Crosslinking and Stabilization of Nanoparticle Filled Poly(1-trimethylsilyl-1-propyne) Nanocomposite Membranes for Gas Separations

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ABSTRACT: Poly(1-trimethylsilyl-1-propyne) (PTMSP) has been crosslinked using 4,4′-diazidobenzophenone bisazide to improve its chemical and physical stability over time. Crosslinking PTMSP renders it insoluble in good solvents for the uncrosslinked polymer. Gas permeability and fractional free volume decreased as crosslinker content increased, while gas sorption was unaffected by crosslinking. Therefore, the reduction in permeability upon crosslinking PTMSP was due to decrease in diffusion coefficient. Compared with the pure PTMSP membrane, the permeability of the crosslinked membrane is initially reduced for all gases tested due to the crosslinking. By adding nanoparticles (fumed silica, titanium dioxide), the permeability is again increased; permeability reductions due to crosslinking could be offset by adding nanoparticles to the membranes. Increased selectivity is documented for the gas pairs O_2/N_2, H_2/N_2, CO_2/N_2, CO_2/CH_4, and H_2/CH_4 using crosslinking and addition of nanoparticles. Crosslinking is successful in maintaining the permeability and selectivity of PTMSP membranes and PTMSP/filler nanocomposites over time. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3078–3088, 2009

Key words: crosslinking; membrane; gas permeation

INTRODUCTION

Poly(1-trimethysilyl-1-propyne) (PTMSP) has the highest gas permeability among all existing polymers,[1] but consequently it also exhibits relatively low selectivity. It is a stiff chain, high free volume glassy polymer.[1] The high permeability of PTMSP is attributed in part to its extremely high fractional free volume (FFV) of 0.29.[2–5] The high gas permeability of the polymer is, however, not stable over time. It has been reported[6,7] that the oxygen permeability of PTMSP decreased by 1 order of magnitude during storage at 25°C for 30 days under vacuum. The gas permeability in this polymer also seems to be sensitive to processing history.[8] PTMSP undergoes significant physical aging over time caused by the gradual relaxation of non-equilibrium excess free volume in glassy polymers. The chemical stability of PTMSP is low, and it is soluble in a wide range of organic solvents, including both aliphatic and aromatic.[9] These phenomena may compromise the practical use of this high permeation polymer unless it can be stabilized.

It was recently reported that the addition of non-porous fumed silica (FS) nanoparticles to PTMSP increased the permeability.[10,11] This behavior is contrary to the observed fact that permeability typically decreases with increasing filler loading in traditionally filled polymer system. The increased permeability in PTMSP has been ascribed to the increased free volume sizes in the polymer caused by the nanosized FS particles disrupting the packing of the polymer chains. This enhanced free volume of the filled superglassy polymer has been confirmed by both positron annihilation lifetime spectroscopy (PALS)[11] and ^{129}Xe NMR.[12]

To improve the use of PTMSP, the chemical and physical stability of PTMSP needs to be improved. PTMSP has been chemically and physically modified using many different methods to improve its stability.[13–16] Jia et al.[16] reported that crosslinking PTMSP with bis(aryl azides) has been shown to increase the chemical and physical stability. Crosslinked PTMSP membranes are insoluble in common PTMSP solvents such as toluene, and the nitrogen and oxygen permeabilities of crosslinked PTMSP are reported to be almost constant over time.[16] The crosslinking reaction described in this report capitalized on the ability of aryl azides ($R-N_3$) to decompose to molecular

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nitrogen (N_2) and reactive nitrenes (R—N) at photochemical irradiation or thermal treatment. Nitrenes readily add to alkenes to form three-membered heterocycles, known as aziridines, or insert into carbonehydrogen bonds to form substituted amines.[17] Since the azide decomposition reaction generates nitrogen gas and reactive nitrene intermediates as its exclusive products, bis(azide)s are ideal for crosslinking PTMSP because no low volatility, low molecular weight byproducts are formed that could contaminate the polymer.[16]

In this study, the chemical stability of PTMSP crosslinked with 4,4′-diazidobenzophenone (BAA) is reported (Fig. 1). The permeability, solubility, and diffusivity of various gases in crosslinked PTMSP are presented, and the effect of addition of nanoparticles (FS and TiO_2) on uncrosslinked and crosslinked PTMSP transport properties is reported.

BACKGROUND

Gas transport and free volume in polymers

The permeation of gases and vapors through a dense polymeric membrane is generally described as a solution-diffusion process where permeability, P, is the produce of the gas diffusivity, D, and solubility, S, i.e.,

$$P = DS \qquad (1)$$

The ability of a membrane to separate two molecules, A and B, is the ratio of their permeabilities; here expressed as ideal selectivity $\alpha_{A/B}$,

$$\alpha_{A/B} = P_A/P_B = (D_A/D_B)(S_A/S_B) \qquad (2)$$

where the first-term on the right-hand side is the diffusivity selectivity and the second is the solubility selectivity. The balance between the solubility selectivity and the diffusivity selectivity relates strongly to the material properties and the properties of gases A and B to be separated. The temperature dependency of solubility, diffusivity and permeability may be expressed as the van't Hoff – Arrhenius relationships.[18–20]

$$S = S_0 \exp(-\Delta HS/RT) \qquad (3)$$

$$D = D_0 \exp(-Ed/RT) \qquad (4)$$

$$P = P_0 \exp(-Ep/RT) \qquad (5)$$

where S_0, D_0, and P_0 are pre-exponential factors, ΔH_S is the enthalpy of sorption, E_d is the activation energy of diffusion, E_p ($=E_d + \Delta H_S$) is the activation energy of permeation, R is the ideal gas constant, and T is the absolute temperature.

Molecular diffusion through a dense polymer depends strongly on the amount of free volume that a material possesses; i.e., depending on the structure and the state of the polymer (glassy or rubbery). The quantity used to compare the amount of free volume in polymers is the FFV; usually estimated according to Bondi's method:

$$FFV = (V - 1.3V_W)/V \qquad (6)$$

where V is the polymer specific volume (i.e., reciprocal of geometric density) and V_w is the specific van der Waals volume, which can be calculated by group contribution methods.[21–23] The FFV of PTMSP is 0.29, which is one of the highest values of any known polymer.

