

Boltorn-modified polyimide gas separation membranes

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Abstract

This paper describes the preparation, characterization and permeation properties of polyimide BTDA-AAPTMI (Matrimid 5218) and co-polyimide BTDA-TDI/MDI (P84) dense polymer films containing aliphatic hyperbranched polyesters, Boltorn (H40). The H40 are dispersed in the polymers at various concentrations.

For Matrimid–H40 1.0 wt% membrane the nitrogen permeability increases but with significant loss in selectivity, while at higher H40 concentrations (5.0 and 10.0 wt%) the permeability becomes lower than of the pure polymer and the selectivity generally stays constant. The dispersion of various concentrations of H40 (1.0, 5.0 and 10.0 wt%) in P84 membranes decreases gas permeability in comparison to pure P84, while the selectivity generally stays constant.

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1. Introduction

Over the last decades, polymeric membranes have proven to operate successfully in industrial gas separations [1]. Special attention has been concentrated on the relationship between polymer structure and gas separation properties. Most of the polymers that have been investigated, however, show the general trend that highly permeable polymers possess rather low selectivity (permeability/selectivity trade off relationship [2]). In the last two decades, various polyimide glassy polymers have been developed which combine high selectivity with acceptable permeability coefficients [3]. In fact, polyimides, like BTDA-AAPTMI (Matrimid 5218) or BTDA-TDI/MDI (P84), show excellent intrinsic gas separation properties and robust mechanical properties to withstand high-pressure gas feeds [4].

A considerable interest has also been shown in dendritic polymers as the hyperbranched polymers (HBP). The exceptional features of the dendritic architecture [5–7] result directly from the repetitive branching giving access to large number of reactive end-groups. In previous work, we mixed various generations

of dendrimers, Boltorn, into poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) polymers [8]. The permeability of various gases (O_2 , N_2 , CO_2) showed a maximum at low Boltorn concentration (1 wt%). There, the gas permeability was in fact 2–3 times higher than the permeability of pure PPO. At higher Bolton concentrations however, the permeability decreased and became even lower than that of the pure PPO. For all Boltorn concentrations the ideal gas selectivity was constant. Our results showed that the maximum in gas permeability is due to increase of polymer free volume at low Bolton concentration while at higher concentrations clustering of Bolton leads to phase separation and decrease of permeability.

This work investigates the gas permeability of Matrimid 5218 and co-polyimide P84 membranes containing Boltorn (H40). Compared to PPO, the polyimides have high gas selectivity; however, their gas permeability is rather low. Therefore, the increase of their permeability by adding dendrimers would be highly desirable. Our results show that small amounts of H40 dispersed into Matrimid increase N_2 and O_2 permeability in comparison to pure Matrimid, while at higher amounts of H40, gas permeability decreases. For P84–H40 membranes the gas permeability is always lower than pure P84. A systematic investigation of the structure of Matrimid–H40 and P84/Boltorn membranes is performed (using scanning electron microscopy

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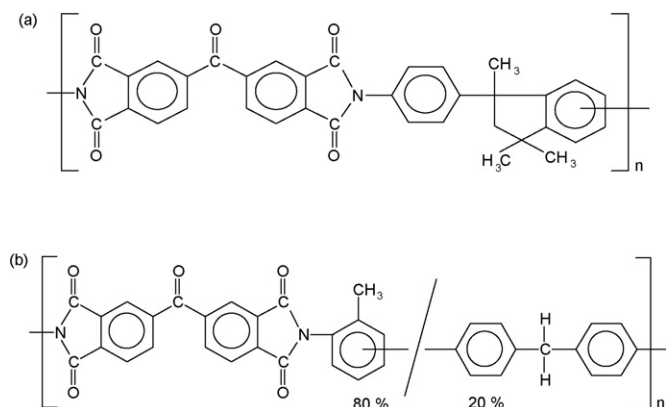


Fig. 1. Chemical structure of (a) Matrimid 5218 polyimide and (b) BTDA-TDI/MDI (P84) co-polyimide.

(SEM), differential scanning calorimetry (DSC), wide angle X-ray scattering (WAXS), contact angle measurements) in order to understand the membrane permeation performance.

2. Experimental

2.1. Materials

For the membrane preparation the following materials were used: BTDA-AAPTMI polyimide (known as Matrimid 5218, from Ciba Specialty Chemicals Corp.) and co-polyimide BTDA-TDI/MDI (known as P84, from Lenzing) (see Fig. 1).

