Ultraviolet-ray treatment of polysulfone membranes on the O_2/N_2 and CO_2/CH_4 separation performance

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ABSTRACT: UV irradiation on polysulfone (PSF) membranes was studied to improve their gas-separation properties. Membranes with 19–25% PSF contents were prepared by the phase-inversion method, and the membrane surface was modified with UV rays with a wavelength of 312 nm and a power of 360 μw/cm^2. Measurements of gas permeation were conducted with pure carbon dioxide (CO_2), methane (CH_4), oxygen (O_2), and nitrogen (N_2) gases under 3–8 bar pressure at 25°C. Fourier transform infrared spectrometry revealed that the polar functional groups of hydroxyl and carbonyl were introduced by UV irradiation. The water contact angle of the treated membrane was reduced from 70–75° to 10–12° after 12 h of UV exposure. Scanning electron microscopy observation showed that the dense skin layer increased as the polymer concentration increased. After UV treatment, the permeation of O_2 decreased from 0.4–3.4 to 0.2–2.3 m^3 m^{-2} h^{-1} bar^{-1}, whereas that of N_2, CO_2, and CH_4 increased for all of the pressures used from 0.1–1.7 m^3 m^{-2} h^{-1} bar^{-1} to about 0.1–3.4 m^3 m^{-2} h^{-1} bar^{-1}; this depended on the applied pressure and the PSF content. As a result, the selectivity ratio of O_2/N_2 decreased from 1.9–7.8 to 0.6–1.5, whereas that of CO_2/CH_4 increased from 0.9–2.6 to 1.1–6.1. Moreover, the O_2/N_2 and CO_2/CH_4 of the untreated and the treated membranes decreased with increasing pressure and increased with increasing polymer concentration. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42074.

INTRODUCTION

Recently, polymeric membrane technology has become increasingly attractive to scientists for gas-separation tasks. Generally, an increased concentration of carbon dioxide (CO_2) in the atmosphere is a major contributor to global warming. Not only is CO_2 released every day from vehicles, but it is also commonly found in natural gas streams, biogases from anaerobic digestion, flue gases from fossil fuel combustion, and products of coal gasification with pipeline specifications below 2% (in the United States).[1] It is classified as an acid gas, similar to H_2S and SO_2, and several steps are required remove it from gas streams. In many industrial processes, such as natural gas sweetening, biogas upgrading, oil recovery enhancement, and landfill gas purification, a mixture of CO_2 and methane (CH_4) commonly remains as waste. The separation of CO_2 from CH_4 can benefit both the environment and energy-recovery aspects. The separation and sequestration of CO_2 by pumping and storage deep underground is a feasible approach for dealing with greenhouse gas emissions.[2]

Another type of gas separation is the separation of nitrogen and oxygen from the air or oxygen enrichment.[3] Enriched oxygen generation from an air mixture is an important process for hospitals and for the effectiveness of combustion systems and greenhouse gas emissions.[4] Therefore, effective techniques for these separations have attracted great interest from workers in many laboratories.

The conventional processes for gas separation are absorption, adsorption, and cryogenic distillation.[5] These conventional methods usually involve substantially complicated equipment and higher energy consumption and capital costs,[6,7] whereas membrane gas separation does have advantages in its energy efficiency, simple process design, modular design (permitting easy expansion), compactness, light weight, low labor intensiveness, low maintenance, low cost, and environmental friendliness.
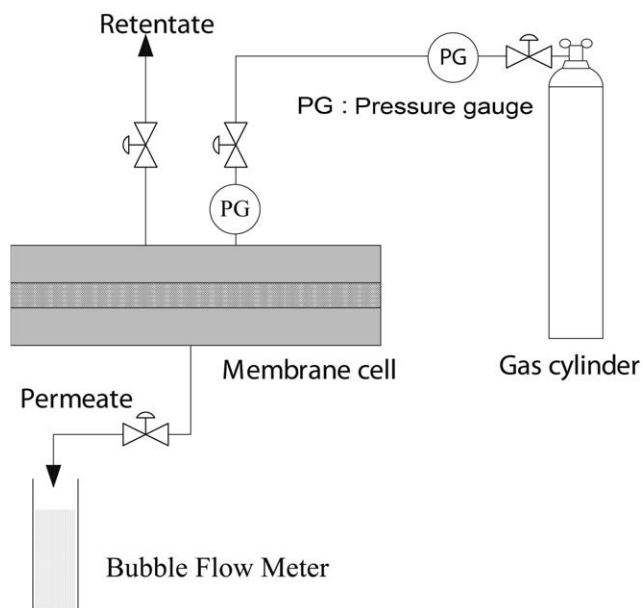
Table I. Compositions of the PSF Membranes According to the PSF Content

| Sample	PSF (wt %)	DMAc (wt %)	Ac (wt %)
PSF19%	19	54	27
PSF22%	22	52	26
PSF25%	25	50	25

The ratio of DMAc to Ac was fixed at 2 : 1 w/w.