A number of techniques may be used to study free volume in polymers, including spin probe methods,[24] molecular modeling,[25,26] inverse gas chromatography,[27] small-angle X-ray scattering,[28] ^{129}Xe NMR,[12,29] and positron annihilation lifetime spectroscopy (PALS).[11,30–32] PALS is one of the most widely applied techniques and provides the most direct and detailed information on the size and concentration of free volume elements in the materials.

EXPERIMENTAL

Instrumental characterization

NMR spectra were recorded on Bruker Avance DPX 400 with chemical shifts reference to tetramethylsilane for deuteriochloroform. Fourier Transform Infrared (FTIR) spectra were recorded on a Thermo Nicolet FTIR Nexus spectrometer. NMR and FTIR spectra were used to confirm chemical structure. UV-vis spectra were recorded on a Varian Cary 50 UV-vis spectrophotometer. Morphology of cross sectional nanocomposites was examined by scanning electron microscopy (LV FESEM, SUPRA^{TM} 55, Zeiss) operating in variable pressure (VP) mode. In such a VP mode, the SEM analysis could be directly performed on non-conducting polymers without coating. The SEM images were acquired collecting the secondary electrons induced by using 5 k eV electron beam and 8 mbar partial pressure.

Synthesis of crosslinking agent

The synthesis and structure of bis azide cross-linking agent is shown in Figure 2. BAA was obtained by diazotization of the corresponding amine (Aldrich Chemicals) followed by nucleophilic displacement of the diazonium salt with NaN_3. The synthetic procedure follows that reported in the literature.[33–36]

BAA (0.50 g, 2 mmol) was dissolved in 2 mL of water containing 1.1 mL of concentrated HC1, and cooled to 0°C, then treated dropwise with a solution of sodium nitrite (0.34 g, 5 mmol) in 1.2 mL of water. After the addition, the reaction was
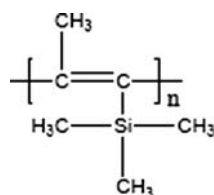
Figure 1 Chemical structure of PTMSP.

maintained at 0–5 °C for 1.5 h. To the resultant clear orange solution was added dropwise 0.31 g (5 mmol) of sodium azide in 1.2 mL of water. The solution was stirred for 15 min, a white precipitate was formed. The solid was collected, washed with water, allowed to dry, dissolved in dichloromethane, and heated with activated charcoal. Filtration and solvent evaporation gave 0.51 g (84%) of pale yellow BAA. ^1H and ^{13}C NMR and FTIR analyses of the product confirmed the chemical structure of BAA (Fig. 2).

Membrane preparation and crosslinking

PTMSP was purchased from Gelest. Before membrane preparation, PTMSP was purified via reprecipitation with methanol. Dense membranes of pure PTMSP, and PTMSP/BAA were cast from toluene solution containing 2.0 wt % polymer. The nanocomposite membranes were prepared by a three-step solvent casting procedure. Filler nanoparticles (FS, TiO_2) were initially dissolved in toluene at room temperature with ultrasonic treatment at 0°C for 30 min followed by stirring with a magnetic stirrer at room temperature for 5 h. The PTMSP (or PTMSP with BAA added) was then dissolved in the filler/toluene dispersion with magnetic stirring for 3 days, after which the solution was poured into a casting ring placed on a glass plate and covered with a funnel to allow for slow solvent evaporation. The casted membranes were dried at room temperature for 6 days and then placed in a vacuum oven at room temperature for at least 24 h to completely remove residual solvent. The final as-cast membrane thicknesses varied from 40 to 50 μm. All membranes were crosslinked by photoirradiation in a vacuum oven at room temperature for 90 min. After 90 min, the peak associated with the azide group in the FTIR spectrum at 2110 cm^{-1} disappeared, indicating that the azide molecules had reacted to form nitrenes. Crosslinking time was kept constant so that each sample had the same photochemical crosslinking history.
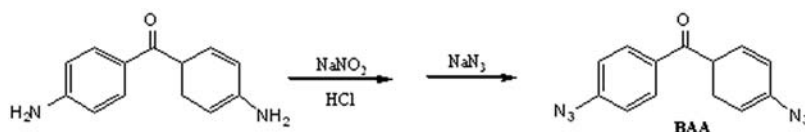
The irradiating wavelength for photochemical crosslinking was set to correspond to the peak of the absorption band for the bisazide BAA, the peak of the absorption is near 302 nm (Fig. 3). Thus 302 nm UV light was used for crosslinking membranes.

Permeability measurements

The membranes were masked using an impermeable aluminum tape, leaving open a defined permeation area. Epoxy was then applied along the interface of the tape and the membrane. A sintered metal disc covered with a filter paper was used as support for the membrane in the test cell. Single gases (N_2, O_2, H_2, CH_4, and CO_2) were measured at 35°C with feed pressure of 2.0 bar using a constant volume/variable-pressure method in a standard pressure–rise setup (MKS Baratron® pressure transducer, 0-134 mbar range) with LabView® data logging. The experimental method and equipment are described elsewhere.[37,38]

The membrane thickness was measured by an electronic Mitutoyo 2109F thickness gauge (Mitutoyo Corp., Kanagawa, Japan). The gauge was a nondestructive drop-down type with a resolution of 1 micron. Flat sheet membrane was scanned at a scaling of 100% (uncompressed tiff-format) and analyzed by Scion Image (Scion Corp., MD) software. This image tool is available from www.scioncorp.com at no cost. The effective area was sketched with the draw-by-hand tool both clockwise and counterclockwise 3-5 times, and the average value of the measurements was used for calculations.

Sorption measurements

The sorption tests were performed in a single chamber apparatus as indicated in Figure 4. For the sorption measurements the following factors received special attention: (1) The volume of the sample cell, the pressure transducer, the tubes and valves were all carefully volume calibrated, and (2) the pressure transducer was kept inside the temperature-regulated chamber to minimize temperature gradients.[39,40]

Sufficient sorption time was always applied, i.e., the evacuation time was as a rule of thumb at least twice the time it took to obtain stable sorption measurement.

