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**Multilayer composite membranes for gas separation based on crosslinked PTMSP gutter layer and partially crosslinked Matrimid® 5218 selective layer**

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# Multilayer composite membranes for gas separation

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## 1. Introduction

In the last decades we can observe an increasing motivation to utilize polymer membranes in industrial gas separation processes (eg. nitrogen production from air, CO<sub>2</sub> removal from natural gas, dehydration of gas streams, separation of organic vapors from air and many others) For some of these applications membrane separation has lower energy consumption and investment costs [1-3]. Additionally, they are environmental friendly compared to traditional thermally driven processes.

For most commercial membrane-based gas separation applications non-porous membranes are being used. The transport of gases in dense polymeric films can be described by the solution-diffusion model [4]. Different diffusivities and solubilities of gases in a polymer determine the dense polymer membrane separation factor. In order to obtain sufficiently high gas fluxes the film thickness should be as low as possible. On the other hand, low membrane thickness causes poor mechanical stability and/or membrane handling difficulties. These problems could be overcome by using composite membranes consisting of a thin selective layer on a microporous support [5,6].

Essential requirement for poly[1-(trimethylsilyl)prop-1-yne] composite membranes is a defect-free selective top-layer which is often problematic to prepare especially from glassy polymers. Each microscopic defect (pinhole) enables a viscous and / or Knudsen flow through it and drastically decreases the top layer selectivity. Effect of pinholes could be eliminated by coating a selective layer with a other thin layer of a highly permeable polymer such as PDMS. PDMS seals microdefects and significantly increases membrane selectivity with almost no permeability drop [7,8].

Penetration of glassy polymer into the support pores has another negative influence on the membrane performance. The penetrated polymer causes pore blockage and gas molecules should pass longer distances in a very low-permeable selective polymer. When a support with lower porosity is coated with a selective layer, the gas flux through the membrane is reduced due to an increasing effective thickness. A simplified geometry of a composite membrane is shown in Fig. 1 and the effective thickness of the membrane is defined by equation 1. This equation can be found in ref. [9]. We use it in corrected version here. Furthest point to closest pore is represented by letter A,  $l_{\max}$  represents longest distance that diffusing gas molecules should pass,  $l_0$  is selective layer thickness and  $r$  is pore radius. Support porosity  $\varepsilon$  is defined for cylindrical pores by equation 2, where  $n_p$  is number of pores present in membrane area  $A_m$ .

$$l_{\text{eff}} = \varepsilon l_0 + (1-\varepsilon) \frac{l_{\max} + l_0}{2} = \varepsilon l_0 + (1-\varepsilon) 0.5 \left[ \sqrt{r^2 \frac{(1-\varepsilon)^2}{\varepsilon^2} + l_0^2} + l_0 \right] \quad (1)$$

$$\varepsilon = n_p \cdot \pi r^2 / A_m \quad (2)$$



Figure 1  
Simplified geometry of the composite membrane crosssection used for effective thickness derivation (a); introduction of gutter layer between support and selective layer (b)

The introduction of an additional “gutter” layer between the selective top-layer and porous support can help overcome both these problems at once. The pore-free and highly permeable gutter layer acts as adhesion and channeling medium [10,13]. The gutter layer could virtually decrease the effective thickness of the selective layer by providing rapid penetration of gas molecules from the selective layer to closest pores.

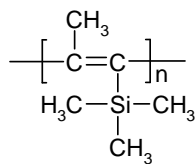
In our work we designed new multilayer composite membranes based on soluble polyimide (Matrimid 5218) as a selective layer, poly[1-(trimethylsilyl)prop-1-yne] (PTMSP) as an interlayer and microporous supports developed in GKSS. Matrimid 5218 is an attractive material for gas separation membranes due to a combination of relatively high gas permeability coefficients and separation factors coupled with excellent mechanical properties, solubility in non-hazard organic solvents and, last but not least, commercial availability [14,15]. PTMSP is the most permeable polymer known and it has better adhesion to other materials than PDMS. Because PTMSP is soluble in many solvents, coating its layers with other polymer solutions is complicated, crosslinking of PTMSP with bis(3-azidophenyl) sulfone (BAPS) was performed [16,17]. The effect of the gutter layer on gas transport properties of composite membranes was studied in comparison with the effect of PDMS sealing layer.

## 2. Experimental

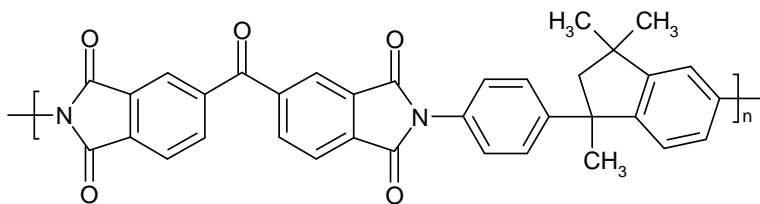
### 2.1 Materials

PTMSP was purchased from Gelest, Inc. Philadelphia, USA and was used without further purification. IR spectra of PTMSP were measured and they corresponded to the expected structure for the pure polymer [18]. Molecular weight of purchased PTMSP was estimated on 210 kDa (see 2.4.1).

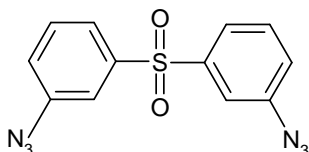
Matrimid<sup>®</sup> 5128 was purchased from Ciba Specialty Chemicals Company and Huntsman in powder form. The polymer was used as received due to TGA investigation showing no volatile residues. Elastosil<sup>®</sup> A43 – poly(dimethylsiloxane) (PDMS) containing acetic acid crosslinking system active at room temperature was supplied by Wacker Chemie AG, Germany. Crosslinking agents bis(3-azidophenyl) sulfone (BAPS) and 1,2-xylylendiamine (XDA) was supplied by Sigma-Aldrich and used without further purification. Polymers and crosslinking agents are shown in Figure 1. Solvents as cyclohexane, isooctane, chloroform and tetrahydrofuran (THF) were purchased from Merck and used as received. Gases were purchased from Air Liquide, Linde AG and Messer and had a purity of at least 99.99 %.