Other chemicals used: 1-methyl-2-pyrrolidinone (NMP, 99%, Acros Organics), and hyperbranched polymers commercially available as Boltorn® H40 (kindly supplied by Perstorp Specialty Chemicals AB, Sweden). They are aliphatic polyesters using ethoxylated pentaerythritol as central cores and 2,2-bis(methylol)propionic acid (bis-MPA) as dendritic units [8]. The products are all hydroxyl functional. Hydroxyl number, molecular weight and polydispersity of Boltorn polymers from the data sheet provided by Perstorp are presented elsewhere [6,8,9].

2.2. Membrane preparation

For the preparation of pure Matrimid membranes, the polymer was dissolved in NMP solvent (10 wt% polymer solution). The solution was cast on a glass plate and dried first under nitrogen atmosphere at room temperature (20–25 °C) for 7 days, then in a vacuum oven at 80 °C for 7 days, and finally in a vacuum oven at 100 °C for 7 days. Dry films with a thickness of 40–50 μm were obtained.

For the preparation of Matrimid membranes dispersed with Boltorn (H40), the Matrimid and H40 were dissolved in NMP (10 wt% polymer solution). The solution was stirred for 3–4 h at room temperature until complete dissolution. The membranes were cast and dried using the same method as for the pure Matrimid. Dry films with a thickness of 40–50 μm were obtained. Films containing 1.0, 5.0 and 10.0 wt% of H40/g of dry membrane were prepared. All membranes were kept in vac-

uum oven at 30 °C until constant weight (for approximately 2 months).

The pure P84 and P84-H40 membranes were prepared in NMP solvent following similar procedure as for the pure Matrimid and Matrimid-H40 membranes.

2.3. Characterization of membranes

2.3.1. Density measurements

The density measurements of all membranes were performed using an AccuPyc 1330 Pycnometer with a 0.1 cm³ sample insert. The pressures observed upon filling the sample chamber with the gas and then discharging it into a second empty chamber allows computation of the density of the sample.

2.3.2. DSC measurements

The thermal properties of pure Matrimid, pure P84, Matrimid-H40 and P84-H40 were measured using a PerkinElmer DSC-7 (differential scanning calorimeter) in nitrogen atmosphere. The samples were initially heated from –50 °C until 380 °C, cooled with liquid nitrogen, held for 5 min, and reheated two more times following the same steps. The heating rate was 10 °C/min and the cooling rate was 20 °C/min. The glass transition temperature, T_g , of the polymer was obtained from the third scan.

2.3.3. Scanning electron microscopy (SEM)

The morphology of all membranes was determined using a Jeol JSM-5600 LV scanning electron microscope. The samples were freeze fractured in liquid nitrogen and sputtered with a thin layer of gold using a Balzers Union SCD 040 sputtering apparatus.

2.3.4. Contact angle measurements

Static liquid–air contact angles were measured with a goniometer (OCA 15, Data Physics). Drops of 1 μl Milli-Q water were formed at the needle tip and contact angles were measured 10 s after placing the drop on the substrate. The equilibrium contact angle (θ) of a liquid with a solid substrate is determined by Young's equation:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (1)$$

where, γ_{LV} , γ_{SV} , γ_{SL} is the surface tensions of the liquid/vapor, solid/vapor and solid/liquid, respectively.

2.3.5. Gas permeability and sorption

The permeation of pure nitrogen (N₂), oxygen (O₂), and carbon dioxide (CO₂) through the membranes was investigated at 3.5 bar feed pressure, using the set up described elsewhere [10]. Pure gas permeability coefficients were calculated from the steady state pressure increase in time in a calibrated volume at the permeate side using the equation:

$$\frac{P}{l} = \frac{V 273.15 (p_{pt} - p_{p0})}{A T ((p_{fr} + p_{f0})/2) 76 t} 10^6 \quad (2)$$

where the ideal gas law is assumed to be valid, p_{pt} , p_{ft} (bar) is the pressure at the permeate and feed side at time t , p_{p0} , p_{f0} is the permeate and feed pressure at $t=0$, T (K) is the temperature, V (cm³) is the calibrated permeate volume, and A (cm²) the membrane area. The gas permeance (P/l) is expressed in GPU, i.e. 10^{-6} cm³ cm⁻² s⁻¹ cmHg⁻¹. Multiplying the gas permeance with the thickness of dense membrane, l (cm), gives the permeability coefficient in barrer. All the gas permeation experiments were performed at 35 °C. Values and error bars reported in the tables and figures are based on measurements of two different membrane samples.