The volume calibration was performed in a careful way; evacuating and refilling step-by-step each part of the equipment (chambers, valves, tubing) with an inert gas (helium); all the time keeping control of
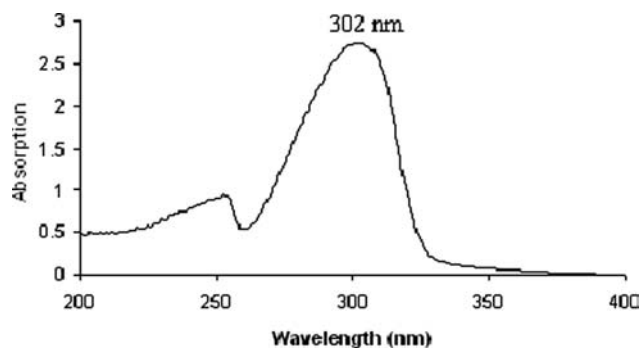

Figure 2 Synthesis of 4,4'-diazidobenzophenone (BAA).

Figure 3 UV-vis spectra of the bis(aryl azide) BAA crosslinking agent used for crosslinking PTMSP membranes.

pressure and perform accurate registrations. An additional known volume is needed to calculate the absolute volumes. This was done by inserting two calibration spheres (known volume of 2.1544 cm³) into the sample chamber. Then by applying the ideal gas law, volumes could be calculated, and volume of the sample chamber, Vol_{ch}, could be determined from ratios, as indicated by eq. (7), where $R2$ and $R2'$ are the volume ratio without and with the calibration sphere, respectively.[39,40]

$$Vol_{ch} = \frac{V_{sphere}}{1 - \left(\frac{R2}{R2'}\right)} \qquad (7)$$

After the membrane sample was loaded into the sample chamber, the sorption system was evacuated for at least 24 h before each test. The sorption was measured as cm³ (STP) gas adsorbed per cm³ material. The tests were performed at 35°C with the pressure range of 1–4 bar. Further details on the experimental method and sorption system can be found elsewhere.[39,40]

RESULTS AND DISCUSSION

Effect of photochemical crosslinking on PTMSP permeation

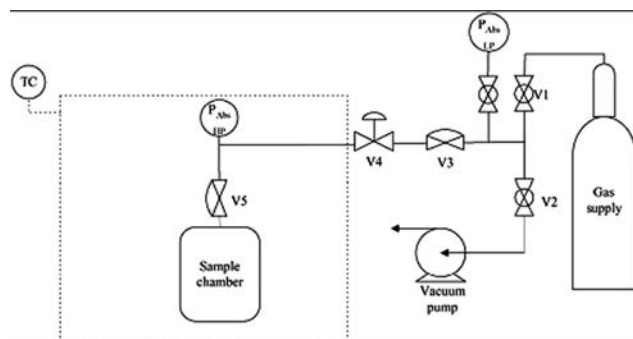The bis azide BAA was used as crosslinking agent. This bis azide easily dissolved in the PTMSP with

solvent to form homogeneous mixtures. At high loadings (> 4.5 wt % BAA) the membranes became cloudy and optical microscopy confirmed phase separation of crosslinker and polymer. All crosslinking studies reported here were performed on clear membranes with a maximum content of 3 wt % BAA, and showed no apparent signs of phase separation. The dried membranes were clear, and UV-vis and FT-IR spectra show that the spectra of the as-prepared membranes are simply the linear combination of the spectrum of PTMSP and that of the azide crosslinker. The reaction between the bis azide crosslinker and PTMSP was observed using FTIR analysis. The stretching vibration for the azide at 2110 cm⁻¹ is easily monitored in the FTIR, and the loss in its intensity can be correlated with the progress of the crosslinking reaction (Fig. 5).

A preliminary indication of significant crosslinking is the lack of solubility of crosslinked membranes in standard solvents for PTMSP. In this regard, crosslinked PTMSP was insoluble in toluene and cyclohexane, which are known to be good solvents for uncrosslinked PTMSP.[16] It was found that when BAA concentration was about BAA 1.0 wt % or higher, PTMSP membranes were insoluble in toluene. The insolubility of crosslinked PTMSP membranes is defined when there is less than 0.5% weight loss in a dry membrane before and after soaking in toluene for 24 h. The crosslinking reactions were studied, a plausible mechanism for the reactions is shown in Figure 6.[16,41] Under photochemical irradiation or thermal treatment the bis azide decomposes to nitrogen gas and reactive nitrenes, the reactive nitrenes insert into a carbon-hydrogen bond in PTMSP to form a substituted amine. Since the carbon-hydrogen bonds in $Si(CH_3)_3$ (~ 100 kcal/mol)[42] are significantly stronger than the carbon-hydrogen bonds in allylic methyl groups
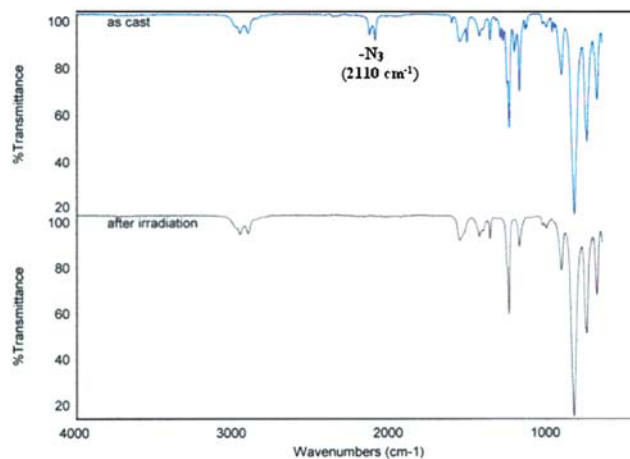