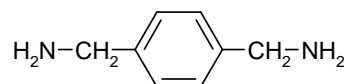
poly[1-(trimethylsilyl)prop-1-yne]  
(PTMSP)



Matrimid<sup>®</sup> 5128



Bis(3-azidophenyl) sulfone (BAPS)



1,2-xylylendiamine (XDA)

## 2.2 Homogeneous dense membrane preparation

### 2.2.1 PTMSP and modified PTMSP membranes

The membranes were prepared by casting a 2wt.% PTMSP solution in cyclohexane, previously filtered (18  $\mu\text{m}$  metal mesh filter), onto a Teflon<sup>®</sup> casting ring plate at room temperature. The cast solution was partly covered to permit slow solvent evaporation. The membranes were dried for 24 h, then easily removed from the plate, and further dried in a vacuum oven at 45 °C for 12 h to remove residual solvent. To prepare modified membranes, PTMSP and 5 wt.% of BAPS were codissolved in cyclohexane, and membranes were then cast from the solution (previously filtered).

Crosslinking of BAPS containing membranes was induced either thermally or by UV irradiation. Thermal crosslinking of the membranes was carried out in a vacuum oven at 175 °C for 2-4 h depending on the membrane thickness. Photo crosslinking was performed in Helios Italquartz U.V. polymerization unit with Zp-type lamp (emission maximum at 300 – 310 nm) in nitrogen atmosphere for 10 min.

### 2.2.2 Matrimid<sup>®</sup> 5218 and modified Matrimid<sup>®</sup> 5218 membranes

Dense homogeneous membrane of Matrimid<sup>®</sup> 5218 was prepared by casting 5 wt. % polymer solution in chloroform, previously filtered, on a leveled glass plate and drying under a dry nitrogen flow. Glass plate was slightly heated at 35 °C. When the solvent evaporation was complete the membrane was delaminated from the glass with deionized water and placed into the methanol bath for 24 h for solvent exchange. The membrane was dried for 24 h at 100 °C under vacuum for complete removal of any volatile impurities.

Modified Matrimid<sup>®</sup> 5218 membranes were prepared similarly from 5 wt. % chloroform polymer solutions which were stirred with 0.5 – 5 wt.% (relative to polymer) of XDA crosslinking agent at 35 °C. Temperature dependence was measured in interval of 20 – 50 °C for system containing 1 wt. % of XDA. Polymer solutions were stirred for 2 – 180 min before

the polymer gel formation. The solution was diluted to 3 wt. %, then filtered and cast onto glass plates and treated as in case of purchased Matrimid<sup>®</sup> 5218.

## 2.3 Preparation of multilayer composite membranes

### 2.3.1 Preparation of asymmetric porous support membrane

Polyacrylonitrile (PAN) solution dissolved in N-methylpyrrolidone (NMP) was cast with a pilot scale membrane casting machine onto a moving belt of poly(1,4-phenylene sulfide) (PPS) non-woven support. The belt then passed into a cold water bath which precipitated the polymer to form the asymmetric, microporous support membrane (later called PAN/PPS porous support). The membrane was then washed for several hours and dried at 80 °C.

### 2.3.2 Preparation of multilayer composite membranes

*Laboratory scale:* Two-sided 10x15 cm envelopes made from PAN/PPS asymmetric porous support membrane were hand-dipped into the bath of a filtered 0.5 wt. % PTMSP solution in cyclohexane containing dissolved BAPS (5 wt. % relative to PTMSP). Envelopes were immersed for 5 s and then gently removed from bath and dried in an air flow oven at 40 °C for 20 min. The same procedure was also performed with the envelopes, in which the pores were filled with deionized water and their surface was gently dried with precision cellulose wipes (wet supports). Dried membrane envelopes were heated in vacuum oven at 175 °C for 30 min or irradiated on the top in a 500 W Helios Italquartz U.V. Polymerization unit for 1 min to crosslink the PTMSP gutter layer. After thermal and also photo treatment, the membranes were slightly curled. Envelopes were then hand-dipped in the bath of 0.25 – 1 wt. % Matrimid<sup>®</sup> 5218 or modified Matrimid<sup>®</sup> 5218 solution in chloroform or THF and dried in an oven in nitrogen flow at 40 °C for 20 min.

*Pilot scale:* Similarly as on the laboratory scale, the same PTMSP solution with the crosslinking agent was cast on the moving 50-cm wide belt of asymmetric porous support membrane using the pilot scale casting machine. The belt then passed the drying section at 40 °C with the movement speed 4 m/min. The belt was then continuously irradiated with 500 W Helios Italquartz U.V. Polymerization lamp at movement speed of 0.5 m/min to crosslink the PTMSP gutter layer. Finally a 0.5 wt. % Matrimid<sup>®</sup> 5218 or modified Matrimid<sup>®</sup> 5218 solution in chloroform was cast on the crosslinked PTMSP gutter layer at a speed of 4 m/min and then dried in air flow at 45 °C. From each fabrication step, representative samples were taken out.

## 2.4 Measurements

### 2.4.1 Viscosity measurement

Intrinsic viscosities ( $\eta$ ) of purchased PTMSP were determined with an Ostwald type viscometer (capillary diameter  $D_1 = 0.51$  mm) using solutions of cyclohexane at 30 °C, with polymer concentrations ranging from 0.10 to 0.50 (g/dL). Molecular weight was determined according to the Mark – Houwing – Sakurada equation  $[\eta] = K \times (M_w)^a = 4.46 \times 10^{-6} (M_w)^{1.04}$  [19].

To determine optimal time of the crosslinking reaction of Matrimid® 5218 with XDA, a filtered sample of reaction system was taken out in the selected time periods to measure its viscosity by cone-plate Brookfield R/S-CPS rheometer with cone spindle C25-1. Measurements were performed at constant temperature (20 °C) and constant shear rate and viscosity was measured as a function of time.

#### 2.4.2 Thermal analysis

Differential scanning calorimetry (DSC) was conducted with a Netsch DSC 204 at a heating range of 20 K/min with nitrogen used as a protective gas. The thermogravimetric analyses (TGA) were conducted with a Netsch TGA 209 at a heating rate of 10 K/min in an argon atmosphere.

