Effects of Crosslinking Modification on the O_2/N_2 Separation Characteristics of Poly(phenyl sulfone)/Poly(bisphenol A-*co*-4-nitrophthalic anhydride-*co*-1,3-phenylenediamine) Blend Membranes

Tzu-Hsiang Weng,[1] **Hui-Hsin Tseng,**[2,3] **Ming-Yen Wey**[1]

[1] *Department of Environmental Engineering, National Chung Hsing University, Taichung 402, Taiwan, Republic of China*
[2] *School of Occupational Safety and Health, Chung Shan Medical University, Taichung 402, Taiwan, Republic of China*
[3] *Department of Occupational Medicine, Chung Shan Medical University Hospital, Taichung 402, Taiwan, Republic of China*

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ABSTRACT: A series of blend membranes of poly(phenyl sulfone) (PPSU) with poly(bisphenol A-*co*-4-nitrophthalic anhydride-*co*-1,3-phenylenediamine) (PBNPI) were prepared through a solution casting method. This was done to examine the permeation characteristics of oxygen and nitrogen. The effect of the PPSU/PBNPI ratio on the membrane structure and O_2/N_2 separation performance were investigated. The results show that the permeability increased remarkably with the content of PPSU, whereas the selectivity decreased slightly. To enhance the selectivity of O_2/N_2, the blend membranes were further crosslinked with a *p*-xylylenediamine agent via the immersion method. According to the Fourier transform infrared analysis, the N—H group was formed on the imide group of PBNPI. Therefore, we suggest that during the crosslinking modification, the PBNPI served as a crosslinkable polymer; this resulted in increased crosslinking efficiency with PBNPI content. The high-resolution X-ray diffraction and melting point method results show that crosslinking modification improved the selectivity with an acceptable loss in permeability along with increased crystallinity. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1254–1263, 2010

Key words: crosslinking; gas permeation; selectivity

INTRODUCTION

Gas separation with a polymeric membrane has been recognized as an energy-efficient and economical process.[1] A preferred polymeric membrane would have to deal with high gas permeability and selectivity, durability, strong chemical resistance, and thermal stability in complex and harsh environments.[2–4] Gas transport through a nonporous permeability membrane often follows the solution–diffusion mechanism. In other words, gas separation through this kind of membrane will depend on the kinetic diameter of the gas. However, the kinetic diameters of the pure gases O_2 and N_2 are very similar; this makes it difficult to obtain excellent selectivity for the separation of these two gases.

Several studies focusing on single polymeric membranes, membrane blends,[5–9] or modification with a crosslinking agent[10,11] have been applied to the separation of gases with similar kinetic diameters to enhance their permeability and selectivity. Among these, crosslinking has been widely used to restrict the mobility of polymer chains by covalent bond formation. With appropriate tailoring, this may result in membranes with a higher selectivity with permeability maintained.[12–14] A number of crosslinking methods have also been used to modify polymer membranes, such as the widely used UV-irradiation method.[15–17] In their study, Kita et al.[15] used the UV-irradiation method to modify benzophenone-containing polyimide, thereby demonstrating a significant increase in gas selectivity. Liu et al.[17] further extended UV irradiation for a stipulated period of time, which eventually led to a higher gas selectivity from hydrogen to nitrogen. Although this method yielded the desired results, it evidently left more time for modification.

Another proposed crosslinking procedure is the immersion method, in which a chemical crosslinking agent is used to modify the polymer chain. Unlike the UV-irradiation method, the immersion method can yield good results and retrench the reaction

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Correspondence to: M.-Y. Wey (mywey@dragon.nchu.edu.tw).

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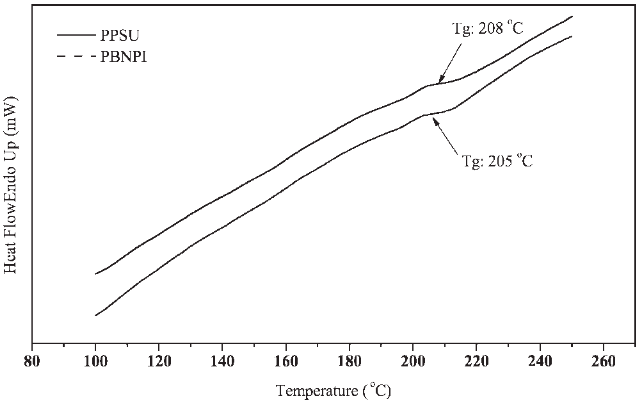

Figure 1 DSC curves showing the T_g values of pure PPSU and PBNPI.

time. In another study, Staudt-Bickel and Koros[10] used ethylene glycol as a crosslinking agent to modify polyimide. In their study, modification by immersion remarkably improved the CO_2/CH_4 selectivity because of decreased swelling and polymer chain mobility. Sridhar et al.[11] used the crosslinking method by immersing the membrane in a 2,4-toulene diisocyanate agent for diverse periods. The study showed that crosslinking for a long span of time (60 min) resulted in good selectivity in CO_2/CH_4 because the carbonyl groups of 2,4-toulene diisocyanate tended to interact with all available reactive polyether monomers. Moreover, this crosslinking method also leads to the compression of Pebax polymer chains, which enhances the selectivity.[11] Although the crosslinking method for polymer membranes obtains excellent selectivity, it has a single deficiency: the crosslinked membranes have lower permeabilities than the unmodified ones. This can be attributed to the close compaction of chains via the reaction caused by crosslinking with the polymer. Nevertheless, the immersion crosslinking method is a simple and effective way to alter the membrane structure and improve the selectivity compared with the UV method.[18] Hence, this crosslinking method makes the polymer membrane more durable; in addition, modification generally enhances the selectivity and renders the polymer suitable for various applications.[19,20] Therefore, the enhanced selectivities of gas separation can account for the restriction of mobility and the increase in the packing density of polymer chains due to crosslinking.

In our previous study, poly(phenyl sulfone) (PPSU) was blended with various amounts of poly(bisphenol A-*co*-4-nitrophthalic anhydride-*co*-1,3-phenylenediamine) (PBNPI) and then applied to gas separation.[21] In this study, we investigated the effects of crosslinking on the O_2 and N_2 gas permeabilities and selectivity properties of PPSU/PBNPI blend membranes. Overall, this study serves as a follow-up study in this line of research. The objectives of this study were as follows: (1) to take advantage of the PPSU/PBNPI blend membrane and then use the *p*-xylylenediamine agent for modification with the immersion crosslinking method, (2) to investigate the variation in O_2 and N_2 permeability and O_2/N_2 selectivity after the crosslinking of the PPSU/PBNPI membranes, and (3) to evaluate the diffusivity and solubility mechanisms through the crosslinked membrane gas separation.