Figure 5 FTIR spectra of PTMSP /3 wt % BAA composite membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]
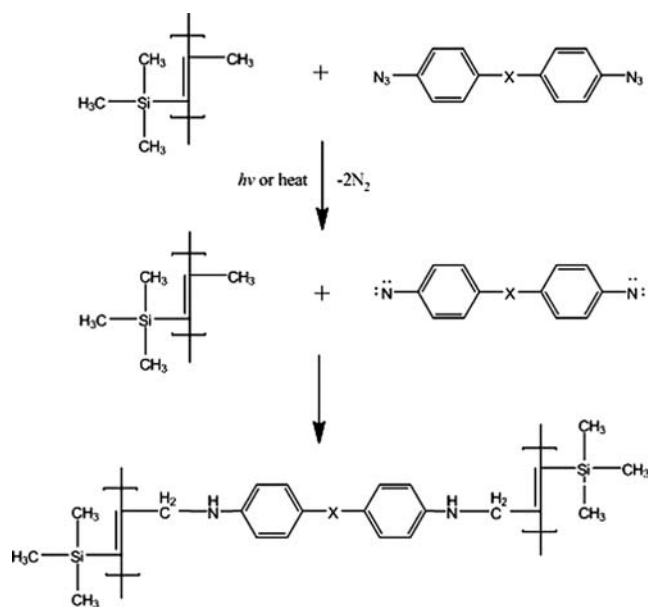

Figure 4 Flow scheme of the sorption apparatus.[40]

Figure 6 Illustration of crosslinking reaction of PTMSP.[16,41]

(C≡C═CH$_3$) (~ 85 kcal/mol)[42], the crosslinking reaction at the allylic methyl groups along the PTMSP backbone should be strongly favored. The azide peak at 2110 cm^{-1} disappears after the PTMSP membrane is crosslinked.

Photochemical crosslinking of membranes with BAA was performed at 302 nm using a lamp at room temperature for 90 min in a vacuum oven. The irradiating wavelength for photochemical crosslinking was set to correspond to the peak of the absorption band for the azide (302 nm).

Permeability data in Table I show membranes with different amounts of crosslinker. For all gases considered with the exception of that for CH$_4$ and N$_2$ (two larger molecules), the addition of bis azide to PTMSP decreased the permeability only slightly before photo-irradiation, with hardly any improvement of selectivity (Table II); again with the exception of that for CO$_2$/CH$_4$ and CO$_2$/N$_2$. The crosslinked membranes show a significant decrease in permeabilities (Table I) for all gases except for H$_2$

(the smallest molecule), steadily decreasing with crosslinker content increase. The selectivities of O$_2$/N$_2$, H$_2$/N$_2$, CO$_2$/N$_2$, CO$_2$/CH$_4$ and H$_2$/CH$_4$ increased with increasing amount of crosslinker. Higher degrees of crosslinking resulted in a lower gas permeability and higher selectivity.

Blanks were run for photochemical reactions (row 1 in Tables I and II), to study the effects of irradiation on the properties of pure PTMSP. When membranes were irradiated at 302 nm for 90 min (the condition used for the irradiation of PTMSP/BAA composites), the selectivities of O$_2$/N$_2$, H$_2$/N$_2$, CO$_2$/N$_2$, CO$_2$/CH$_4$ and H$_2$/CH$_4$ improved and the permeabilities decreased. There is a large reduction in permeation for N$_2$ and CH$_4$.

For photochemical crosslinking, the permeability changes in going from pure PTMSP, to PTMSP with azide additive, to the crosslinked membrane were predictable. For example, the azide additive in composite membranes is expected to occupy much of the free volume in the polymer and thus the permeability is lower compared with pure PTMSP membranes. Crosslinking connects adjacent chains, increases the local segment density, and causes a further decline in the permeability.

The initial permeability of PTMSP decreased with increasing crosslinking due to the loss in FFV. The selectivities of O$_2$/N$_2$, H$_2$/N$_2$, CO$_2$/N$_2$, CO$_2$/CH$_4$ and H$_2$/CH$_4$ increased as the FFV decreased, showing that crosslinked PTMSP is more size selective to gases than uncrosslinked PTMSP.

Permeation through uncrosslinked PTMSP nanocomposite membranes

FS and TiO$_2$ were used as fillers, and the membranes prepared as described above. The data in Table III and Table IV show that the permeation and selectivity results obtained with the uncrosslinked filled PTMSP membranes increased for all gases as the filler content increased. The permeability increased about 38%–66% for all the gases in the PTMSP membrane filled with 35 wt % FS, and about 35%–63% for all the gases in the PTMSP membrane filled with 35 wt % TiO$_2$. The

TABLE I
Gas Permeabilities [Barrer][a] of Uncrosslinked and Photochemically Crosslinked PTMSP Membranes at 35°C and Feed Pressure of 2.0 Bar

Crosslinking agent		Before crosslinking					After crosslinking				
Azide	Azide wt%	N$_2$	O$_2$	H$_2$	CH$_4$	CO$_2$	N$_2$	O$_2$	H$_2$	CH$_4$	CO$_2$
None[b]	0	5180	7870	13850	12670	28590	4280	7120	13110	9350	25890
BAA	1.1	4470	6930	13020	9050	24980	1150	3670	9960	2140	13680
BAA	2.0	3560	6170	12560	7580	22770	780	2790	9120	1430	11120
BAA	3.0	2750	5020	11530	5980	19810	590	2230	7850	1070	8870

[a] Perneability is in unit of Barrer (1 Barrer = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1}cmHg $^{-1}$).
[b] Irradiated at 302 nm for 90 min.