#### 2.4.3 Gas separation

Gas permeability, diffusion and solubility coefficients were determined for dense, isotropic membranes using a time-lag apparatus based on the barometric method described elsewhere [20]. Permeability values were determined from the slope of a plot of downstream pressure versus time after attainment of the steady state [21]. Gas diffusivities were estimated from the time-lag data ( $\theta$ ), using the relation:

$$D = \frac{l^2}{6\theta} \quad (1)$$

where  $l$  is the film thickness and  $\theta$  is the time-lag [21]. A precision of 0.1 s for the time lag determination allowed the determination of the diffusion coefficients of helium and hydrogen. Apparent solubility coefficients were calculated using the following equation:

$$S = P / D \quad (2)$$

The overall selectivity of a polymer membrane for a pair of gases  $i$  and  $j$  is commonly expressed in terms of an ideal separation factor,  $\alpha_{ij}$ , defined by the following relation:

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{S_i}{S_j} \cdot \frac{D_i}{D_j} \quad (3)$$

where  $P_i$  and  $P_j$  are pure gas permeabilities,  $D_i/D_j$  is the mobility (or diffusivity) selectivity and  $S_i/S_j$  the solubility selectivity. All time-lag measurements were performed at 30 °C.

Asymmetric membranes were tested for gas permeance using the semiautomatic apparatus based on the mentioned barometric method. The setup allows to program the testing sequence with up to 6 individual gases at feed pressures up to 1.3 bar in the temperature range 20– 80 °C.

The thickness of all homogeneous membranes was determined using a Fischer Deltascope MP2C electronic micrometer having the accuracy 0.2  $\mu\text{m}$ . Only membranes having a thickness deviation lower than 0.5  $\mu\text{m}$  were used for gas transport tests.

#### 2.4.4 *Infrared spectroscopy*

The chemical structure changes of modified PTMSP and Matrimid were monitored with a Bruker Equinox55 using the transmission method for very thin homogenous dense films and total reflection method (FT-IR-ATR) for composite membranes.

#### 2.4.5 *Electron microscopy*

The morphology of the prepared membranes was analyzed by scanning electron microscopy (SEM). Samples were immersed in isopropyl alcohol and fractured in liquid nitrogen. The non-woven support was cut with a scalpel. The samples were coated with Au/Pd by sputtering and observed in a field emission scanning electron microscope LEO Gemini 1550 VP.

### 3. Results and discussion

#### 3.1 Dense PTMSP membranes

5 wt. % of the crosslinking agent BAPS was dissolved in PTMSP solution in cyclohexane. During solvent evaporation from the cast films, no apparent signs of phase separation were observed. The dry films were transparent; IR and also UV/vis spectra showed combination of spectrum of PTMSP and that of the azide crosslinker. The stretching vibration of the azide group at  $2100\text{ cm}^{-1}$  could be easily monitored in IR, and loss in its intensity could be correlated with the progress of crosslinking. During crosslinking, most of azide groups were converted to nitrene groups which then reacted with PTMSP chains to form polymer network. There are two possible crosslinking sites on the PTMSP backbone: double bonds and methyl groups in the side chains, but the latter are more probable since the access to double bonds is sterically hindered [16,22,24]. After crosslinking, the characteristic intensity of the azide stretching vibration at  $2100\text{ cm}^{-1}$  significantly decreased or disappeared completely (Fig. 2).

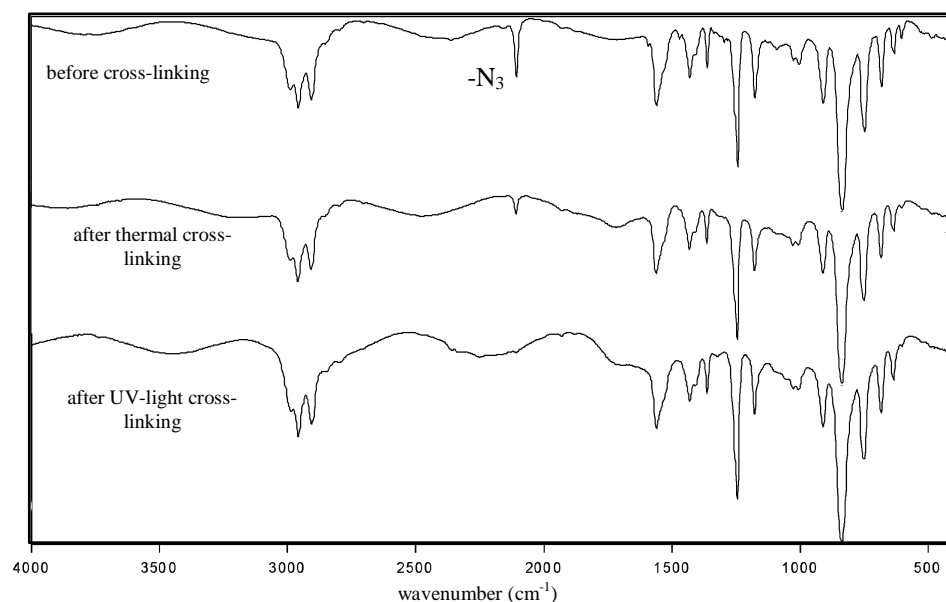


Figure 2  
IR spectra of dense PTMSP membranes with dissolved BAPS before and after crosslinking; the intensity of the azide stretching vibration at  $2100\text{ cm}^{-1}$  corresponds to the crosslinking degree



Two types of crosslinking procedures were carried out: thermal crosslinking at 175 °C and UV light-induced crosslinking at room temperature. The irradiation wavelength for photochemical crosslinking was found on the basis of UV/Vis spectrum of BAPS which showed maximum of absorption at 295 nm. Because UV/Vis absorption of PTMSP is around 280 nm, and irradiation at this wavelength could negatively influence the PTMSP structure, crosslinking was performed at a slightly higher wavelength – 300 nm. The temperature for thermal crosslinking was determined by DSC measurement of PTMSP/BAPS composite which showed an onset of N<sub>2</sub> loss at 175 °C. Similar temperature was also reported [16,17].

