I), again, ablation dominated, and the selectivity decreased with the increase in CH_4 permeance.

The O_2 plasma treatment increased both the CO_2 permeability and CO_2/CH_4 permselectivity of the

six PSf membranes (samples A, B, C, F, H, and I) simultaneously. This favorable phenomenon has been previously observed by Kumazawa and co-workers[27–29] after the N_2 and NH_3 plasma treatment of different glassy and rubbery polymer membranes.

Furthermore, it seemed that ablation and etching were very effective on the membranes treated by plasma irradiation. Particularly, when the membrane selective layer was thin, this effect was more pronounced. In our research, it seemed that in cases in which the CH_4 permeability was drastically increased, the CH_4 just did not permeate through solution–diffusion, and part of the permeated molecules went through the defects caused by etching. This phenomenon was also applicable for the permeation of CO_2 molecules. However, because the permeation rate of CO_2 was much higher and also because plasma treatment increased it even more, the efficacy of the increase of CO_2 permeability caused by etching and ablation was not as dominant and observable as CH_4.

ATR–FTIR spectroscopy

IR spectroscopy in ATR mode is broadly used to investigate chemical changes that occur on a membrane surface during the modification process. However, the sensitivity of this characterization technique is not quite satisfactory because of the sampling depth, which is much greater than the thickness of the modified layer. Thus, some absorption bands of functional groups introduced by plasma irradiation might be of very low intensity. The FTIR spectra of the PSf membrane surface, both before and after O_2 plasma modification, are presented in Figure 1.

The intensities of all of the absorption bands of PSf decreased after plasma treatment. This was probably due to the presence of a thin modified layer on top of the PSf membrane. With the shorter treatment time (sample D), the change in the spectrum was not quite distinctive. With the increase in treatment duration

TABLE III
Water Contact Angles of the O_2-Plasma-Treated and Untreated PSF Membranes

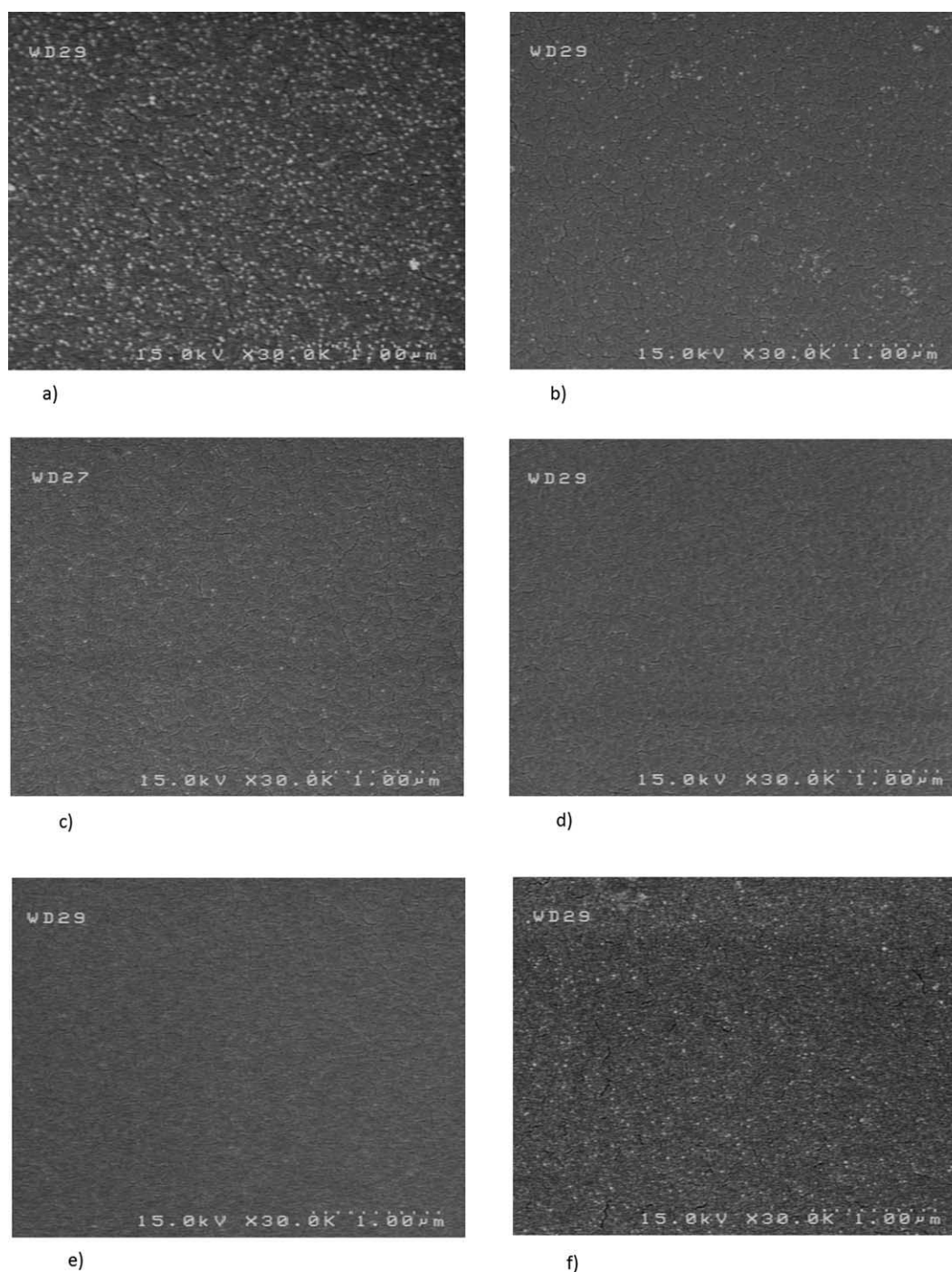| Membrane ID | Plasma parameter | | Contact angle (°) |
	Time (s)	Power (W)	
Virgin	—	—	76.7
A	30	6	52.4
B	60	6	41.3
C	150	6	39.3
D	30	12	41.7
E	60	12	37.8
F	150	12	35.2
G	30	20	37.2
H	60	20	35.7
I	150	20	34.5