TABLE II
Selectivities[a] of Various Gas Pairs in Uncrosslinked and Photochemically Crosslinked PTMSP Membranes

Crosslinking agent		Selectivity (before crosslinking)					Selectivity (after crosslinking)				
Azide	wt % Azide	O_2/N_2	H_2/N_2	CO_2/N_2	CO_2/CH_4	H_2/CH_4	O_2/N_2	H_2/N_2	CO_2/N_2	CO_2/CH_4	H_2/CH_4
None[b]	0	1.5	2.7	5.5	2.3	1.1	1.7	3.1	6.0	2.8	1.4
BAA	1.1	1.6	2.9	5.6	2.8	1.4	3.2	8.7	11.9	6.4	4.7
BAA	2.0	1.7	3.5	6.4	3.0	1.7	3.6	11.7	14.3	7.8	6.4
BAA	3.0	1.8	4.2	7.2	3.3	1.9	3.8	13.3	15.0	8.3	7.3

[a] Selectivity is the ratio of the permeabilities for the pure gases.
[b] Irradiated at 302 nm for 90 min.

selectivities of CO_2/N_2, CO_2/CH_4, and CH_4/N_2 decreased slightly as the filler content increased. For these gas pairs at the temperature measured (35°C) in this high free volume polymer, the selectivity is determined primarily by differences in the sizes and hence the diffusion coefficients of the gases. The non-ideal properties of CO_2 also contributes to the relatively higher selectivity of CO_2/N_2 compared with CO_2/CH_4. The slight loss of selectivity indicates that the addition of the filler to the PTMSP matrix created larger gaps in the interconnected free volume of the filled membranes, thereby increasing the diffusion coefficient of the larger molecule proportionately more than the smaller molecule. The selectivities of O_2/N_2 and CH_4/N_2 remained about the same as loading increased, because the CH_4 and N_2 molecules are similar in size and not to different in physical properties, so both diffusion coefficients increases by roughly the same factor. The same holds for the gas pair $O_2 - N_2$. The selectivity of H_2/CH_4 increased slightly as the filler content increased, which indicates that there is a relatively higher increase in the permeability of H_2 than that of CH_4 with increasing the filler to the PTMSP matrix.

As mentioned above, the particle sizes of FS and TiO_2 are different (FS with a primary particle size of 7 nm and TiO_2 with a primary particle size of 21 nm), the data obtained in Tables III and IV showed that at a fixed filler volume fraction, these two different PTMSP/filler nanocomposites showed a small difference in gas permeability; the smaller FS particles

seem to produce a larger increases in permeability at a constant filler volume fraction. This result is most likely related to smaller particles yielding larger polymer/particle interfacial area, since at a fixed volume fraction of particles there is a large number of small particles per unit volume of nanocomposite, which gives them a greater capacity to disrupt chain packing, thereby affecting transport property.

Permeation through crosslinked PTMSP nanocomposite membranes

Repeated permeability measurements were performed with the same fillers (FS, TiO_2) at the same concentrations, however, now crosslinked using 2 wt % of the crosslinker BAA. The results are presented in Figure 7(a–e).

The effect of increasing the filler content on CO_2 permeability, CO_2/N_2 and CO_2/CH_4 selectivities of crosslinked PTMSP membranes containing 2 wt % BAA is shown in Figure 7(a-b). Compared with the pure PTMSP membrane, the CO_2, N_2, and CH_4 permeabilities of the crosslinked membrane are now initially being reduced due to the crosslinking with a fairly large increase in selectivities. By adding the nanoparticles (FS, TiO_2), the permeabilities are again increased, whereas the CO_2/N_2 and CO_2/CH_4 selectivities show only a small decrease. However, with the filler content increased, the selectivities of crosslinked PTMSP/filler nanocomposite membranes are significantly increased compared with the pure

TABLE III
Gas Permeabilities and Selectivies of Pure PTMSP and PTMSP/FS Nanocomposite Membranes at 35°C and Feed Pressure of 2.0 Bar

Silica content (wt %)	Permeability[a]					Selectivity[b]					
	N_2	O_2	H_2	CH_4	CO_2	O_2/N_2	H_2/N_2	CO_2/N_2	CH_4/N_2	CO_2/CH_4	H_2/CH_4
0 (pure PTMSP)	5180	7870	13850	12670	28590	1.5	2.7	5.5	2.4	2.3	1.1
15	5340	8120	14110	12970	28960	1.5	2.6	5.4	2.4	2.2	1.1
25	7120	10980	19470	16750	36750	1.5	2.7	5.2	2.4	2.2	1.2
35	8210	11960	22960	18320	39280	1.5	2.8	4.8	2.2	2.1	1.3

[a] Perneability is in unit of Barrer (1 Barrer = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cmHg $^{-1}$).
[b] Selectivity is the ratio of the permeabilities for the pure gases.

TABLE IV
Gas Permeabilities and Selectives of Pure PTMSP and PTMSP/TiO₂ Nanocomposite Membranes
at 35°C and Feed Pressure of 2.0 Bar

TiO$_2$ (wt %)	Permeability[a]					Selectivity[b]					
	N$_2$	O$_2$	H$_2$	CH$_4$	CO$_2$	O$_2$/N$_2$	H$_2$/N$_2$	CO$_2$/N$_2$	CH$_4$/N$_2$	CO$_2$/CH$_4$	H$_2$/CH$_4$
0 (pure PTMSP)	5180	7870	13850	12670	28590	1.5	2.7	5.5	2.4	2.3	1.1
15	5230	7980	13940	12780	28870	1.5	2.7	5.5	2.4	2.3	1.1
25	6910	10230	18760	16210	36210	1.5	2.7	5.2	2.3	2.2	1.2
35	7950	11540	22810	18220	38980	1.5	2.9	4.9	2.3	2.1	1.3

[a] Perneability is in unit of Barrer (1 Barrer = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cmHg $^{-1}$).
[b] Selectivity is the ratio of the permeabilities for the pure gases.