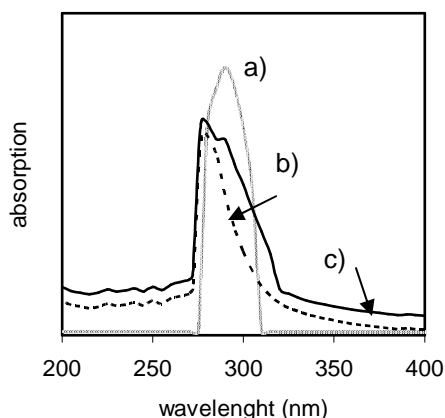


Figure 3  
UV/vis. spectra of (a) BAPS; (b) PTMSP; (c) PTMSP containing 5 wt% of BAPS

Crosslinked membranes were tested for solubility in common PTMSP solvents like cyclohexane, toluene and THF. All crosslinked membranes were insoluble in these solvents and their swelling degree in toluene was 85 % for photocrosslinked and 97% for thermally crosslinked PTMSP.

Gas transport properties of PTMSP and crosslinked PTMSP membranes were measured on a time-lag apparatus using light gases (He, H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>); the results are shown in Table 1. The highest permeability to all gases has the membrane made from neat PTMSP. When this membrane was exposed to the same thermal or UV irradiation conditions as the membranes for crosslinking (blank test) their permeabilities slightly dropped but selectivities were almost the same as PTMSP without any treatment. The blank experiments were performed to see the influence of thermal or UV light irradiation on transport properties. Transport properties of membranes containing dissolved BAPS had lower permeabilities and considerably higher selectivities than the neat PTMSP membrane; thus BAPS could behave like a filler, which occupies the free-volume elements and blocks this transport channel [25]. These membranes were then thermally or photochemically crosslinked and were again tested for gas transport. For both types of crosslinking procedures the permeabilities considerably decreased and selectivities improved. The thermally crosslinked membranes had higher permeabilities and slightly lower selectivities than membranes crosslinked with UV radiation. These results are in accord with the fractional free volume (FFV) determination by swelling measurements of crosslinked PTMSP in toluene reported by Jia and Baker [16], which showed that thermally crosslinked PTMSP has higher FFV than photo-chemically crosslinked PTMSP. The higher permeabilities might be attributed to the higher crosslinking temperature of the thermal process, when the polymer network is formed in the state of thermal expansion of the polymer, and after cooling, the links between PTMSP stiff chains partly hinder the contraction.

Table 1

Gas transport properties of PTMSP and dense crosslinked PTMSP membranes

Membrane	Permeability ( $10^{-10}$ cm <sup>3</sup> (STP)cm/(cm <sup>2</sup> s cmHg)) at 30 °C						Selectivity		
	He	H <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub> /CH <sub>4</sub>	O <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>
PTMSP	2167	6324	12496	4034	2222	5427	1.17	1.82	2.30
PTMSP - therm (blank) <sup>a</sup>	1952	5499	10866	3334	1852	4829	1.14	1.80	2.25
PTMSP/BAPS <sup>b</sup>	1723	4985	9792	2773	1175	4123	1.21	2.36	2.38
PTMSP/BAPS - therm. cross. <sup>d</sup>	1351	3146	7375	1854	526	2085	1.51	3.53	3.54
PTMSP - photo (blank) <sup>a</sup>	1913	5444	10540	3267	1796	4636	1.17	1.82	2.27
PTMSP/BAPS <sup>c</sup>	1637	5118	9777	2456	1004	4112	1.24	2.45	2.38
PTMSP/BAPS - photo cross. <sup>d</sup>	1013	2454	5458	1346	372	1474	1.66	3.61	3.70

<sup>a</sup> Membrane from neat PTMSP treated under the same conditions of thermally / photochemically crosslinked PTMSP/BAPS membranes<sup>b</sup> Membrane from PTMSP with dissolved BAPS measured before thermal crosslinking<sup>c</sup> Membrane from PTMSP with dissolved BAPS measured before photochemical crosslinking<sup>d</sup> Membrane from PTMSP with dissolved BAPS measured after thermal (175 °C / 30 min) or photochemical crosslinking (300 nm / 1min)

### 3.2 Dense Matrimid 5218 membranes

The thickness of a selective polymer layer cast on the top of a porous support is controlled by polymer concentration in solvent. To prepare a very thin selective layer (100 - 500 nm) on the top of a porous support, it is necessary to operate with dilute solutions (0.1 – 1%) which are usually low viscous. Coating solutions then easily penetrate into the support pores where cause pore blocking and the resulting permeability decrease. Penetration additionally decreases liquid film thickness and significantly enhances formation of many defects. An easy way of increasing viscosity at the same polymer concentration is partial crosslinking of the polymer to increase its molecular weight. In our work we used the XDA crosslinking agent for modification of Matrimid 5218 as selective polymer. Even though XDA has negligible solubility in chloroform, it reacts readily with in chloroform dissolved Matrimid 5218. Different amounts of XDA were added to Matrimid 5218 to find out an optimal crosslinker concentration. From the kinetics of crosslinking reaction (manifested by viscosity increase), the optimal crosslinker concentration and reaction time were sought to achieve high-molecular-weight Matrimid 5218 and prevent gel formation. Viscosity measurements of 5 wt. % Matrimid 5218 solutions in chloroform containing 0.5, 0.75, 1, 2 and 5 wt. % of XDA (relative to Matrimid 5218) were performed at 35 °C. The results are shown in Fig. 4. For content of 0.5 and 0.75 wt. % XDA, the viscosity increase with the time of crosslinking is relatively low, for 1 wt. % moderate and for higher loadings (2 and 5 wt. %) is notably steep. Approximately, a temperature increase of 10 °C halves a time necessary to achieve the same viscosity as the same polymer solution at lower temperature. The most convenient crosslinking procedure, which was studied in more detail, was a system with the 1 wt. % XDA content in Matrimid 5218 at 35 °C.