EXPERIMENTAL

Materials and membrane preparation

The PBNPI and PPSU powder used in this study were both purchased from Sigma–Aldrich Chemical Co. (St. Louis, MO). The PBNPI molecular weight of the repeating unit was 622 g/mol, and the PPSU molecular weight ranged from 53,000 to 59,000 g/mol. As shown in Figure 1, the values of the glass-transition temperature (T_g) of PBNPI and PPSU were 205 and 208°C, respectively; meanwhile, Figure 2 shows the chemical structures of PBNPI and PPSU. *N*-Methyl-2-pyrrolidone (NMP), from Mallinckrodt Chemicals Co., was used as a solvent, whereas the *p*-xylylenediamine (>99%) crosslinker was also purchased from Sigma–Aldrich. Oxygen (99.99%) and nitrogen (99.99%) were obtained from Toyo Gas Co. (Taiwan). Overall, PBNPI, PPSU, NMP, *p*-xylylenediamine, and the two pure gases were used directly. All of the polymer blend membranes were made out of PBNPI and PPSU at different concentration ratios with the solution casting technique. Details for this technique were given elsewhere.[22] The PBNPI and PPSU powders were dissolved in NMP to form 15 and 5 wt % solutions, respectively. To prepare the blend membranes, the PPSU solution was added to the PBNPI solution. From this mixture, different volumes were added to the PBNPI solution to create different ratios in the blend membranes. The details

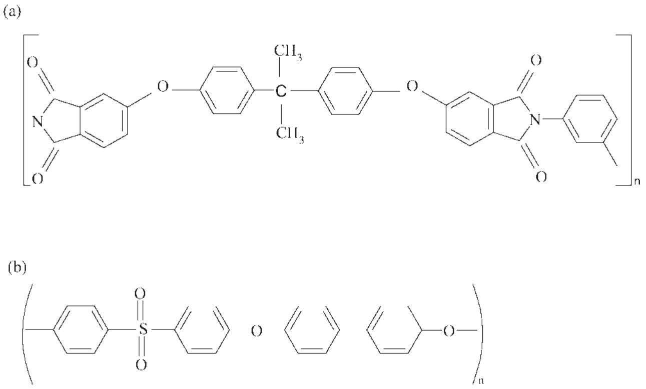

Figure 2 Scheme of the repeating unit of (a) PBNPI and (b) PPSU.

of the preparation procedure of these PPSU/PBNPI blend membranes (50/50, 67/33, 75/25, and 84/16 wt %) were also given elsewhere.[21]

Membrane modification by crosslinking

A 5% (w/v) crosslinking reagent was prepared by dissolution of the *p*-xylylenediamine powder in methanol and with stirring for a uniform agent. The crosslinking of the resulting blend membranes was performed by immersion of the membranes into the crosslinking reagent for 2 h and by subsequent washing of these with fresh methanol.[2,10,23] Immediately after taking the membranes out of the methanol reagent, we washed the residual solution on the film's surface away with deionized water. Afterward, the membranes were dried at ambient temperature.

Characterization of the polymer membrane

The X-ray diffraction (XRD) measurements of the blended membranes were recorded on a Bruker D8 SSS (Karlsruhe, Germany) multipurpose thin-film X-ray diffractometer system (high-resolution XRD). The X-rays ($\lambda = 1.5418$ Å) were generated by a Cu Kα source. The 2θ values of the radiation ranged from 5 to 30, whereas the XRD measurements were carried out within the range $5^\circ \leq 2\theta \leq 35^\circ$ with a step increment ratio of 0.4°/s. This was done to identify the changes in the crystal structure and intermolecular distances between the polymer matrix's intersegmental chains.[11] The Fourier transform infrared (FTIR) spectra of the crosslinked and uncrosslinked membranes were measured on a Jasco 4100 (Hachioji, Tokyo, Japan) Fourier transform infrared/attenuated total reflection (FTIR–ATR) spectrometer over the wave-number range 4000–400 cm^{-1}. An FTIR–ATR spectroscope was then used to measure the change in the membrane's polymer chemical function group before and after crosslinking. Furthermore, the *p*-xylylenediamine agent among amide bands at 1634 (C=O) and 1525 cm^{-1} (C—N) were identified for the purpose of tracking the changes in the polymer's structure.[23] The melting temperature (T_m) and crystallinity of the crosslinked and uncrosslinked membranes were measured with a PerkinElmer STA 6000 differential scanning calorimeter at a heating rate of 40°C/min in an N_2 atmosphere. The crystallinity percentage (x) was obtained from the following equation[24,25]:

$$x = \frac{\Delta \text{H}}{\Delta \text{H}_m} \times 100$$

where ΔH is the heat produced by the fusion of the PPSU/PBNPI blend sample and amorphous plus crystalline parts (J/g) and ΔH_m is the heat of fusion of 100% crystalline PBNPI (J/g).

Gas-permeation measurement

For nonporous membranes, the gas-separation mechanism, based on the solution–diffusion model, occurs in three stages. These are sorption, diffusion, and desorption under a pressure gradient.[26] The gas-permeation performance of the PPSU/PBNPI blend membranes before and after crosslinking modification was measured with a constant volume/variable pressure approach with a self-built vacuum time-lag apparatus. Details of the self-built vacuum time-lag apparatus were presented elsewhere.[21] The operation temperature and feed pressure were 26°C and 2 kg/cm^2, respectively. A circular stainless permeability cell (47-mm disc filters, Millipore, Billerica, MA) was used to measure the transport properties of the membrane. The effective area inside the cell was 17.34 cm^2; in addition, O_2 and N_2 with kinetic diameters of 3.46 and 3.64 Å,[27,28] respectively, were tested as penetrants. After both sides of the membrane were evacuated, the pure gas was introduced to the upstream side of the membrane, after which it was allowed to permeate to the downstream side. After a certain period of time, a steady state was reached, at which the amount of the gas permeating increased linearly with time. The pressure levels at both the upstream (kg/cm^2) and downstream sides were measured by pressure sensors and recorded with the help of Visidaq Builder software (Sunnyvale, CA). This software ensured automated measurement with an automatically adapting data-sampling rate (1 datum/s) to yield downstream pressure data points and to completely describe the time lag and steady-state gas transport. The permeability coefficient (*P*), solubility coefficient (*S*), and diffusion coefficient (*D*) were all calculated according to the Daynes–Barrier time-lag (θ) method[29] with the following equation:

$$P = \left(\frac{dp}{dt}\right) \frac{VT_0}{A \Delta P} \times \frac{L}{TP_0} \tag{1}$$

where P is expressed in barrers [1 barrer = 1×10^{-10} cm^3 cm (STP) cm^{-2} s^{-1} cmHg^{-1}], dp/dt is the slope of the straight line in the steady-state region at which the permeate pressure increases with time on the downstream side, V is the calibrated downstream volume (cm^3), ΔP is the transmembrane pressure difference between the two sides (cmHg), A is the effective area of the membrane (cm^2), L is the membrane thickness (cm), T is the measured temperature (K), and T_0 and P_0 are the standard temperature and pressure, respectively. The ideal separation factor of pure gas A over pure gas B (α_{AB}) is defined as the ratio of the permeation rate of A (P_A) to the permeation rate of B (P_B):

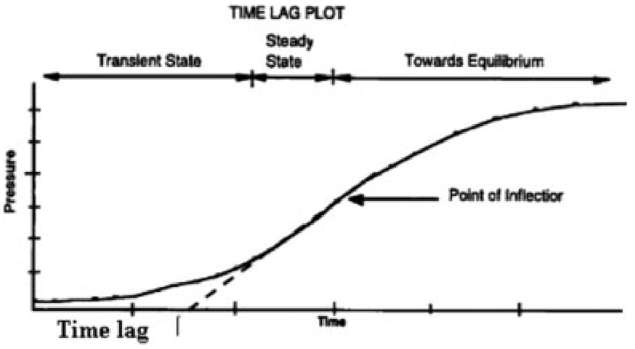

Figure 3 Pressure response in the downstream volume with the approach to equilibrium.[29]

$$\alpha_{AB} = P_A / P_B \tag{2}$$

In this study, the gas-separation phenomenon produced through the dense polymeric membrane was found to be in accordance with the solution and diffusion mechanism. D was determined with the following equation[29]:

$$D = \frac{L^2}{6\theta} \tag{3}$$

where L is known (measured with a micrometer). As Figure 3 shows, for the time-lag (θ) diffusion experiment, we obtained the gradient of the curve of the outgoing pressure against time. We used this to evaluate D, noting that the product of the steady-state slope and the time lag was independent of the diffusivity.

The rate-determining parameter is D, which can be obtained as the product of S:

$$S = \frac{P}{D} \tag{4}$$

RESULTS AND DISCUSSION

FTIR–ATR

The typical infrared bands for the blend membranes with or without modification by crosslinking were monitored by FTIR–ATR spectroscopy. Figure 4(a) shows the spectrum of PBNPI, which exhibited characteristic imide-group absorptions around 1775 cm^{-1} (asymmetric C=O stretching), 1718 cm^{-1} (symmetric C=O stretching), and 1355 cm^{-1} (C—N stretching).[2] The intensities of these characteristic peaks were found to gradually decrease with decreasing PBNPI weight ratio in the blend membranes [see Fig. 4(c–f)]. Meanwhile, the PPSU spectrum [Fig. 4(b)] showed a major characteristic peak at about 1147 cm^{-1}, which indicated the stretching of S=O in the sulfone group. The intensities of this characteristic peak were also found to change with the variation in the weight ration of PPSU in the blend membranes [Fig. 4(c–f)]. Compared with the uncrosslinked membrane, the transmittance percentage of the spectra for the crosslinked blend membranes

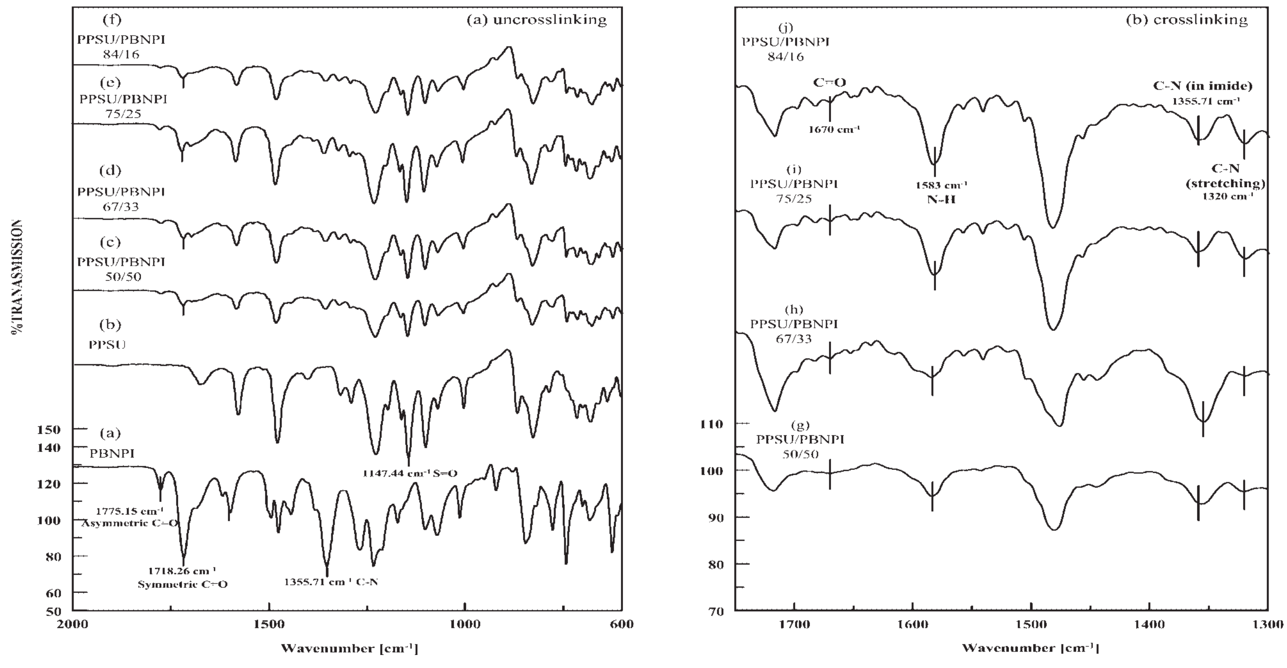

Figure 4 FTIR–ATR spectra of (a) PBNPI; (b) PPSU; (c–f) uncrosslinked PPSU/PBNPI blend membranes with weight ratios of 50/50, 67/33, 75/25, and 84/16, respectively in the region of 2000–600 cm^{-1}; and (g–j) crosslinked PPSU/PBNPI blend membranes in the region of 1750–1300 cm^{-1}.