PTMSP membrane. The data obtained show that at a fixed filler volume fraction, crosslinked PTMSP/FS nanocomposites have a little higher CO$_2$ permeability and a trend of a little lower selectivities of CO$_2$/N$_2$ and CO$_2$/CH$_4$, compared with crosslinked

PTMSP/TiO$_2$ nanocomposites. The increase in permeability upon filling was attributed to increased free volume in the nanoparticle-filled PTMSP nanocomposites as compared to the unfilled polymer. In the crosslinked PTMSP it was documented that with
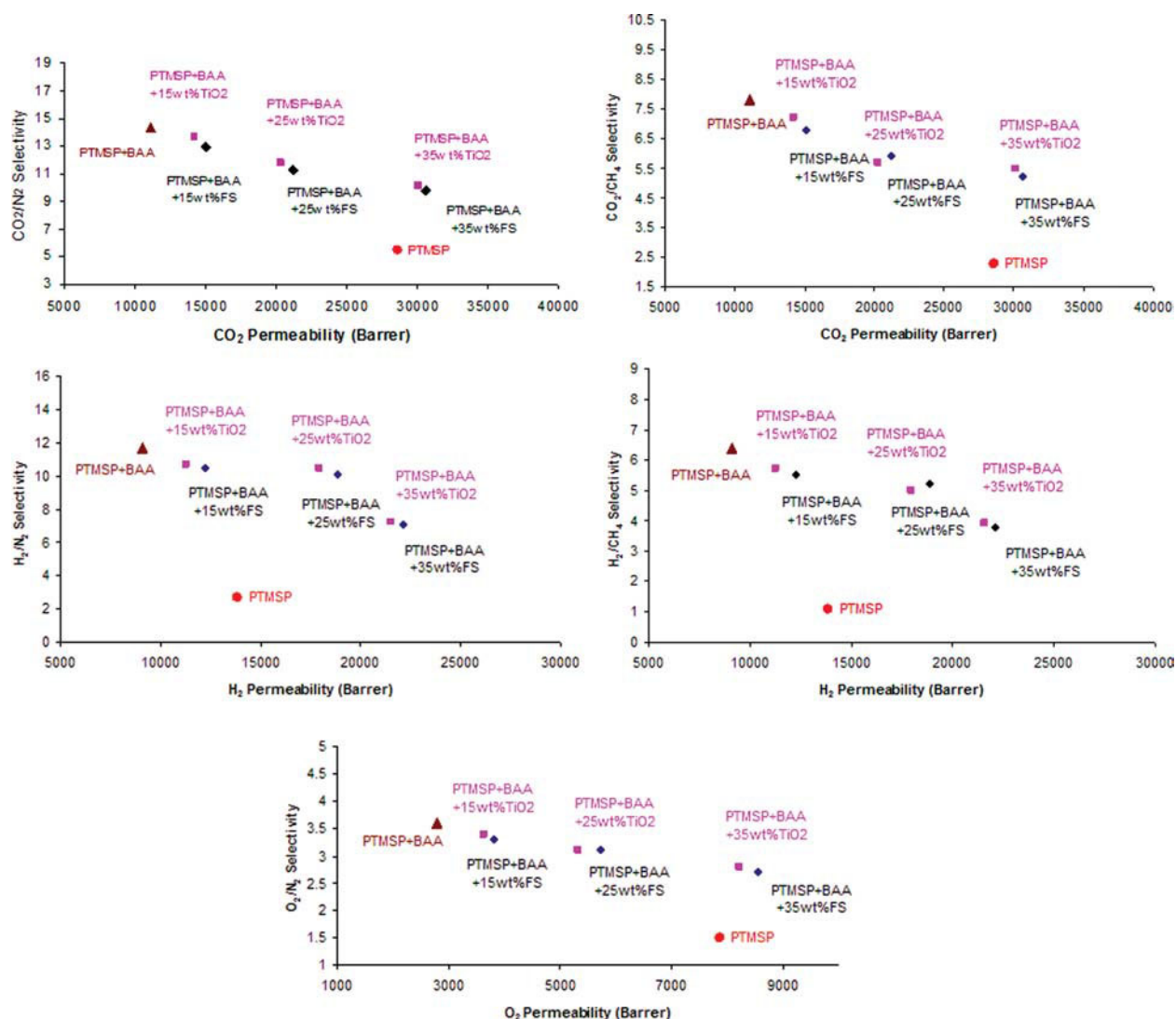

Figure 7 (a–e) The effect of nanoparticles (FS, TiO$_2$) content on gas permeabilities and selectivities of crosslinked PTMSP membranes containing 2 wt % BAA crosslinker. Temperature: 35°C; Feed pressure: 2.0 bar. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]
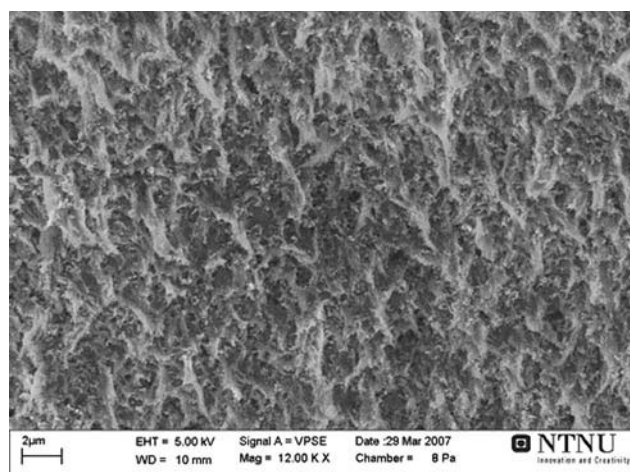
Figure 8 SEM photomicrograph of cross-section of crosslinked PTMSP + 2 wt % BAA + 25 wt % FS membrane.

a filler content of around 35 wt % FS or TiO_2, the permeability of the CO_2 is about the same as that of pure PTMSP, but the selectivity of both CO_2/CH_4 and CO_2/N_2 in the crosslinked PTMSP is now doubled. The decrease in selectivity with increased filler content for the crosslinked nanocomposite membranes, indicates that the addition of the filler to the PTMSP matrix creates larger gaps in the interconnected free volume of the filled membranes, thereby increasing the diffusion coefficient of the larger molecule proportionately more than the smaller molecule.

The effect of increasing the filler content on H_2 permeability, H_2/N_2 and H_2/CH_4 selectivities of crosslinked PTMSP membranes containing 2 wt % BAA is shown in Figure 7(c,d). Similarly, the H_2 permeability of the crosslinked membrane is also initially reduced because of crosslinking compared with the pure PTMSP membrane. After adding nanoparticles (FS, TiO_2), the H_2 permeability is increased again, while the H_2/N_2 and H_2/CH_4 selectivities decreased as the filler content increased. Howerer, compared with the pure PTMSP membrane, the selectivities of crosslinked PTMSP/filler nanocomposites are also increased significantly. Already at a filler content of 25 wt %, the H_2 permeability is restored more than the pure PTMSP, while the selectivities are increased about four times.