A series of dense membranes made from partially crosslinked Matrimid 5218 containing 1 wt. % XDA with different crosslinking times were prepared. They were characterized by IR and gas transport measurements. IR spectra were comparable with those given in ref. [26]. They showed that intensities of the characteristic imide ring peaks (1780 cm<sup>-1</sup> for asymmetric C=O stretching, 1713 cm<sup>-1</sup> for symmetric C=O stretching and 1380 cm<sup>-1</sup> for C-N stretching) decreased with increasing BAPS concentration and with the time of crosslinking. This indicates that XDA amino groups open imide rings and link Matrimid 5218 macromolecules by amide groups.

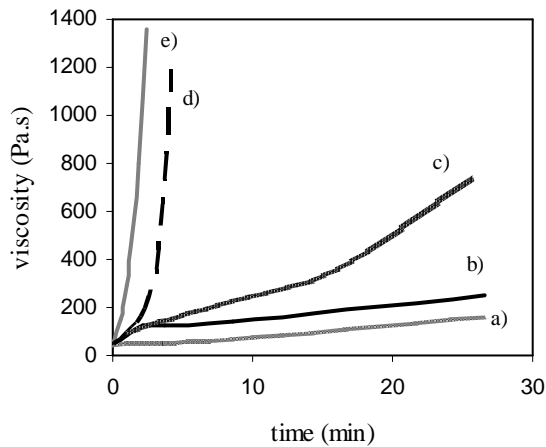


Figure 4  
Time dependences of viscosities of 5 wt. % Matrimid 5218 solutions in chloroform during crosslinking reaction with different contents of XDA: (a) 0.5 wt. %; (b) 0.75 wt. %; (c) 1 wt. %; (d) 2 wt. %; (e) 5 wt. % of XDA (relative to Matrimid 5218) at 35 °C

Gas permeability dependences on the crosslinking time of modified dense Matrimid 5218 membranes are shown in Table 2, Fig. 5. For short crosslinking times, the permeabilities are approximately the same; with increasing time permeabilities slightly decreased. The decrease in gas permeabilities was most apparent for CO<sub>2</sub> and methane. This could probably correspond to a larger kinetic diameter of gas molecules, which leads to smaller molecule mobility. For preparation of composite membrane we modified the Matrimid 5218 with the XDA content 1 wt. % and the crosslinking time was set to 3 h.

Table 2  
Gas separation properties of original and crosslinked dense Matrimid 5218 membranes.

Time of cross-linking (h)	Permeability ( $10^{-10} \text{ cm}^3 \text{ (STP)cm}/(\text{cm}^2 \text{ s cmHg})$ ) at 30 °C						Selectivities		
	He	H <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub> /CH <sub>4</sub>	O <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>
0	24.2	26.70	10.80	2.51	0.38	0.26	104.34	6.61	42.02
3	21.3	25.60	10.50	2.40	0.35	0.25	106.66	6.92	41.69
6	15.9	18.50	7.94	2.04	0.28	0.18	104.03	7.24	44.67
12	11.0	12.30	3.55	1.05	0.13	0.10	117.49	7.76	33.88

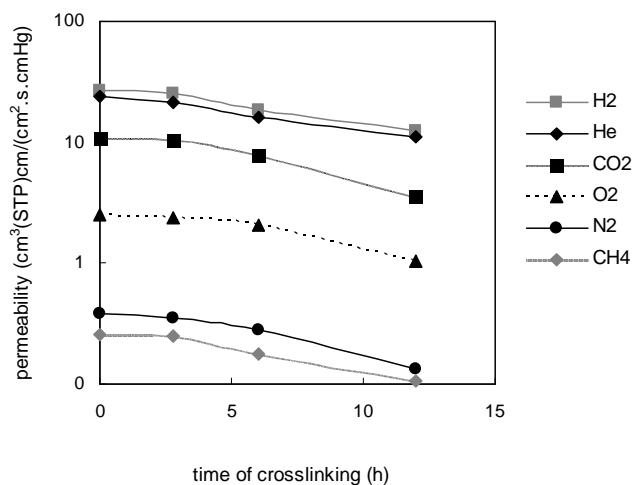


Figure 5  
Permeabilities of dense Matrimid 5218 membranes as a function of crosslinking time.

### 3.3 Composite membranes

Selection of suitable polymer porous support is crucial for preparation of durable and effective composite membranes. For multilayer composite membranes based on PTMSP and Matrimid 5218, the porous support should be stable to chloroform, cyclohexane, high crosslinking temperature (175 °C) and UV light irradiation. These requirements are fulfilled when using a poly(acrylonitrile) (PAN) porous support reinforced with poly-1,4-phenylenesulfide) (PPS) non-woven fabric.

An influence of crosslinking conditions on the N<sub>2</sub> permeabilities through PAN/PPS porous support was studied on laboratory scale. The PAN/PPS support exhibits a high N<sub>2</sub> permeability, 85 m<sup>3</sup>/(m<sup>2</sup>.h.bar), but, when kept for 5 min in a vacuum oven at 175 °C, its permeability decreases to 66 m<sup>3</sup>/(m<sup>2</sup>.h.bar) and, after another 20 min, to 39.5 m<sup>3</sup>/(m<sup>2</sup>.h.bar). Further thermal treatment does not significantly change this value. Changes in PAN/PPS support permeabilities could be due to a decrease in the PAN pore size due to PAN structure deformation above the T<sub>g</sub>. The tested PAN/PPS supports exhibited slight curling caused probably by asymmetric heat distribution in vacuum oven which can also affect PAN deformation.

Composite membranes consisting of the PAN/PPS porous support and the PTMSP top layer containing BAPS (5 wt.%) (coated from 0.5 wt.% solution) were prepared in as pilot scale machine. Samples of this membrane were thermally or photochemically crosslinked and the O<sub>2</sub> and N<sub>2</sub> permeabilities were measured for different crosslinking times (Table 3). The measured data, which are also plotted in Fig. 6, show that even short crosslinking time caused a strong permeability decrease. On the other hand, after longer periods (>2.5 h for thermal crosslinking, 1 min for UV light), permeabilities remain almost the same. The strong permeability drop is not sufficiently explained; it is probably caused by structure changes on the interface between the support and modified PTMSP because of high temperature or high energy irradiation stress. In UV light-crosslinked membranes with shorter expositions, the permeabilities are generally higher (selectivities are similar compared with thermal treatment) and with long expositions, a partial degradation of membrane appears and selectivities drop almost to unity. From the results, we determine the optimal crosslinking time, which is 0.5 h at 175 °C for thermal crosslinking and 45 s for UV light crosslinking.