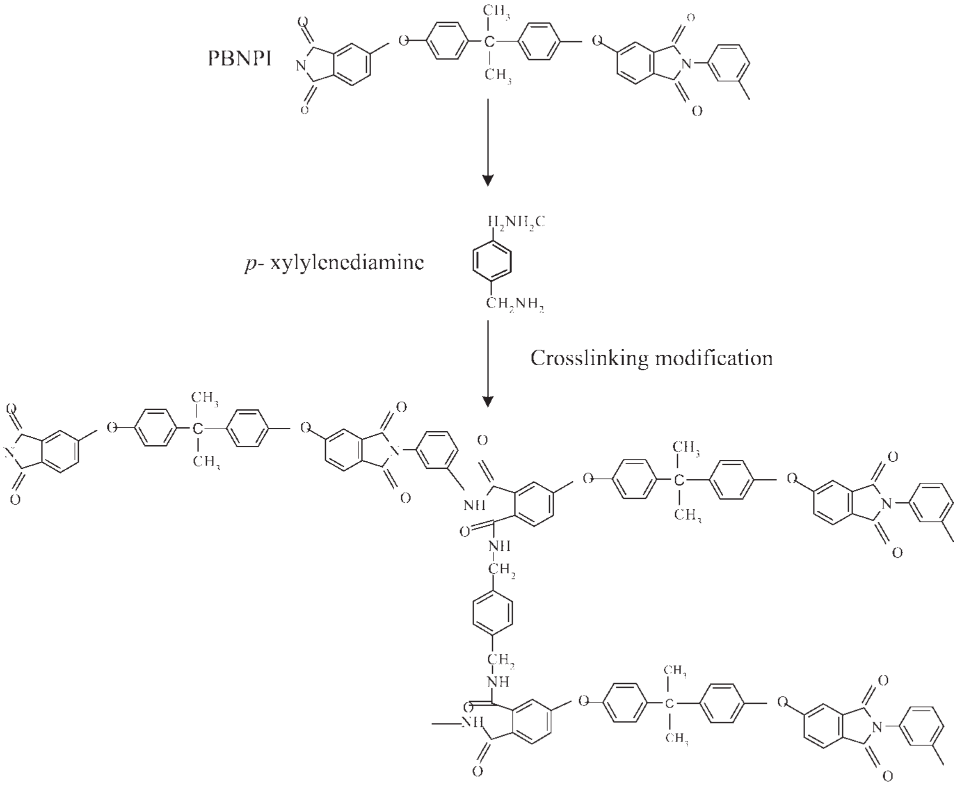

Figure 5 Mechanism of the chemical crosslinking modification and possible crosslinking structure.

ranging from 1750 to 1300 cm^{-1} [see Fig. 4(g)] presented two characteristic peaks: C=O stretching in the amide group at 1670 cm^{-1} and a strong amine band (stretching of C—N and/or band of N—H in the amide group) at 1320 and 1583 cm^{-1}, respectively. Furthermore, after crosslinking, the transmittal intensities of imide characteristic bands increased and were substituted by the characteristic bands of the amide group, together with aromatic polyamide N—H stretching bands at 1583 cm^{-1}. The results indicate that the crosslinking reaction could be conducted by simple immersion of the membrane in a *p*-xylylenediamine solution at ambient temperature, from which the crosslinking mechanism could be deduced (Fig. 5). The crosslinking modification process was initiated by the swelling of methanol, followed by the assault of the imide functional groups of PBNPI from the amino groups in *p*-xylylenediamine. Furthermore, the variations of different blending ratios of the PBNPI/PPSU membrane's function group before and after crosslinking were also estimated with an FTIR spectrum pattern. Figure 4(g–j) shows that the N—H functional group was formed in the amide group of PBNPI after crosslinking. Furthermore, by comparing the FTIR patterns in Figure 4(g–j), we found that the transmittal intensities of the N—H group increased when the PBNPI content decreased. This suggests that the PBNPI served as a crosslinkable polymer in this study and that the crosslinking efficiency slightly decreased with decreasing PBNPI content.

XRD

Figure 6 shows the XRD patterns of the uncrosslinked and crosslinked PPSU/PBNPI membranes. As shown, the uncrosslinked PPSU/PBNPI blend membrane [Fig. 6(a–d)] had a crystalline peak at a 2θ of 12° and wide amorphous structural regions at 2θ's of 15–25°, all of which were already examined in a previous study.[21] These results indicate that blending PBNPI with PPSU can reduce the crystalline structure of PBNPI polymers; all of the related details were given elsewhere.[21] However, compared with crosslinked membranes, the crystalline peak at $2\theta = 12°$ obtained from the crosslinked PPSU/PBNPI blend membranes [Fig. 6(e–h)] completely disappeared after crosslinking modification. Moreover, the crosslinking reaction caused more intensive diffraction patterns of partially crystalline peaks at $2\theta = 18–19°$. Table I summarizes the crystallinity percentages of the uncrosslinked and crosslinked PPSU/PBNPI blend membranes. The summary shows that after crosslinking, the crystallinity percentages of the PPSU/PBNPI blend membranes were all enhanced. Furthermore, the percentages of increase in the crystallinity of the PPSU/PBNPI blend membranes increased with increased PPSU