In addition, gas-separation membrane units are smaller than other types of plants and are potentially beneficial to offshore gas processing.[7,8]

A high gas permeability and selectivity are always desirable for polymeric membranes. In most cases, an increase in the gas permeability often causes a decrease in the gas selectivity. Asymmetric membranes with a highly selective thin layer on top are known as high-performance membranes.[5,9] However, the gas-transport properties of polymeric membranes depend on the physicochemical interactions between various gas species and polymer molecules.[6] A difficulty in the gas-separation process falls on the fact that the gas molecules to be separated are relatively small. Also, differences do exist in the membrane material properties and electronic properties, such as in the polarizability and quadrupole moment of the gases.[10] In addition, membrane modification with polarity addition to the surface is of interest for the improvement of the absorption and adsorption properties for gas separation.

Figure 1. Schematic view of the experimental setup.
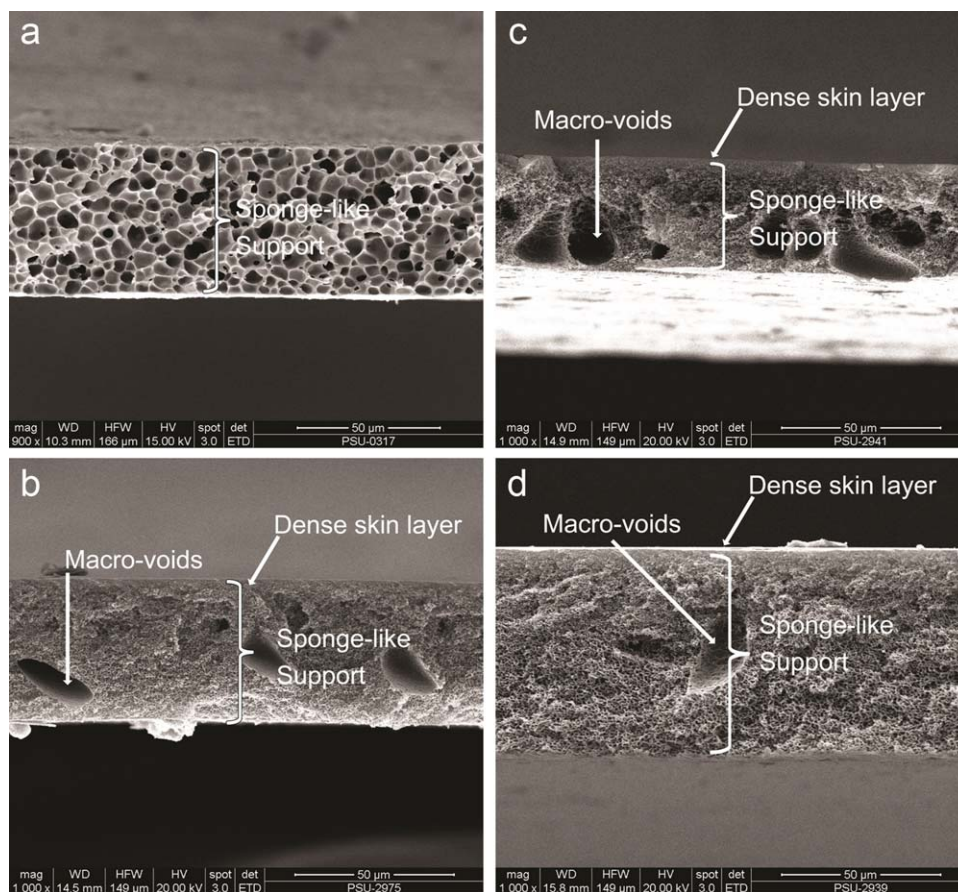
Figure 2. Scanning electron micrographs of the PSF membranes prepared without and with Ac: (a) 20% PSF (without Ac), (b) 19% PSF, (c) 22% PSF, and (d) 25% PSF.
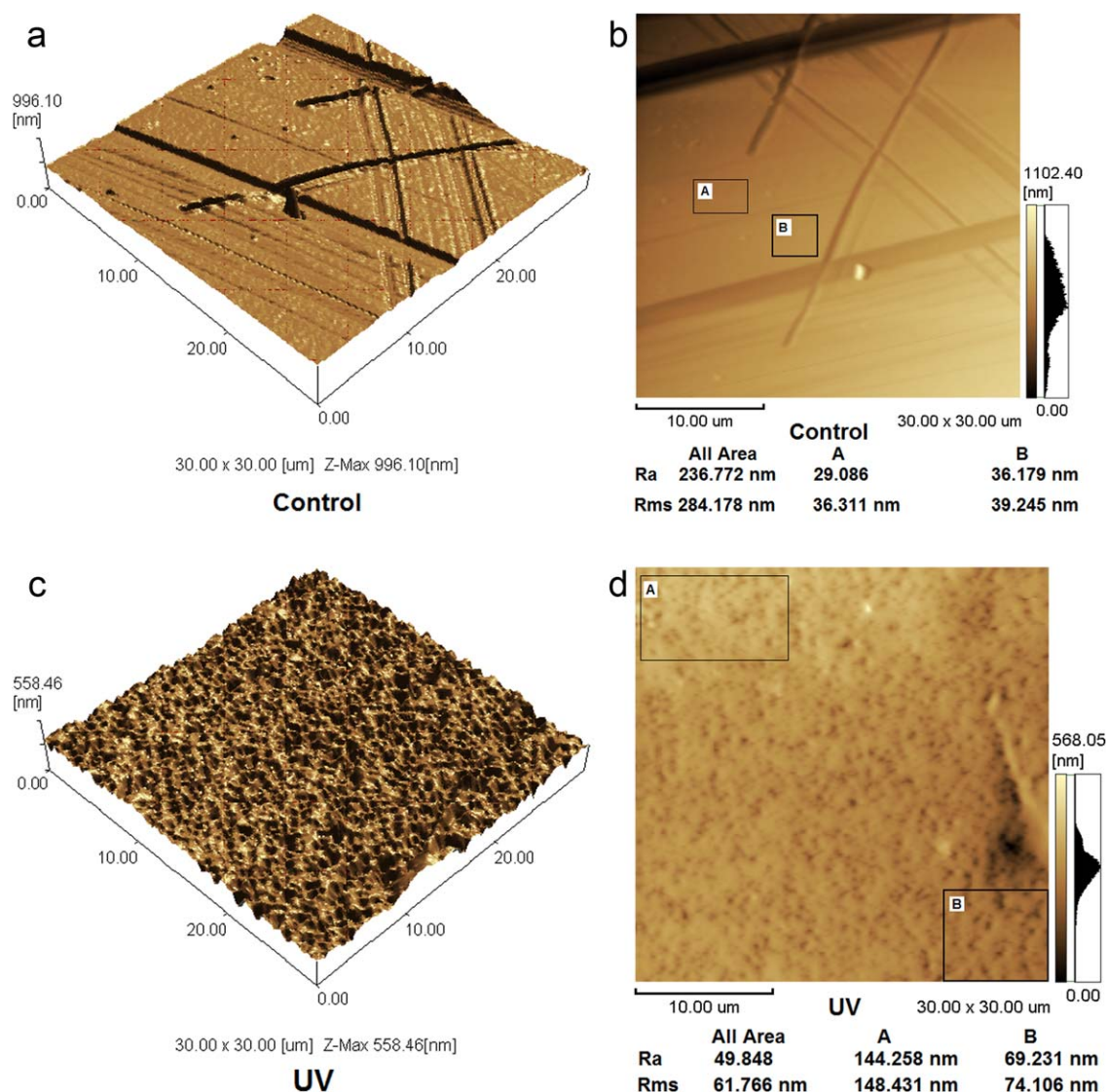
Figure 3. Atomic force microscopy images of the (a) untreated (control) and (b) 12-h UV-treated membranes (22% PSF). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