Table 3  
Transport properties of crosslinked PTMSP composite membranes

Thermal crosslinking at 175 °C				UV light cross-linking			
Time of cross-linking (h)	<i>P</i> (O <sub>2</sub> ) m <sup>3</sup> /(m <sup>2</sup> .h.bar)	<i>P</i> (N <sub>2</sub> ) m <sup>3</sup> /(m <sup>2</sup> .h.bar)	α (O <sub>2</sub> /N <sub>2</sub> )	Time of cross-linking (min)	<i>P</i> (O <sub>2</sub> ) m <sup>3</sup> /(m <sup>2</sup> .h.bar)	<i>P</i> (N <sub>2</sub> ) m <sup>3</sup> /(m <sup>2</sup> .h.bar)	α (O <sub>2</sub> /N <sub>2</sub> )
0	16.39	9.965	1.6	0	16.23	9.777	1.7
0.5	0.637	0.213	3.0	0.5	2.450	1.161	2.1
1	0.174	0.059	3.0	1	0.720	0.250	2.9
1.5	0.160	0.051	3.2	2	0.220	0.086	2.6
5	0.140	0.044	3.2	10	0.115	0.058	2.0
10	0.135	0.041	3.3	20	0.130	0.108	1.2

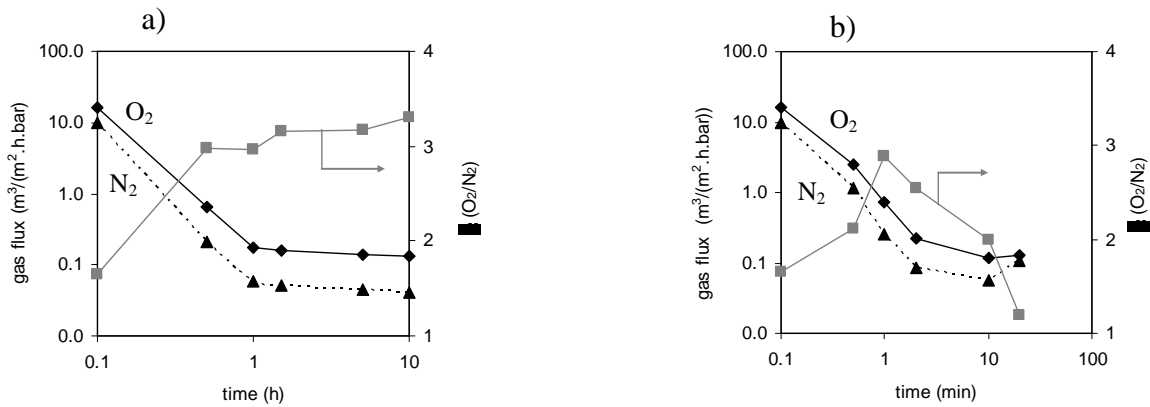


Figure 6 Influence of the time of crosslinking on transport properties of crosslinked PTMSP composite membranes; a) thermal crosslinking; b) UV light induced crosslinking

To compare the effect of the modified PTMSP gutter layer with the PDMS sealing layer a basic composite membrane using modified Matrimid 5218 selective layer was prepared in a pilot scale machine. Due to higher viscosity of a modified Matrimid coating solution, the penetration into the support pores significantly decreased. Generally, the layers of modified Matrimid 5218 on the PAN/PPS support had considerably better quality and homogeneity than the layers of unmodified Matrimid 5218. Gas transport properties of this membrane shown in Table 4 naturally exhibit low gas fluxes typical of glassy polymer top-layers whereas low selectivities of typical gas pairs in comparison with dense Matrimid 5218 membranes indicate the existence of pinholes. On the same sheet of the membrane, an additional PDMS layer was made by coating with 2 wt. % solution in isooctane. This treatment sealed pinholes and expectedly enhanced selectivities with a very small gas flux decrease. The highest selectivity increase was observed for  $H_2/CH_4$  (23 %) and  $O_2/N_2$  (20 %) whereas selectivity of  $CO_2/CH_4$  increased just about 4.7 %. The composite membrane containing a modified PTMSP gutter layer between the PAN/PPS porous support and Matrimid 5218 selective layer exhibited higher gas fluxes than composite membranes based on Matrimid 5218 with a PDMS sealing layer, which has almost the same thickness as the PTMSP gutter layer. The gas flux enhancement decreased in the order:  $CO_2$  (37 %) >  $O_2$  (31 %) >  $H_2$  (25 %) > He (12 %) >  $N_2$  (7 %), only  $CH_4$  flux was slightly reduced. The higher gas flux most probably consist in that high-permeable PTMSP prevent a Matrimid coating solution from penetrating into the porous support pores, which leads to a considerable gas flux decrease. Additionally, the PTMSP gutter layer better distributes gas molecules diffusing from the Matrimid 5218 selective layer into the porous support pores. A significant selectivity increase for  $H_2/CH_4$ ,  $O_2/N_2$  and  $CO_2/CH_4$  gas pairs suggest the effect of pinholes; selectivities are closer to the values for dense (modified) Matrimid 5218 membrane. The highest flux increase for  $CO_2$  could be explained by the resistance model, which describes the behavior of composite gas separation membranes [6,27].  $CO_2$  has a high permeability coefficient in both Matrimid 5218 and PTMSP, so the resistance is relatively low while  $CH_4$  has high permeability in PTMSP but very low permeability in Matrimid. Thus the overall resistance is higher. This leads to a slight reduction in  $CH_4$  flux.

Table 4

Transport properties of composite membranes consisting of Matrimide 5218 selective layer and additional sealing (PDMS) or gutter (PTMSP) layer.