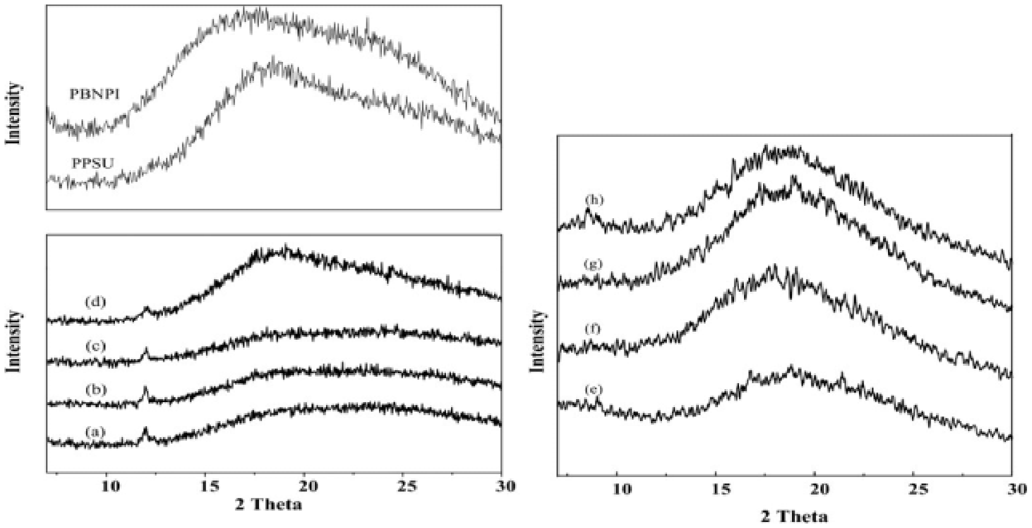

Figure 6 XRD patterns of pure PPSU; pure PBNPI; uncrosslinked PPSU/PBNPI blend membranes with weight ratios of (a) 50/50, (b) 67/33, (c) 75/25, and (d) 84/16; and crosslinked PPSU/PBNPI blend membranes with weight ratios of (e) 50/50, (f) 67/33, (g) 75/25, and (h) 84/16.

content. We inferred, therefore, that crosslinking function improved the crystallinity of the PPSU/PBNPI blend membranes.

Meanwhile, Sridhar et al.[11] also obtained a corresponding crystalline region diffraction peak at $2\theta = 18°$ for the modified polymeric membrane; this showed a reduction in the packing size or intersegmental spacing, which improved the membrane's selective permeation properties.[30] On the other hand, the patterns obtained from the crosslinked PPSU/PBNPI membranes peaked at $2\theta = 15$–$25°$; these were more intensive than the diffraction pattern of the uncrosslinked PPSU/PBNPI membranes.

According to the changes in Dgr;*H* [obtained from the differential scanning calorimetry (DSC) results; see Fig. 7], Table I shows that the crystallinity in the crosslinked blend membranes ranged from 31.31–44.43%, which was higher than that of uncrosslinked blend membranes. From this, we assumed that the crosslinked blend membranes possessed some crystalline structure within the wide amorphous diffraction peak at $2\theta = 15$–$25°$. Furthermore, the XRD pattern shown in Figure 6 (e–h) indicated that after crosslinking of the PPSU/PBNPI blend membranes, the wide amorphous regions at $2\theta = 15$–$25°$ slightly changed to a semicrystalline structure. This result showed a slight increase in the partially crystalline polymer at $2\theta = 18$–$19°$ for the crosslinking of the 75/25 wt % PPSU/PBNPI blend membrane among all of the crosslinked blended PPSU/PBNPI blend membranes. As Table I shows, the 75 and 84% contents of PPSU increased in crystallinity at 91 and 98%, respectively, for the crosslinked PPSU/PBNPI blend membrane.

Gas-permeation properties of the blend membranes

Table II summarizes the gas permeabilities of O_2 and N_2 passing through the PPSU/PBNPI blend membranes with or without crosslinking modification. For the uncrosslinked PPSU/PBNPI blend membranes, the gas permeabilities of O_2 and N_2 initially increased with increased PPSU content up to 67% and then decreased against the PPSU content. The table shows that the blend membrane with a weight ratio of 67/33 had the highest O_2 and N_2 permeation rates of 23.2 and 22.42 Barrer, respectively; these were higher than those of others. Meanwhile, the permeability obviously decreased with increased PPSU content (from 67 to 84%). The minimum permeability was observed in the 75/25 wt % PPSU/PBNPI blend membrane. Comparatively, the

TABLE I
Crystallinity of the Uncrosslinked and Crosslinked PPSU/PBNPI Blend Membranes

Polymer membrane	wt %	Crystallinity (%)		Increase in crystallinity (%)
		Uncrosslinked	Crosslinked	
PPSU/PBNPI	50/50	27.35	44.43	62
PPSU/PBNPI	67/33	23.64	42.08	78
PPSU/PBNPI	75/25	17.33	33.17	91
PPSU/PBNPI	84/16	15.84	31.31	98

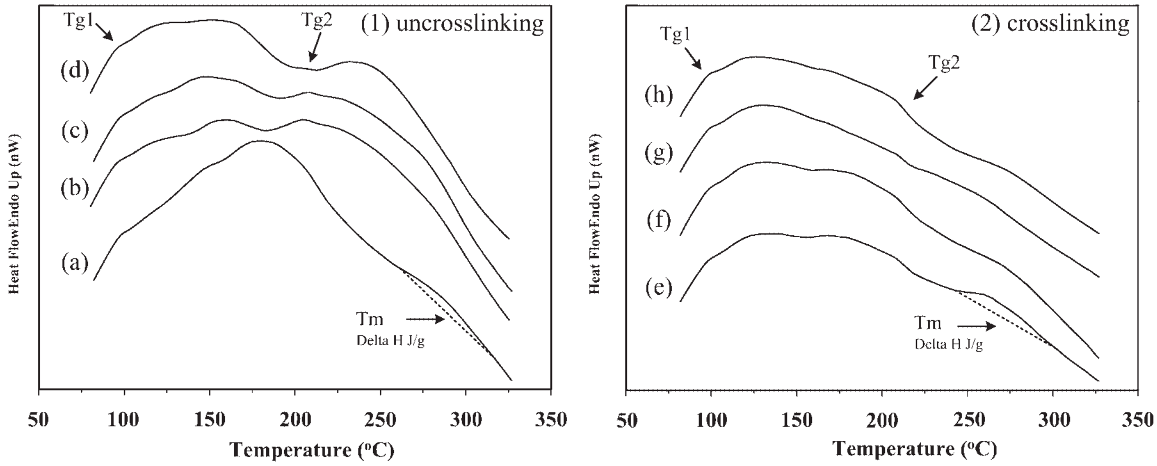

Figure 7 DSC curves showing the T_g and T_m values of uncrosslinked PPSU/PBNPI blend membranes with weight ratios of (a) 50/50, (b) 67/33, (c) 75/25, and (d) 84/16 and crosslinked PPSU/PBNPI blend membranes with weight ratios of (e) 50/50, (f) 67/33, (g) 75/25, and (h) 84/16.

permeability of O_2 was almost higher than that of N_2 in all of the different ratios of PPSU/PBNPI blend membranes. However, blending modification resulted in a slight decrease in the selectivity of O_2 over N_2. The primary factor causing the change in the permeability of both O_2 and N_2 was the effective permeation volume change caused by the decrease in crystallinity (see XRD results). In the low PPSU content region (50%), the crystallinity decreased with increasing PPSU content; this led to higher O_2 and N_2 permeation rates. However, when the PPSU content was higher than 50 wt %, the O_2 and N_2 permeation rates decreased (in fact, even the crystallinity also decreased with the PPSU content). These phenomena may have been due to the increased gap volume caused by the phase separation of the component polymers.