There are many methods for modifying the membrane surface; these include plasma treatment and ultraviolet (UV) irradiation. Kim et al.[11] and Jaleh et al.[12] reported changes from hydrophobicity to hydrophilicity in polymeric membranes after oxygen plasma treatment. However, this technique has a very short lifetime effect, showing hydrophobicity recovery within hours; this was explained as being due to the migration of short uncrosslinked chains to the surface.[13] An equally effective method for the surface modification is an exposure of a membrane to UV irradiation. Nystrom and Jarvinen[14] reported increases in the flux and hydrophilicity of polysulfone (PSF) membranes after UV irradiation. In addition, Hsu et al.[15] revealed that UV irradiation of poly(trimethylsilyl propyne) membranes resulted in an improvement of the O_2/N_2 selectivity from 1.4 to approximately 4 after treatment. Information about the membrane surface modification by UV irradiation is rather scarce, although the technique has distinct advantages over others because of its simplicity, inexpensiveness, and widespread industrial applications.[16]

In this article, we report the surface modification of PSF asymmetric membranes by UV ray irradiation to investigate its effects on CO_2/CH_4 and O_2/N_2 separations.

Table II. Water Contact Angles of the PSF Membranes versus the Irradiation Time

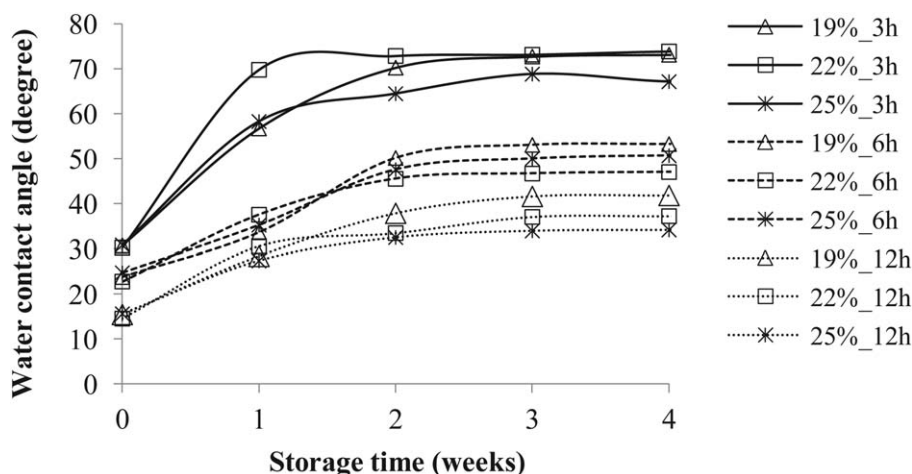| Irradiation time (h)	Water contact angle (°)		
	19% PSF	22% PSF	25% PSF
0	76.5 ± 0.2	72.1 ± 1.8	71.4 ± 3.4
3	40.4 ± 2.0	38.9 ± 0.1	36.5 ± 2.7
6	15.9 ± 0.5	18.8 ± 1.3	14.8 ± 0.4
12	11.5 ± 0.5	11.9 ± 0.8	10.4 ± 1.0

Data were averaged from three experiments.

Figure 4. Changes in the water contact angles on UV-treated membranes versus the storage time.

EXPERIMENTAL

Preparation of Asymmetric Flat-Sheet Membranes

The polymeric solution in this study consisted of PSF (Udel P-3500) supplied by Solvay (China). N,N-Dimethylacetamide (DMAc) and acetone (Ac) were used as solvents for the PSF membrane and were supplied by Sigma–Aldrich Co. and Guang-dong Guanghua Chemical Factory Co., Ltd. (China), respectively. Tap water was used as a coagulation medium. PSF resin was dried in an oven at a temperature of about 80°C for 24 h to remove the humidity before use. Asymmetric PSF flat-sheet membranes were prepared by casting with a solution consisting of PSF (polymer), DMAc (less volatile solvent), and Ac (more volatile solvent) of various concentrations (Table I), whereas the ratio of DMAc and Ac was fixed at 2 : 1 w/w. The solutions were mixed at 60°C for 24 h and placed in an ultrasonic water bath to remove air bubbles. Casting was carried out on a clean glass plate under an ambient atmosphere (25°C and 85% relative humidity). The thin polymer sheet was immersed in a coagulation bath at 25°C and remained there for 24 h. The wet membranes were dried at room temperature for 24 h before use.

Three pieces of dried PSF membranes in the form of squares with areas of approximately 2 cm^2 were irradiated by UV

radiation in air at room temperature within a basement. The exposure area was 20 cm^2. Membranes were exposed to a UV source (Vilber Lourmat, Vl-215.MC), and the distance between the source and sample holder was kept constant at 3 cm, where the light intensity was measured within 360 μw/cm^2 of all position of the sample holder. Membranes were exposed for various times, such as 3, 6, and 12 h. The control (0 h) was placed in the box without humidity.

Membrane Characterization

The permeation performance of the PSF membranes were evaluated by two parameters: the permeability (P) and the selectivity. The gas permeation measurements were conducted with a gas permeation unit, as shown in Figure 1. The PSF membranes were cut into a circle area of 3.14 cm^2 and mounted in the gas permeation unit. The testing temperature was room temperature (25°C). The testing pressure was controlled from 3 to 8 bar, and the testing gases were O_2, N_2, CO_2, and CH_4. The feed gas was fed into the upside, and the permeating gas was at the downside of the membrane. The gas flow rate (Q) was determined by bubble flow meters. The pure gas permeance (P/l) of the membrane was calculated by the following equation:[17]
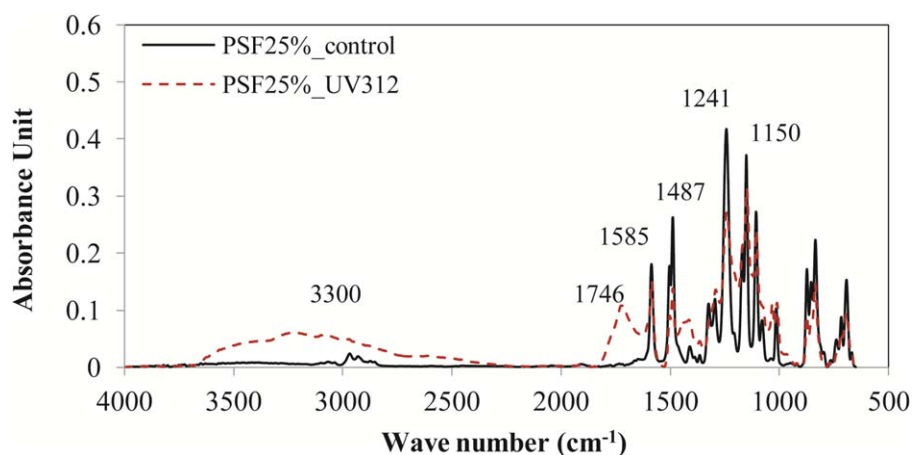