Similarly, the O_2 permeability of the crosslinked membrane is also initially reduced due to crosslinking compared with the pure PTMSP membrane. After adding nanoparticles (FS, TiO_2), the O_2 permeability is increased again, while the O_2/N_2 selectivity showed very little decrease with the filler content increased. Compared to the pure PTMSP membrane, the O_2/N_2 selectivity of crosslinked PTMSP/filler nanocomposite is significantly increased [Fig. 7(e)].

The distribution of FS nanoparticles in crossliked PTMSP/FS membrane is shown in the scanning elec-

tron microscopy (SEM) image presented in Figure 8. It can be seen that these particles are relatively well dispersed in PTMSP, consistent with weak polymer-filler interactions. In addition, the SEM images also indicate that some nanoparticles aggregate into clusters. The concentration of particles increases with nanoparticles loading.

Effect of pressure and temperature on gas transport properties of crosslinked PTMSP/FS nanocomposite membranes

The permeabilities of crosslinked PTMSP/FS nanocomposite membranes were determined as a function of feed pressure at 35°C. The measurements were carried out with N_2 and CO_2, two very different gases. As shown in Figure 9, the permeabilities of N_2 and CO_2 are essentially independent of gas pressure under the experimental conditions of this study (up to 10 bar). These results are similar to the results of pure PTMSP membranes reported in the literature.[11]

The permeabilities of crosslinked PTMSP/FS nanocomposite membranes to N_2 and CO_2 were determined at temperatures ranging from 35 to 70°C; the feed pressure was 2.0 bar. The results are shown in Figure 10. The permeabilities of N_2 and CO_2 decreased significantly with increasing temperature. These results are similar to the results of pure PTMSP membranes reported in the literature.[11]

The activation energy of permeation, E_p, is the sum of the activation energy of diffusion, E_d, and the heat of sorption, ΔH_S. Diffusion through polymers is an activated process; therefore, diffusion coefficients always increase with temperature, that is, E_d is always positive (see eq. (4)). In most polymers, solubility of gases decreases with temperature; therefore, ΔH_s is generally negative. In conventional glassy polymers, such as low free volume polyimide, gas permeabilities increase with increased temperature for both permanent and condensable gases,
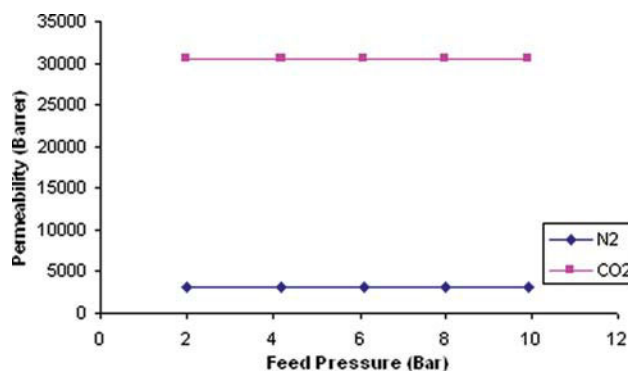

Figure 9 Gas permeabilities of crosslinked PTMSP + 2 wt % BAA + 35 wt % FS nanocomposites as a function of feed pressure; T = 35°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]
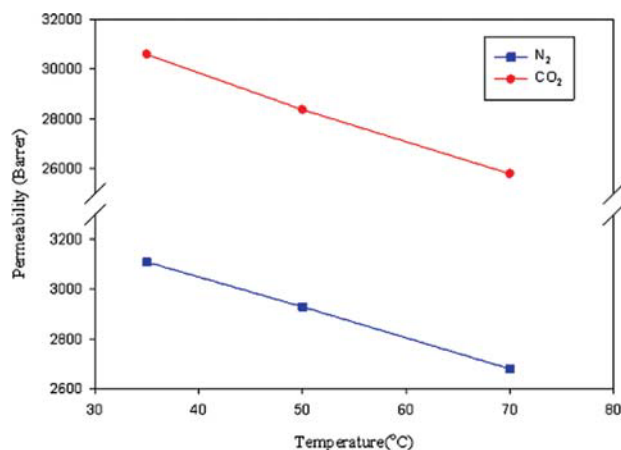
Figure 10 Gas permeabilities of crosslinked PTMSP + 2 wt % BAA + 35 wt % FS nanocomposites as a function of temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

because the positive value of E_d is typically much larger than that of the negative heat of sorption.[43,44] Conventional glassy polymers show positive activation energy of permeation because the activation energy of diffusion is larger than the heat of sorption. Two notable exceptions to this behavior are PTMSP and PMP;[11,45] in these high free volume, glassy polymers the activation energy of permeation is always negative, even for small permanent gases, such as helium, hydrogen, and nitrogen. Hence, in these high free volume acetylene-based polymers, permeability decreases with increasing temperature. A comprehensive investigation of this was, however, not undertaken in the current project.

Solubility of nitrogen and methane

Figure 11 presents nitrogen sorption isotherms in uncrosslinked PTMSP, crosslinked PTMSP containing 3.0 wt % BAA and crosslinked PTMSP/FS containing 2.0 wt % BAA crosslinker at 35°C. Within experimental uncertainty, nitrogen sorption levels in uncrosslinked PTMSP, crosslinked PTMSP and PTMSP/FS are equivalent. The permeability (P) is described as the product of the gas diffusivity (D) and solubility (S) [eq. (1)]; hence the decrease in permeability in crosslinked PTMSP and PTMSP/FS is most likely due to a decrease in the diffusivity caused by a reduced FFV. This trend would also be expected for an ideal gas like nitrogen with very low sorption level.