The gas sorption isotherms of N₂, O₂ and CO₂ in dense Matrimid pure and P84 pure, Matrimid and P84 dispersed with H40 (1.0 and 10.0 wt%) films were measured at 35 °C, using a magnetic suspension balance [11] (MSB, Rubotherm). The experimental procedure has been described in detail elsewhere [12]. The equilibrium mass increase was corrected for buoyancy by subtracting the weight at zero sorption at a certain pressure from the vacuum weight of the sample. Using the equilibrium weight increase and the density of the polymer, the concentration (in cm³ STP) inside the polymer (cm³ polymer) was calculated [11].

The ideal Fickian sorption of a penetrant into a polymer matrix is proportional to the square root of time, assuming a constant diffusion coefficient [13]. The mass uptake (g) in time ($M(t)$) can be described with the following equation:

$$\frac{M(t)}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp \left\{ -\frac{D(2m+1)^2 \pi^2 t}{l^2} \right\} \quad (3)$$

where M_{∞} is the mass uptake at infinite time (equilibrium sorption), D is the diffusion coefficient (m²/s) and t is the time

(s). Fitting of sorption data to this equation gives the ideal gas diffusion coefficients [14].

2.3.6. WAXS measurements

Wide angle X-ray scattering (WAXS) experiments were performed using a Bruker-Nonius D8-Discover equipped with 2D detector. Standard background (air and sample holder) subtraction measured at the same time and conditions were applied to all data. The sample–detector (S–D) distance was set at 10 cm and the incident beam wavelength was 1.54 Å (Cu Kα). Measurements were performed both perpendicular and in the plane of the membrane [12]. In the first case, the sample thickness as seen by the incident beam was always less than 0.5 mm.

3. Results and discussion

3.1. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to investigate the distribution of H40 in Matrimid and P84 membranes. Figs. 2–4 show some typical results obtained using magnification of 1000× and 5000×. A two-phase morphology seems to be characteristic of all samples, with more or less spherical droplets of the minor phase (H40) dispersed in a continuous matrix phase, comparable with the findings of Mulkern and Tan [5] for polystyrene-Boltorn. Both pure Matrimid and pure P84 have similar dense and compact structure (surface and cross-section). It seems that at various H40 concentrations (1.0 and 10.0 wt%) in Matrimid, phase separation occurs resulting in a dispersed particulate structure (see Fig. 2). Similar results were also found by Boogh et al. [15] for modified DGEBF epoxy resin with Boltorn. Furthermore, at the top side of P84–H40

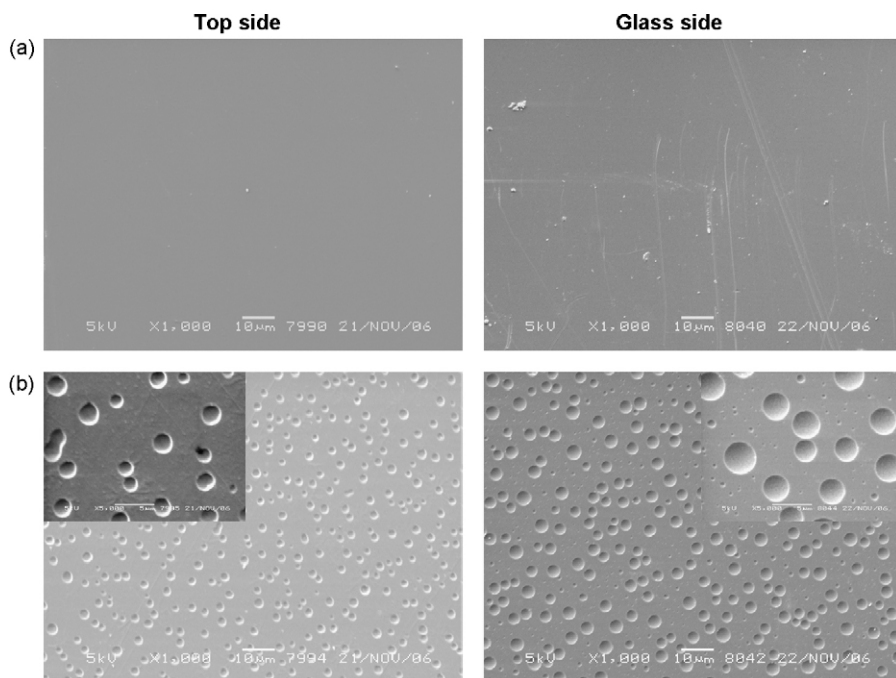


Fig. 2. SEM micrographs of (a) pure Matrimid, and (b) Matrimid–H40 1.0 wt% membranes (insets are zoom at magnification 5000×).