Figure 5. Comparison of the Fourier transform infrared spectra of the untreated membrane and the membrane treated with UV rays. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
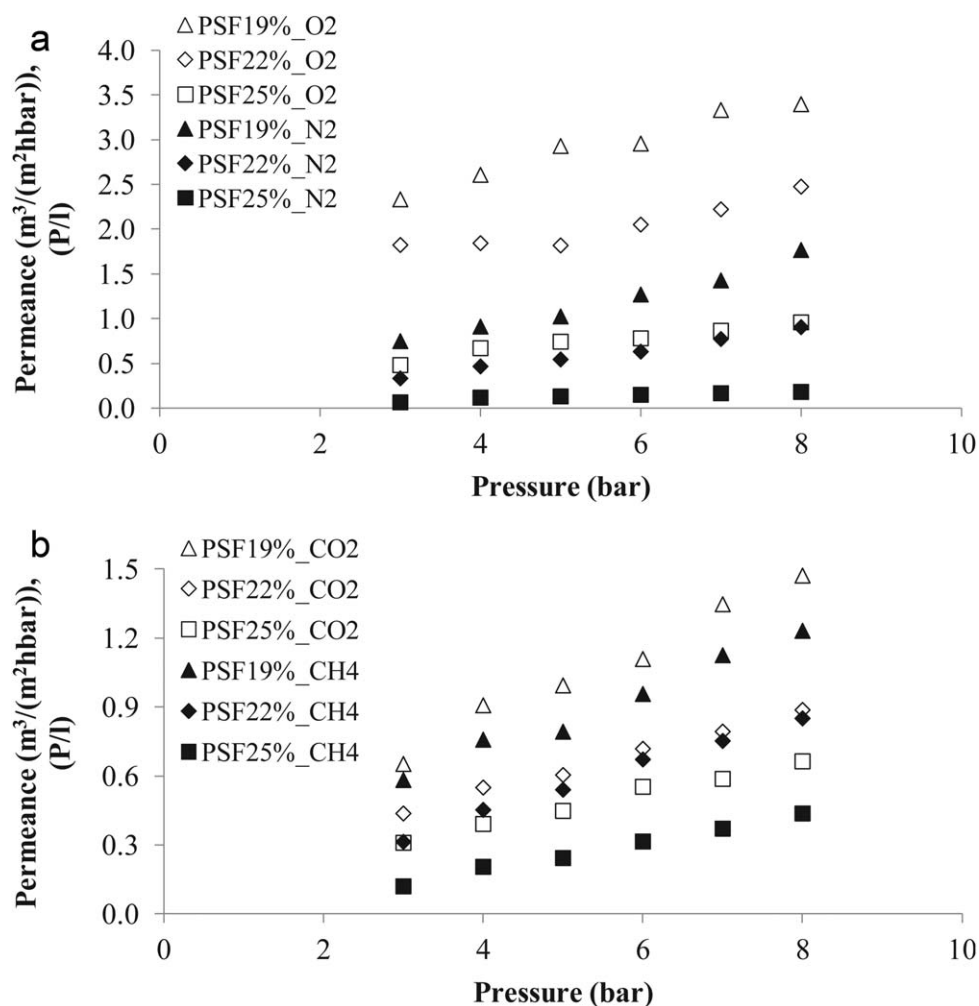
Figure 6. Permeation of (a) O_2 and N_2 and (b) CO_2 and CH_4 through several untreated PSF membranes.

$$\frac{P}{l} = \frac{Q}{A\Delta P} \tag{1}$$

where ΔP is the pressure difference across the membrane, A is the membrane effective surface area, and l is the membrane skin thickness. Each membrane was tested three times for each gas, and the results are presented as averages. The selectivity (α) was defined by the following equation:[1,17]

$$\alpha_{ij} = \frac{\left(\frac{P}{l}\right)_i}{\left(\frac{P}{l}\right)_j} \tag{2}$$

where $(P/l)_i$ and $(P/l)_j$ are the permeances of gases i and j, respectively. The reported values are the average of three measurements.