Membrane	layer thickness <sup>b</sup> ( $\mu\text{m}$ )	Gas flux, $\times 10^2 \text{ m}^3 \text{ (STP)}/(\text{m}^2 \cdot \text{h} \cdot \text{bar})$						selectivities			
		He	H <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub> /CH <sub>4</sub>	H <sub>2</sub> /CO <sub>2</sub>	O <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>
PDMS <sup>a</sup>	0.94	102.7	184.8	804.4	167.2	79.8	253.5	0.73	0.23	2.09	3.17
PTMSP	0.89	1049.9	1945.7	2431.3	1069.4	654.7	943.6	2.06	0.80	1.63	2.58
UV cross-linked PTMSP	0.91	147.3	207.6	260.7	68.1	25.2	29.8	6.98	0.80	2.70	8.76
Matrimid <sup>®</sup> 5218	0.33	12.7	13.0	5.41	1.04	0.24	0.27	47.96	2.39	4.33	20.04
Matrimid <sup>®</sup> 5218 / PDMS <sup>c</sup>	0.33 / 1.01	10.9	10.0	4.57	0.94	0.18	0.17	58.82	2.19	5.22	26.88
PTMSP / Matrimid <sup>®</sup> 5218 <sup>d</sup>	1.14 / 0.34	14.3	16.2	7.43	1.37	0.26	0.24	66.80	2.18	5.34	30.58

<sup>a</sup> coated from 2 wt. % PDMS solution in isoocane

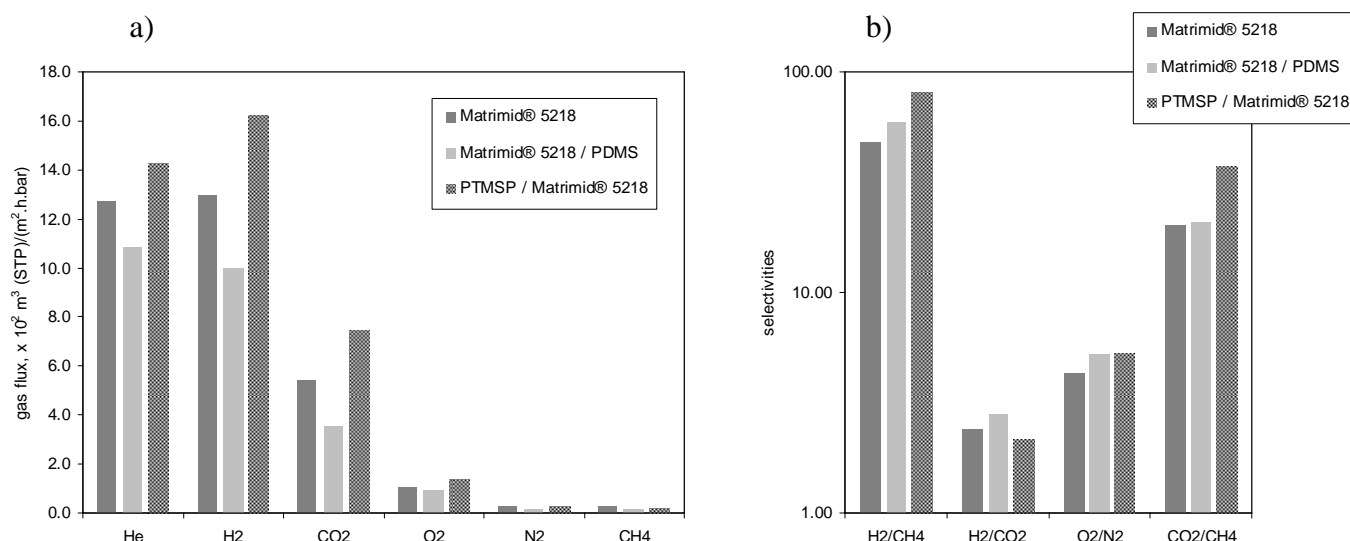
<sup>b</sup> Estimated from flux and SEM micrographs

<sup>c</sup> previous membrane with additional PDMS sealing layer

<sup>d</sup> UV light cross-linked PTMSP as the gutter layer between PAN/PPS porous support and Matrimide<sup>®</sup> 5218 selective layer

Figure 7

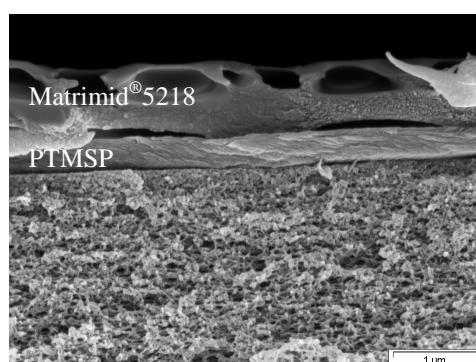
Comparison of gas fluxes through the composite membranes consisting of a Matrimide 5218 selective layer and additional sealing (PDMS) or gutter (PTMSP) layer.



An important parameter of the composite membrane is the thickness of the coating layers, which basically determine gas fluxes. In our work we prepared composite membranes with almost the same thicknesses of each functional layer for correct comparison of transport properties of the studied multilayer composite membranes. Thicknesses were determined mostly by SEM micrographs (Figure 8) and from equation  $l = (P \cdot \Delta p) / J$  for single gas flux ( $J$ ) through the composite membrane, where  $P$  is permeability coefficient,  $\Delta p$  is a pressure difference (resistance of porous support is omitted).

Figure 8

SEM micrograph of multilayer composite membrane consisting of a crosslinked PTMSP gutter layer and Matrimid<sup>®</sup> 5218 selective layer coated on PAN/PPS polymeric porous support



## 4. Conclusions

New multilayer gas separation composite membranes based on the (modified) Matrimid® 5218 selective layer on PAN/PPS polymeric porous support were prepared.

Crosslinking modification of PTMSP using bis(3-azidophenyl) sulfone (BAPS) was successfully performed to obtain an insoluble layer on which another Matrimid 5218 selective layer could be deposited. Gas transport properties of dense crosslinked PTMSP membranes were close to the properties of neat PTMSP. On the other hand, the dependence of gas transport properties of asymmetric PTMSP membranes on the crosslinking time showed that gas fluxes dropped by two orders of magnitude after 10 min for thermal and 2 min for UV light exposition. The optimal crosslinking time for asymmetric membrane preparation was found: 0.5 h at 175 °C for thermal crosslinking and 45 s for UV crosslinking.