Figure 12 presents methane sorption isotherms in uncrosslinked PTMSP, crosslinked PTMSP containing 3.0 wt % BAA and crosslinked PTMSP/FS containing 2.0 wt % BAA at 35°C. The isotherms are slightly concave to the pressure axis, which is typical behaviour for gas sorption of non-ideal gases in glassy polymers.[21] Methane has about the same molecular size as
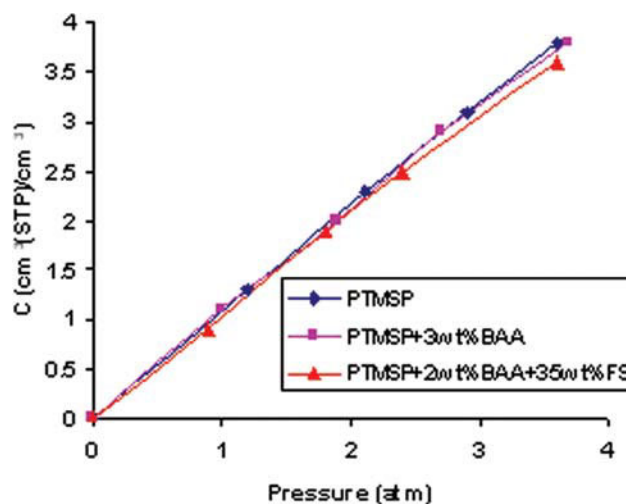

Figure 11 Nitrogen sorption in uncrosslinked PTMSP, crosslinked PTMSP containing 3.0 wt % BAA and crosslinked PTMSP/FS containing 2.0 wt % BAA crosslinker at 35°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

nitrogen, but is less ideal, hence the slightly more concave curve at higher pressures was expected. Consistent with the nitrogen data provided in Figure 11, methane sorption data in PTMSP are independent of BAA crosslinker content, indicating that methane solubility in PTMSP containing varying amounts of BAA is virtually identical to that in the pure polymer – again in this low pressure region.

Membrane stability

The stability of the uncrosslinked and crosslinked PTMSP, crosslinked PTMSP/filler membranes stored
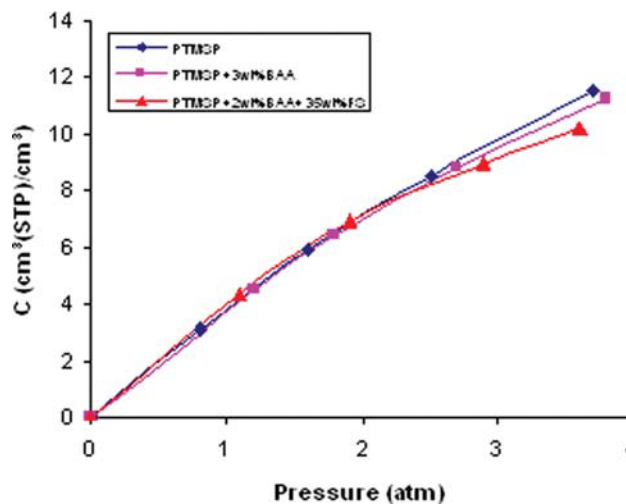

Figure 12 Methane sorption in uncrosslinked PTMSP, crosslinked PTMSP containing 3.0 wt % BAA and crosslinked PTMSP/FS containing 2.0 wt % BAA crosslinker at 35°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]
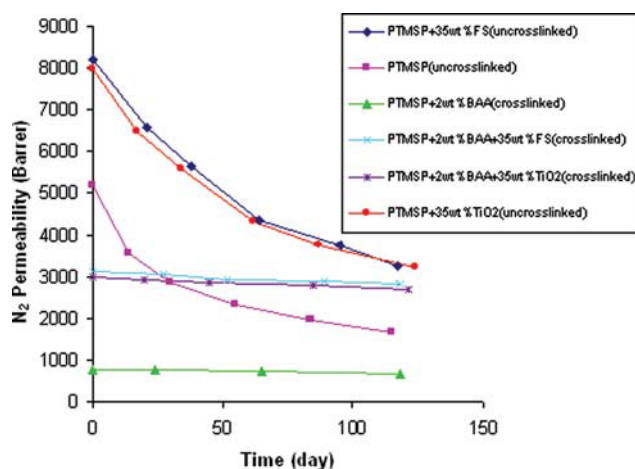
Figure 13 The stability of uncrosslinked and crosslinked PTMSP, PTMSP/filler membranes measured as nitrogen permeability. Temperature: 35°C; Feed pressure: 2.0 bar. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

in air were checked over time. The results are shown in Figure 13. The nitrogen permeabilities of crosslinked PTMSP and crosslinked PTMSP/filler membranes were almost constant over a period of 4 months. The uncrosslinked PTMSP and PTMSP/filler membranes showed a large decrease in the nitrogen permeability during the same time. PTMSP undergoes significant physical aging over time caused by the gradual relaxation of non-equilibrium excess free volume in glassy polymers. The permeability stability of crosslinked PTMSP and crosslinked PTMSP/filler membranes for the gas is clearly improved.

CONCLUSIONS

The chemical stability of crosslinked PTMSP is strongly enhanced using BAA bisazide. After crosslinking, the PTMSP membranes were insoluble in good solvents for PTMSP such as toluene and cyclohexane. Compared with the pure PTMSP membrane, the permeability of the crosslinked membrane is initially reduced for all gases tested due to the crosslinking. By adding nanoparticles (FS, TiO_2), the permeability is again increased. The selectivities of O_2/N_2, H_2/N_2, CO_2/N_2, CO_2/CH_4 and H_2/CH_4 increased with increasing amount of crosslinker. Crosslinking is successful in maintaining the permeability and selectivity of PTMSP membranes and PTMSP/filler nanocomposites over time.

The sorption levels of N_2 and CH_4 were measured and found to be independent of crosslinker content, within experimental uncertainty. Therefore gas solubility in PTMSP does not seem to be affected by the FFV decrease accompanying the increase in crosslinker content. The permeability (P) is described as

the product of the gas diffusivity (D) and solubility (S), hence the decrease in permeability in crosslinked PTMSP is most likely due to a decrease in the diffusivity.

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