The membrane morphology was examined by scanning electron microscopy (FEI, Quanta 400) with 20-kV voltage potentials. In cross-sectional studies, the membrane samples were fractured in liquid nitrogen and coated with gold before scanning. A Fourier transform infrared spectrometer (Bruker, EQUINOX 55) was used to investigate changes in the functional groups of the membranes after UV ray irradiation. The water contact angle values of the membranes were measured with a contact angle device (Dataphysics, OCA 15 EC) immediately after the UV treatment and also after the membranes were left at room temperature for 4 weeks to study the hydrophobic recovery of the treated membranes. The membrane surface topography was observed with an atomic force microscope operated in tapping-

Table III. Comparisons of the Structural, Physical, and Electronic Parameters of Gas Molecules

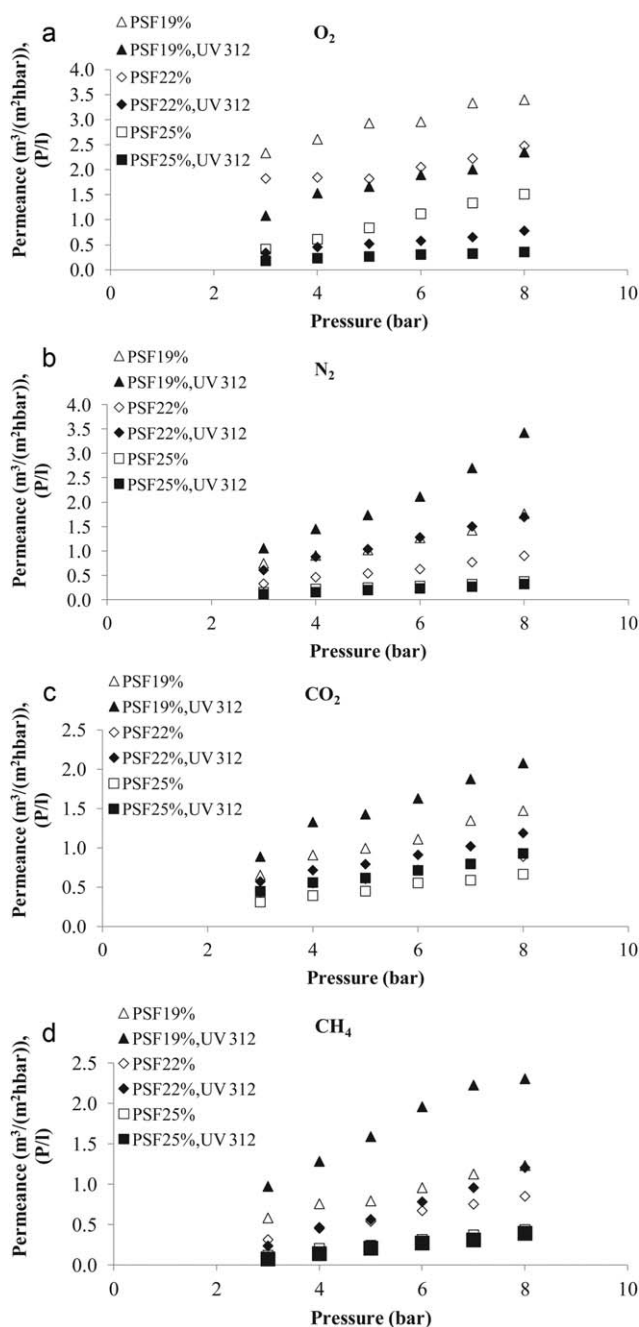| Molecule	Kinetic diameter (Å)[6]	Structure[21]	Quadrupole moment (10^{-40} C m²)[21]	Polarizability (10^{-40} J⁻¹ C² m²)
O_2	3.46	Linear	1.3	1.57[22]
N_2	3.64	Linear	4.7	1.97[21]
CO_2	3.30	Linear	13.4	2.93[21]
CH_4	3.80	Tetrahedral	0	2.89[21]

Figure 7. Comparison of (a) O$_2$, (b) N$_2$, (c) CO$_2$, and (d) CH$_4$ permeation through the untreated membrane and the membrane treated with UV rays.

mode scanning. The membrane sample was prepared at a 1 × 1-cm^2 size for atomic force microscopy scanning and scanned in a 30 × 30-μm^2 area.

RESULTS AND DISCUSSION

The formation of a dense skin layer was investigated by scanning electron microscopy and is shown in Figure 2. Ac was a more volatile solvent. It could rapidly evaporate from the outermost surface of the membrane during polymer casting, which resulted in higher polymer concentration in the upper layer of

the membrane and led to delayed liquid–liquid demixing; as a result, a dense skin layer with less defects and pinholes was prepared.[18] The asymmetric membranes were prepared. The dense skin layer increased, and the macrovoids of the spongelike support decreased with increasing polymer concentration. This was consistent with the results of Madaeni and Moradi.[19]

Atomic force microscopy scanning showed that the membrane surface roughness increased significantly after the UV irradiation compared with the control, as shown in Figure 3. The obtained atomic force microscopy images suggest that chains scission and crosslinking occurred simultaneously in the irradiated membranes by UV radiation.[20]

The water contact angles on the untreated and the treated membranes by UV irradiation are shown in Table II. For the untreated membranes, the contact angles were 71–76°. After 6 h of UV irradiation, they were reduced to 14–18° and stabilized at 10–11° after 12 h of irradiation. Apparently, these membranes possessed similar contact angles regardless of the polymer content. This result indicates that the hydrophilicity of the PSF membranes was increased by UV irradiation.