Penetration of low-viscous Matrimid 5218 coating solutions into the porous support was partly eliminated by a solution viscosity increase achieved by Matrimid 5218 crosslinking modification using XDA as crosslinking agent. Optimal XDA concentration was 1 wt. % relative to Matrimid 5218 and the time of crosslinking was set up to 3 h.

Incorporation of the gutter layer between the modified Matrimid selective layer and PAN/PPS porous support led to enhancement both gas fluxes and selectivities (for example, CO<sub>2</sub> flux increased by cca. 35 % compared with CO<sub>2</sub> flux for single modified Matrimid 5218 layer coated on PAN/PPS). A significant selectivity increase for H<sub>2</sub>/CH<sub>4</sub>, O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> gas pairs to suggests the sealing effect of pinholes. Selectivities are closer to the values for dense (modified) Matrimid 5218 membranes. The prepared composite membranes with incorporated gutter layer exhibit a better gas separation performance than membranes containing a PDMS sealing layer. Properties of the gutter layers and their influence on the transport properties of composite membranes may represent a good potential for industrial applications.

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## 6. References

- [1] P. Pandey, R.S. Chauhan, Membranes for gas separation, *Prog. Polym. Sci.* 26 (2001) 853-893
- [2] W. J. Koros, R. Mahajan, Pushing the limits on possibilities for large scale gas separation: Which strategies?, *J. Membr. Sci.* 175 (2000) 181-196
- [3] J. Crank, G. S. Park, *Diffusion in Polymers*, Academic, London (1968)
- [4] J. G. Wijmans, R. W. Baker, The solution-diffusion model: a review, *J. Membr. Sci.* 107 (1995) 1-21
- [5] W.R. Browall, R.M. Salemme, Laminated porous/nonporous membranes, US Patent 3,874,986 (1975)
- [6] J. M.S. Henis, M.K. Tripodi, Multicomponent membranes for gas separation, US Patent 4,230,463 (1980)
- [7] W.R. Browall, Method for sealing breaches in multi-layer ultrathin membrane composite, US Patent 3,980,456 (1976)
- [8] I. Pinnau, J.G. Wijmans, I. Blume, T. Kuroda, K.-V. Peinemann, Gas permeation through composite membranes, *J. Membr. Sci.* 37 (1988) 81-88
- [9] H. Strathmann, Membranes and membrane processes, *Ullmann's encyclopedia of industrial chemistry* 6<sup>th</sup> Edition, John Wiley & Sons Canada (2002) Vol. A16 187.
- [10] I. Cabasso, K. A. Lundy, Method of making membranes for gas separation and the composite membranes US Patent 4,602,922 (1986)
- [11] K. A. Lundy, I. Cabasso, Analysis and construction of multilayer composite membranes for the separation of gas mixtures *Ind. Eng. Chem. Res.* 28 (1989) 742-756
- [12] T. S. Chung, E. R. Kafchinski, R. S. Kohn, P. Foley, R. S. Straff, Fabrication of composite hollow fibers for air separation, *J. Appl. Polym. Sci.* 53 (1994) 701-709
- [13] T. S. Chung, E. R. Kafchinski, M. Spak, B. Bembry-Ross, G. Wensley, High performance PAN composite membranes, US Patent 5,324,430
- [14] J. Bateman, D. A. Gordon, Soluble polyimides derived from phenylindane diamines and dianhydrides, US Patent 3, 856, 752 (1974)
- [15] O. M. Ekiner, R. A. Hayes, Production of aromatic polyimide membranes, US Patent 4, 983, 191 (1991)
- [16] J. Jia, G.L Baker, Crosslinking of poly[1-(trimethylsilyl)-1-propyne] membranes using bis(aryl azides), *J. Polym. Sci., Part B: Polymer Physics* 36 (1998) 959-968
- [17] S. D. Kelman, B. D. Freeman, Crosslinking of high free volume polymers for the separation of organic vapors from permanent gases, *AIChE Annual Meeting, Conference Proceedings* (2005) 2460-2461
- [18] T. Masuda, E. Isobe, T. Higashimura, Polymerization of 1-(trimethylsilyl)-1-propyne by halides of niobium(V) and tantalum(V) and polymer properties, *Macromolecules* 18 (1985) 841-845
- [19] K. Nagai, T. Masuda, T. Nakagawa, B.D. Freeman, I. Pinnau, Poly[1-(trimethyl)-1-propyne] and related polymers: synthesis, properties and functions, *Prog. Polym. Sci.* 26 (2001) 721-798.
- [20] S. M. Shishatskii, Y u .P. Yampol'skii, K.-V. Peinemann, Novel highly permselective 6F-poly(amide-imide)s as membrane host for nano-sized catalysts, *J. Membr. Sci.* 112 (1996) 275-285.
- [21] M. R. Pixton, D. R. Paul, *Polymer. Gas Separation Membranes*, CRC Press, Boca Raton (1994) 83-153
- [22] T. Higashimura, T. Masuda, K. Takada, Polymer and a membrane having an improved gas-permeability and selectivity, US Patent 4,755,193 (1988)
- [23] J. Kunzler and V. Percec, *Polym. Prepr., ACS Div. Polym. Chem.* 28 (1988) 252
- [24] J. Kunzler and V. Percec, *New Polym. Mater.* 1(1990) 252
- [25] J. Qiu, J.-M. Zheng, K.-V. Peinemann, Gas transport properties in novel poly(trimethylsilylpropyne) composite membrane with nanosized organic filler trimethylsilyl glucose, *Macromolecules* 39 (2006), 4093-4100
- [26] P.S. Tin, T.S. Chung, Z. Liu, R. Wang, S.L. Liu, K. P. Pramoda, Effects of crosslinking modification on gas separation performance of Matrimid membranes, *J. Mem. Sci.* 225 (2003) 77-90
- [27] G. He, X. Huang, R. Xu, B. Zhu, An improved resistance model for gas permeation in composite membranes, *J. Membr. Sci.* 118 (1996) 1-7