Figure 2 SEM images of the surfaces of the plasma-treated PSf membranes: (a) virgin membrane, (b) A (6 W, 30 s), (c) D (12 W, 30 s), (d) E (12 W, 60 s), (e) F (12 W, 150 s), and (f) I (20 W, 150 s).

from 30 to 150 s, a broad absorption band between 1650 and 1750 cm^{-1} was observed to grow; this indicated the enrichment of carbonyl groups on the membrane surface. The intensity of this absorption band increased with longer treatment time. The intensity of this absorption band also increased with increasing power from 6 to 20 W (samples C, F, and I). A relatively broad absorption band refers to a larger number of different structural features containing carbon–oxygen double bands (C=O), such as those in aldehyde, ketone, acid, and ester groups. This indicates that the O$_2$ plasma is oxidizing the membrane.

Contact angle measurements

The determination of the water contact angle is the most widely used surface characterization technique, with a depth analysis of about 5 Å.[30] The contact

angles of a droplet of pure water on the PSf membrane surfaces treated under various conditions of treatment time and power were measured immediately after plasma exposure and are presented in Table III.

The contact angle significantly decreased with plasma treatment. It could be observed that the reduction of the contact angle increased with increasing treatment time and power. This was directly a result of the introduction of more and more hydrophilic functional groups, as described in the previous section.

SEM

The surface morphologies of the virgin and plasma-treated PSf membranes are shown in SEM images in Figure 2. The virgin PSf membrane surface was contaminated with round, white features and had nonuniformity [Fig. 2(a)]. The effect of O_2 plasma treatment on the smoothness and cleaning of the PSf membrane surface was evident, even for the treatment with lowest treatment power and time [Fig. 2(b)]. For membranes treated with a plasma power of 12 W, a gradual smoothening and clearance of the membrane surface was clearly observable [Fig. 2(c–e)]. This gradual smoothening of the surface was due to redeposition of the sputtered fragments of the polymeric materials after plasma etching.[31] Treatment with O_2 plasma with 20 W and a long treatment time of 150 s caused surface damage. The membrane surface was no longer smooth, and some cracks were observed [Fig. 2(f)].

CONCLUSIONS

The effect of LF O_2 plasma modification on the CO_2 separation and surface properties of PSf membranes was investigated. The CO_2/CH_4 separation properties of the treated membranes were altered significantly with plasma exposure time and power, and the selectivity was enhanced about 50% for one sample (sample C), from 30.88 to 45.34 for treatment conditions of 6 W and 150 s. The FTIR spectra of the membrane surfaces showed the introduction of C=O containing functional groups to the surface of the treated samples, and the water contact angle decreased drastically with plasma exposure; this was due to the surface hydrophilization of the PSf membrane surfaces by O_2 plasma treatment. The nonuniform and contaminated unclear surface of the untreated membrane became smooth and clear with plasma treatment. However, prolonged treatment caused damage and the formation of cracks on the surface.