In addition, the hydrophobic recovery was observed after the irradiated membranes were left in storage for several periods of time. This was indicated by changes in the contact angle with time, as shown in Figure 4. The hydrophobic recovery of the 3-h treated membranes occurred rapidly within 1 week after the treatment ended. The contact angle increased from 30 to 70° and was fairly equal to that of the untreated membranes. It is interesting to point out that for the 6- and 12-h UV irradiation treatment times, the contact angle gradually increased from 25 to 35° and from 15 to 25°, respectively, and this took place for 4 weeks. This result indicates that the membrane hydrophilicity could not be achieved in a short irradiation period. Moreover, the irradiated membranes of greater polymer content exhibited smaller contact angles in all cases, and the hydrophobic recovery seemed to be inhibited.

The Fourier transform infrared spectra of the UV-treated membranes compared to the control are shown in Figure 5, which though describes functional groups of only the greatest PSF containing membrane because all of the membranes showed similar spectral peaks. The PSF consists of a backbone made up of diaryl sulfone (Ar—SO$_2$—Ar) and diaryl ether (Ar—O—Ar) groups, which showed strong bands at 1150 and 1241 cm^{-1}, respectively. The bands at 1487 and 1585 cm^{-1} belonged to the vibrations of the aromatic (C=C) in the PSF. There were two new peaks appearing round 3300 and 1746 cm^{-1}, which should have belonged to the stretching vibrations of hydroxyl (—OH) and carbonyl (C=O) groups, respectively. Because they were polar functional groups,[11] this indicated that polar functional groups were introduced to the PSF membrane by UV ray irradiation, and this led to an increase in hydrophilicity. This was confirmed by contact angle measurements and was consistent with the result of Kim et al.,[11] who modified the surface of PSF membrane by oxygen plasma treatment.

The permeance of four gases through PSF membranes with different polymer concentrations was investigated with eq. (1), and the results are illustrated in Figure 6. The permeance of all of the gases (O$_2$, N$_2$, CO$_2$, and CH$_4$) increased with increasing pressure and decreased with increasing polymer concentration
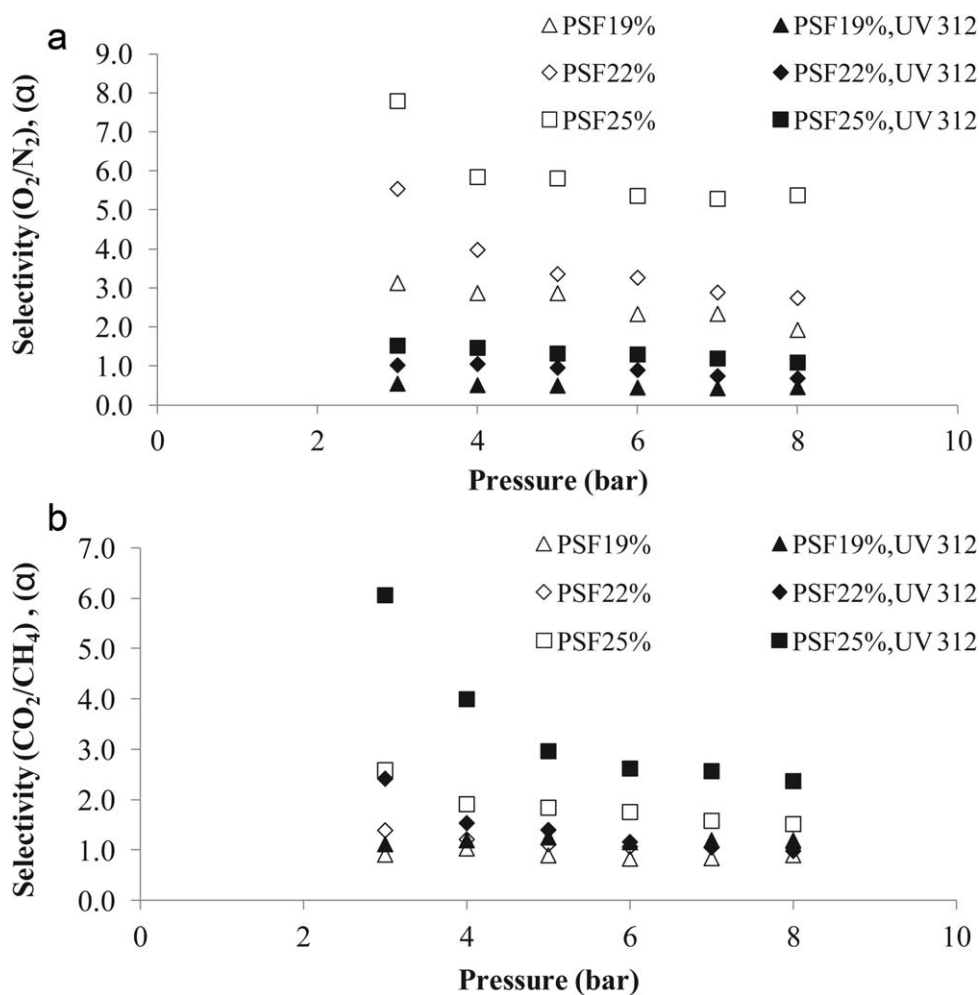
Figure 8. Selectivity of the untreated membrane and the membrane treated with UV rays for (a) O_2/N_2 and (b) CO_2/CH_4.