Meanwhile, Table III shows the T_g values of the pure polymer membrane and the PPSU/PBNPI blend membranes. As phase separation was explained through the T_g, only the second glass-transition temperature (T_{g2}) was observed in the pure polymer membranes; rather, the first occurrence of the glass-transition temperature (T_{g1}) and T_{g2} values were observed in the PPSU/PBNPI blend polymer membranes. This suggests that phase separation resulted in two T_g values in the blend polymer membranes.

Effect of crosslinking on the gas-permeation performance

The gas permeability and ideal selectivity of both O_2 and N_2 through the crosslinked blend membranes are also summarized in Table II. The permeabilities of both gases were found to decrease by modification with the crosslinking agent. Furthermore, the maximum values were still attained in the crosslinking of the 50/50 PPSU/PBNPI blend membrane. This phenomenon was attributed to crosslinking modification. From the FTIR results (see the discussion mentioned previously), new spectra of C=O stretching and C—N and/or the N—H band were formed in the crosslinked PPSU/PBNPI blend membrane. These new bands may have comprised a bridge that could combine the PPSU and PBNPI polymer chains, that is, crosslinking, thereby

TABLE II
Performance Comparison of the Uncrosslinked and Crosslinked PPSU/PBNPI Membranes in Terms of Their O_2 and N_2 Permeabilities and Ideal Selectivities

	Permeability (barrer)				Selectivity	
	Before crosslinking		After crosslinking		Before crosslinking	After crosslinking
PPSU/PBNPI (wt/wt)	O_2	N_2	O_2	N_2	O_2/N_2	O_2/N_2
0/100	0.93	0.72	0.98	0.47	1.29	2.09
50/50	22.13	21.22	21.38	21.35	1.04	1.00
67/33	23.20	22.42	15.69	13.08	1.03	1.20
75/25	7.26	8.30	7.98	5.48	0.87	1.46
84/16	12.67	11.24	9.20	7.20	1.13	1.28
100/0	3.76	3.342	2.66	1.82	1.13	1.46

TABLE III
T_g Values for the Pure Polymer Membranes and PPSU/PBNPI Blend Membranes

Polymer membrane	wt %	T_{g1} (°C)	T_{g2} (°C)
PPSU	100	—	208
PBNPI	100	—	205
PPSU/PBNPI	50/50	101	211
PPSU/PBNPI	67/33	102	210
PPSU/PBNPI	75/25	102	209
PPSU/PBNPI	84/16	101	213

reducing the chain mobility and the interstitial space among the chains. Furthermore, from the XRD and DSC analysis (also see the discussion mentioned previously), the crystallinity of all of the modified blend membranes was enhanced above 62–98%.

We found that the reduction in free volume, chain mobility, and interstitial space among the chains caused the decrease in permeability with crosslinking modification. The decreasing gas permeability followed this order: N_2 (3.64 Å) > O_2 (3.46 Å). It appeared that the decreasing order corresponded to the kinetic diameter of the gas molecules.

Table II also shows the effect of crosslinking modification on the ideal gas selectivity. The improvement of O_2/N_2 selectivity was attributed mainly to the reduced interstitial space of the polymer chains after crosslinking. Generally, when the polymer membrane with the poly(ether imide) family as the precursor was used, after chemical crosslinking with an aromatic diamine, the resistance to chemical influence was promoted.[12,31,32] In addition, the polymer chain mobility was also reduced. As Table II shows, the crosslinked PPSU/PBNPI blend membrane exhibited a higher O_2/N_2 selectivity than did the uncrosslinked one. The selectivity rates of the uncrosslinked PPSU/PBNPI membranes ranged from 0.87 to 1.13. These rates did not increase even with increased PPSU content. However, improved O_2/N_2 selectivity from 1.00 to 1.46 was due mainly to the reduced interstitial space of the polymer chain after crosslinking. Moreover, the crosslinked PPSU/PBNPI 75/25 and 84/16 wt % blend membranes obtained selectivity values of 1.46 and 1.28, respectively. These values were higher than those obtained by the 50/50 and 67/33 wt % blend membranes, whose values were 1.00 and 1.20, respectively. The maximum selectivity was obtained in the PPSU/PBNPI 75/25 wt % blend membrane value (1.46), which according to the FTIR results, seemed to have been caused by the high transmittance percentage of C—N stretching and bending of N—H in the amide group, hence, the lower N_2 permeability and good O_2/N_2 selectivity. Furthermore, a much improved ideal O_2/N_2 selectivity value (1.28) was observed in the 84/16 wt % PPSU/PBNPI membrane. These results were deduced from the FTIR functional group effect on the O_2 and N_2 permeabilities. Moreover, the XRD studies showed a $2\theta = 18°$ improvement in the crystalline peak intensity, which indicated compaction of the chains within the crosslinked PPSU/PBNPI membrane. This inference was quite similar to that of other studies.[11]

Diffusivity and solubility of the crosslinked membranes

In this research, pure gases permeating through the polymer membrane either by diffusion or solution were likewise investigated. The gas diffusivity and solubility of the uncrosslinked and crosslinked PPSU/PBNPI blend membranes as a function of PPSU concentration are shown in Figure 8(a,b), respectively. Figure 8(a) shows that the rate of diffusion of O_2 and N_2 passing through the PPSU/PBNPI blend membranes was higher then that through the pure PPSU/PBNPI polymer membranes. The diffusivity coefficients of O_2 and N_2 slightly increased in the 50/50 wt % blend PPSU/PBNPI membrane.