In sum, despite the lower intensity of LF plasma toward radio frequency and micro wave plasma, this technique effectively altered the surface properties of the PSf membranes, and with optimum treatment conditions, it improved the separation properties of PSf gas-separation membranes without damaging the susceptible thin, selective layer of the membranes.

References

1. Baker, R. W. Membrane Technology and Applications, 2nd ed.; Wiley: Chichester, West Sussex, England, 2004.
2. Pabby, A. K.; Rizvi, S. S. H.; Sastre, A. M. Handbook of Membrane Separations; CRC: Boca Raton, FL, 2009.
3. Shena, J.; Wub, L.; Zhanga, L.; Donga, Y.; Chena, H.; Gao, C. Desalination 2006, 193, 327.
4. Nunes, S. P.; Peinemann, K. V. Membrane Technology in Chemical Industry, 2nd ed.; Wiley-VCH: Weinheim, 2006.
5. Kim, J. H.; Ha, S. Y.; Nam, S. Y.; Rhim, J. W.; Baek, K. H.; Lee, Y. M. J Membr Sci 2001, 186, 97.
6. Matsuyama, H.; Teramoto, M.; Sakakura, H.; Iwai, K. J Membr Sci 1996, 117, 251.
7. Syrtsova, D. A.; Kharitonov, A. P.; Teplyakov, V. V.; Koops, G. H. Desalination 2004, 163, 273.
8. Cao, C.; Chung, T. S.; Liu, Y.; Wang, R.; Pramoda, K. P. J Membr Sci 2003, 216, 257.
9. McCraig, M. S.; Paul, D. R. Polymer 1999, 40, 7209.
10. Yang, Y. S.; Kwak, H.; Bae, S. Y.; Kumazawa, H. J Appl Polym Sci 2007, 103, 1798.
11. Hu, C. C.; Tu, C. Y.; Wang, Y. C.; Li, C. L.; Lee, K. R.; Lai, J. Y. J Appl Polym Sci 2004, 93, 395.
12. Vandencasteele, N.; Reniers, F. J Electron Spectrosc Relat Phenom 2010, 178–179, 394.
13. Gil'man, A. B. High Energy Chem 2003, 37, 17.
14. Xu, Z.; Huang, X.; Wan, L. Surface Engineering of Polymer Membranes; Springer: New York, 2007.
15. Wavhal, D. S.; Fisher, E. R. Desalination 2005, 172, 189.
16. Ilconich, J. B.; Xu, X.; Coleman, M.; Simpson, P. J. J Membr Sci 2003, 214, 143.
17. Hopkins, J.; Badyal, J. P. S. Langmuir 1996, 12, 4205.
18. Le Roux, J. D.; Paul, D. R.; Kampa, J.; Lagow, R. J. J Membr Sci 1994, 94, 121.
19. Choi, S. H.; Lee, M. K.; Oh, S. J.; Koo, J. K. J Membr Sci 2003, 221, 37.
20. Pesek, S. C.; Koros, W. J. J Membr Sci 1993, 81, 71.
21. Pike Technologies. ATR Sampling Products. http://www.piketech.com/products/atr.html. Accessed on December 14, 2010.
22. Matsuyama, H.; Teramoto, M.; Hirai, K. J Membr Sci 1995, 99, 139.
23. Wilken, R.; Hollander, A.; Behnisch, J. Surf Coat Technol 1999, 116–119, 991.
24. Slepicka, P.; Vasina, A.; Kolska, Z.; Luxbacher, T.; Malinskyd, P.; Mackova, A.; Svorcik, V. Nucl Instrum Methods B 2010, 268, 2111.
25. Gancarz, I.; Pozniak, G.; Bryjak, M. Eur Polym J 2000, 36, 1563.
26. Gancarz, I.; Pozniak, G.; Bryjak, M. Eur Polym J 1999, 35, 1419.
27. Nakata, M.; Kumazawa, H. J Appl Polym Sci 2006, 101, 383.
28. Teramae, T.; Kumazawa, H. J Appl Polym Sci 2007, 104, 3236.
29. Kumazawa, H.; Yoshida, M. J Appl Polym Sci 2002, 78, 1845.
30. Bain, C. D.; Whitesides, G. M. J Am Chem Soc 1988, 110, 5897.
31. Pal, S.; Ghatak, S. K.; De, S.; DasGupta, S. J Membr Sci 2008, 323, 1.