from 19 to 25% because of the increased in the dense skin layer and membrane thickness resistance against gas diffusion. However, the O_2 and CO_2 permeances were greater compared, respectively, to those of N_2 and CH_4, respectively, because the O_2 and CO_2 molecules were smaller than the N_2 and CH_4 molecules, respectively. The molecular size of the gas was considered from the kinetic diameters, which are shown in Table III.

The effect of UV irradiation on gas permeation through the membranes is shown in Figure 7. From the contact angle results, the 12-h UV treatment was the optimum condition. So, the membrane treated for 12 h with UV was selected for this study. The result showed that O_2 permeation decreased, whereas the permeation of N_2, CO_2, and CH_4 increased after UV irradiation. This may have been due to gas molecules permeated through the membrane by quadrupole–dipole interactions between the gas molecules and polar segments of membrane.[1] UV irradiation improved the hydrophilicity and polar groups of the membrane; this was confirmed by contact angle measurement (Table II) and Fourier transform infrared analysis.

Therefore, the highly polar groups in the treated membranes should have been more attractive to CO_2, N_2, and CH_4 because the CO_2 molecule has a high quadrupole moment (see Table

Table IV. Surface-Free Energies of the Untreated and Treated PSF Membranes

Sample (%)	Untreated membrane			Treated membrane		
	Surface energy	Dispersive component	Polar component	Surface energy	Dispersive component	Polar component
19	34.91	30.20	4.21	83.58	0.83	82.76
22	31.35	18.08	13.27	84.92	0.79	84.14
25	36.48	31.37	5.11	84.06	0.94	83.12

III) with a high polarizability, whereas the N_2 and CH_4 have a high polarizability and lead to more permeance. However, O_2 has a low quadrupole moment and polarizability, and this leads to a repellence from the polar membrane, and hence, smaller gas permeation was evidenced. This -permeation affected the O_2/N_2 and CO_2/CH_4 selectivities of the membranes because the selectivity was proportional to the permeation of the two gases. Therefore, the O_2 permeance was divided by the N_2 permeance according to eq. (2) and, with the data from Figure 7(a,b), became the O_2/N_2 selectivity, which is shown in Figure 8(a). In the same way, the CO_2/CH_4 selectivity, which is shown in Figure 8(b), was calculated by this method with data from Figure 7(c,d). The result shows that the O_2/N_2 selectivity decreased, whereas the CO_2/CH_4 selectivity increased after UV irradiation. The permeance of O_2 through the treated membranes decreased, whereas that of N_2 increased, and this led to a decrease in the O_2/N_2 selectivity. In the case of CO_2 and CH_4, both permeances increased after UV irradiation, but the CO_2 permeance was greater because of the greater quadrupole moment (Table III). It should be also pointed out that the selectivity decreased with increased pressure and increased when the polymer concentration increased from 19 to 25% because the formation of a dense skin layer in higher polymer content membranes with fewer macrovoids (in Figure 2) lowered the diffusion of gas molecules through the membrane.

To confirm polar segments of the membrane, the surface properties of the PSF membranes were examined by contact angle measurement (Dataphysics, OCA 15 EC). With the contact angles of formamide and ethylene glycol, the surface energy and its polar and dispersive components of the PSF membrane were calculated with SCA20 software. The results are shown in Table IV. The surface free energy increased mainly because of the increase of the polar component, and the dispersive component decreased after UV irradiation. This result was consistent with the results of surface modification of the PSF membrane by the oxygen plasma treatment of Kim et al.[11] This indicates that the UV radiation affected the polar component, which affected the gas permeation of the PSF membranes.

CONCLUSIONS

In this study, we found that UV rays 312 nm in wavelength and 360 $\mu w/cm^2$ in power affected the polar component of the surface free energy. This affected the gas permeation of the PSF membranes. UV irradiation decreased the O_2/N_2 selectivity but increased the CO_2/CH_4 selectivity of the membranes. Hence, the separation of CO_2 from CH_4 was improved only when permanent hydrophilicity of the treated membranes was achieved, and it could be improved further by an increase in the polymer content of the membrane.

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