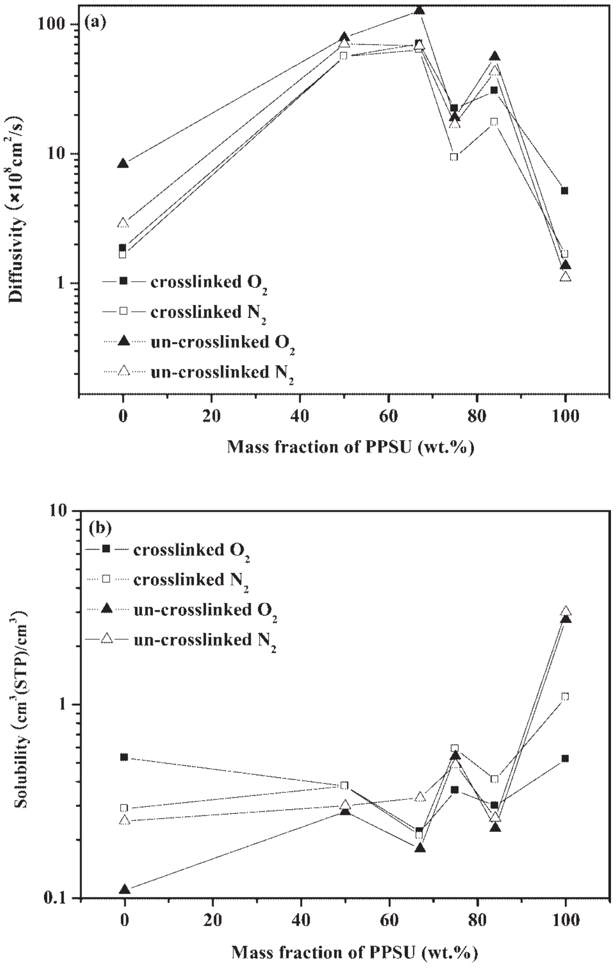

Figure 8 Pure gas diffusivity and solubility properties of the PPSU/PBNPI blend membranes before and after crosslinking.

TABLE IV
XRD Parameters

Polymer membrane	wt %	*d*-spacing (Å) Uncrosslinked membrane (2θ = 12°)	Crosslinked membrane (2θ = 15–20°)
PPSU/PBNPI	50/50	7.45	4.78
PPSU/PBNPI	67/33	7.41	4.75
PPSU/PBNPI	75/25	7.39	4.76
PPSU/PBNPI	16/84	7.36	4.72

When the PPSU content increased to 67 wt %, the diffusivity behavior of O_2 increased remarkably. We observed that the diffusivity behavior of O_2 decreased with increasing PPSU content over 67 wt %. Therefore, the diffusivities of the O_2 and N_2 gases through the uncrosslinked blend membranes increased with increasing PPSU content from 50 to 67 wt %, whereas the slight diffusivity selectivity of the O_2/N_2 gas pair decreased.

As discussed previously, the same variations in permeability and permselectivity with blended composition were observed in Table II. This was attributed to the increase in the free volume on the mixing of the blends. Meanwhile, Table IV shows the *d*-spacing values of the blend membranes. Comparing *D* with the *d*-spacing, we observed slightly higher *d*-spacing values when the PPSU content increased from 0 to 67 wt %. Therefore, we suggest that the PPSU/PBNPI blends were microscopically phase-separated. Blending with PPSU formed a two-phase system with a weak interaction, which developed a phase gap between the interfaces of PPSU and PBNPI and provided more volume for O_2 and N_2 transport.

Figure 8(a) shows the decreased diffusivity of O_2 and N_2 through the crosslinked blend membranes; this was found to be lower than in all kinds of uncrosslinked blend membranes. Meanwhile, the diffusivity of N_2, in comparison with that of the uncrosslinked membranes, decreased remarkably by virtue of the 75 and 84 wt % PPSU of crosslinked blend membranes. This suggests that the crosslinking modification had more influence on the N_2 diffusion behavior than on the O_2 diffusion behavior. Such an explanation may account in part for the PPSU/PBNPI membrane via crosslinking modification, which decreased the volume for the transport of the gases through the blend membranes.

In Table II, the *d*-spacing value of the blend membranes after crosslinking modification is tabulated; it shows the decrease of *d*-spacing from 4.78 to 4.72. This suggests that the decreased *d*-spacing might have reduced the packing size and, consequently, decreased the diffusivity properties of the crosslinked membranes.

Meanwhile, as Figure 8(b) illustrates, when the PPSU content increased from 50 to 67 wt %, the blending ratio did not significantly affect *S* of O_2 and N_2. This suggests that the gas-permeation behavior of O_2 and N_2 in the uncrosslinked blend membranes whose PPSU concentration was lower than 67 wt % was determined by the diffusion mechanism.

Furthermore, when the PPSU content increased from 67 to 100 wt %, the solubility of both gases passing through the uncrosslinking blend membranes slightly increased, whereas their diffusivity decreased. The same variation was also found in permeability. Therefore, the gas-permeation behavior of O_2 and N_2 in the blend membranes with PPSU concentrations higher than 67 wt % was dominated by the solubility mechanism. Table V summarizes the selectivities of both the diffusivity and solubility among the uncrosslinked and crosslinked PPSU/PBNPI blend membranes. Before crosslinking, the diffusivity selectivity ratio of O_2 to N_2 was not significantly influenced by the PPSU content. Furthermore, an unusually high ideal O_2/N_2 diffusivity selectivity of 2.87 was obtained. In addition, Table V shows that after crosslinking, the pure PPSU membrane had a good diffusivity selectivity, but that of the PBNPI decreased remarkably. Meanwhile, the apparent increase in the efficiency of the diffusivity selectivity was accompanied by increased PPSU content in the crosslinked PPSU/PBNPI blend membranes. However, this phenomenon worked against the solubility selectivity. Therefore, in terms of

TABLE V
Diffusivity Selectivity and Solubility Selectivity of the Uncrosslinked and Crosslinked PPSU/PBNPI Blend Membranes

Polymer membrane	wt %	Diffusivity selectivity: O_2/N_2 Before crosslinking	After crosslinking	Solubility selectivity: O_2/N_2 Before crosslinking	After crosslinking
PPSU	100	1.24	3.08	0.91	0.48
PBNPI	100	2.87	1.13	0.45	1.85
PPSU/PBNPI	50/50	1.12	1.00	0.93	1.00
PPSU/PBNPI	67/33	1.87	1.11	0.55	1.08
PPSU/PBNPI	75/25	1.13	2.40	1.11	0.61
PPSU/PBNPI	84/16	1.30	1.70	0.87	0.73

selectivity enhancement, it appeared that the modification of the blend membranes with crosslinking was caused mainly by the reduced interstitial space in the polymer chains after crosslinking.

CONCLUSIONS

In this study, we investigated the gas-permeation and selectivity characteristics of uncrosslinked and crosslinked PPSU/PBNPI blend membranes. The results demonstrate that the crosslinking modification resulted in improved O_2/N_2 separation by immersion of the films in 5% (w/v) of a *p*-xylylenediamine methanol solution for a certain period of time. The changes in the chemical structure were measured by FTIR–ATR spectroscopy before and after the crosslinking process. Here, C═O stretching and strong amine bands (stretching of C─N and/or bending of N─H in the amide group) demonstrated that a crosslinking reaction in the PPSU/PBNPI blend membrane was achieved. Although the crosslinked PPSU/PBNPI blend membrane showed a lower permeability than the uncrosslinked PPSU/PBNPI blend membranes, the former possessed a higher selectivity than the latter because of the compact structure of the polymer chains. In the crosslinked PPSU/PBNPI blend membranes, the gas permeabilities decreased gradually along with increasing PPSU. Furthermore, their maximum values were attained in the 50/50 wt % crosslinked PPSU/PBNPI blend membrane. Meanwhile, an effective improvement in O_2/N_2 selectivity was presented when C─N, C═O and the N─H function group exhibited strongly in the crosslinked membrane. The pure gas permeation in both the uncrosslinked and crosslinked PPSU/PBNPI blend membranes mainly occurred via a diffusivity mechanism. The results show that the crosslinked membrane affected O_2 and N_2 solubility in the gas-permeation process, which also contributed to O_2/N_2 separation.

References

1. Pandey, P.; Chauhan, R. S. Prog Polym Sci 2001, 26, 853.
2. Tin, P. S.; Chung, T. S.; Liu, Y.; Wang, R.; Liu, S. L.; Pramoda, K. P. J Membr Sci 2003, 225, 77.
3. Huang, M. R.; Xu, Q. W.; Gu, S. Y.; Wu, Y. H.; Dong, Z. Q.; Shao, J. W. H. T.; Wang, X. S. J Appl Polym Sci 2003, 87, 1371.
4. Li, X. G.; Huang, M. R.; Lu, Y. Q.; Zhu, M. F. J Mater Chem 2005, 15, 1343.
5. Kapantaidakis, G. C.; Kaldis, S. P.; Dabou, X. S.; Sakellaropoulos, G. P. J Membr Sci 1996, 110, 239.
6. Kim, S. H.; Kim, D.; Lee, D. S. J Membr Sci 1997, 127, 9.
7. Johnson, T.; Thomas, S. Polymer 1999, 40, 3223.
8. Ye, Z.; Chen, Y.; Li, H.; He, G.; Deng, M. Mater Chem Phys 2005, 94, 288.
9. Yi, C.; Wang, Z.; Li, M.; Wang, J.; Wang, S. Desalination 2006, 193, 90.
10. Staudt-Bickel, C.; Koros, W. J. J Membr Sci 1999, 155, 145.
11. Sridhar, S.; Suryamurali, R.; Smitha, B.; Aminabhavi, T. M. Colloid Surf A 2007, 297, 267.
12. Dudley, C. N.; Schöberl, B.; Sturgill, G. K.; Beckham, H. W.; Rezac, M. E. J Membr Sci 2001, 191, 1.
13. Wright, C. T.; Paul, D. R. J Membr Sci 1997, 129, 47.
14. Ruaan, R.-C.; Wu, T.-H.; Chen, S.-H.; Lai, J.-Y. J Membr Sci 1998, 138, 213.
15. Kita, H.; Inada, T.; Tanaka, K.; Okamoto, K. I. J Membr Sci 1994, 87, 139.
16. Matsui, S.; Ishiguro, T.; Higuchi, A.; Nakagawa, T. J Polym Sci Part B: Polym Phys 1997, 35, 2259.
17. Liu, Y.; Pan, C.; Ding, M.; Xu, J. Eur Polym J 1999, 35, 1739.
18. Rao, H. X.; Liu, F. N.; Zhang, Z. Y. J Membr Sci 2007, 303, 132.
19. Anjali Devi, D.; Smitha, B.; Sridhar, S.; Aminabhavi, T. M. J Membr Sci 2005, 262, 91.
20. Smitha, B.; Sridhar, S.; Murthy, G. S.; Mayor, S. J. J Chem Technol Biotech 2005, 80, 1416.
21. Weng, T. H.; Tseng, H. H.; Wey, M. Y. Int J Hydrogen Energy 2008, 33, 4178.
22. Vijay, Y. K.; Wate, S.; Acharya, N. K.; Garg, J. C. Int J Hydrogen Energy 2002, 27, 905.
23. Vanherck, K.; Vandezande, P.; Aldea, S. O.; Vankelecom, I. F. J. J Membr Sci 2008, 320, 468.
24. Charmette, C.; Sanchez, J.; Gramain, P.; Rudatsikira, A. J Membr Sci 2004, 230, 161.
25. Frounchi, M.; Dadbin, S.; Salehpour, Z.; Noferesti, M. J Membr Sci 2006, 282, 142.
26. Rao, P. S.; Wey, M. Y.; Tseng, H. H.; Kumar, I. A.; Weng, T. H. Micropor Mesopor Mater 2008, 113, 499.
27. Kim, T. H.; Koros, W. J.; Husk, G. R.; O'Brien, K. C. J Appl Polym Sci 1987, 34, 1767.
28. Yampolskii, Y.; Pinnaul, I.; Freeman, B. D. Materials Science of Membranes for Gas and Vapor Separation; John Wiley & Sons., Ltd.: England, 2006.
29. Rutherford, S. W.; Do, D. D. Adsorption 1997, 3, 283.
30. Sridhar, S.; Ganga, D.; Smitha, B.; Ramakrishna, M. Sep Sci Technol 2005, 40, 2889.
31. Ismail, A. F.; Lorna, W. Sep Purif Technol 2002, 27, 173.
32. Mika, A. M.; Childs, R. F.; Dickson, J. M.; McCarry, B. E.; Gagnon, D. R. J Membr Sci 1997, 135, 81.