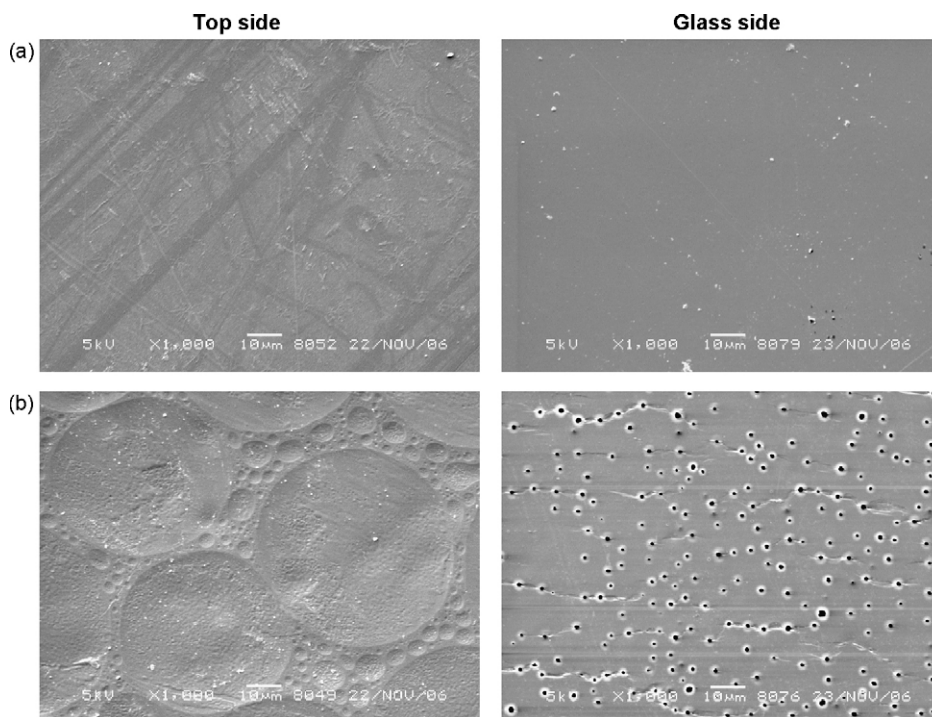


Fig. 3. SEM micrographs of (a) pure P84 and (b) P84–H40 1.0 wt% membranes.

1.0 and 10.0 wt% membranes the dispersed particulate structure consists in big circles surrounded by smaller ones, while at the glass side SEM micrographs show the formation of “holes” (Fig. 3). In contrast to PPO–Boltorn where Boltorn were mostly on the top of the membrane [8], here the dispersed particulate structure seems to be present at both sides (top and glass side) of Matrimid–H40 and P84–H40 membranes. Moreover, the membranes have “holes” in the cross-section (see Fig. 4). This might be due to “washing” out of H40 agglomerates during the sample preparation for SEM analysis.

In order to investigate further the film structure, we kept the Matrimid–H40 and P84–H40 membranes for four days in water (known as solvent for Boltorn, but not for the polymers). The membranes were dried afterwards in N₂ box for 2 days and vacuum oven at 50 °C for 2 days. The SEM micrographs of Matrimid–H40 (1.0 and 10.0 wt%) after “washing” with H₂O look similar with the original sample before “washing” (see Fig. 5a). In contrast, the SEM micrographs of P84–H40 (1.0 and 10.0 wt%) washed in H₂O show bigger “holes” at the glass surface, instead of the dispersed particulate structure seen before (see Fig. 5b). These “holes” were probably created after dissolution of H40 by H₂O, while the top side keeps its particulate structure similar to the original sample (Fig. 5). This test suggests that for P84 membranes, the H40 migrate to both surfaces, although preferentially to the glass side, and form agglomerates. For Matrimid, no differences between the original samples and those “washed” (with H₂O) could be visualized by SEM. This suggests that probably H40 is mixed rather well with the polymer (similar to PPO [8]) perhaps due to hydrogen bond formation between the polymer and H40.

The H40 migration to the membrane surface is supported by the contact angle measurements of both surfaces

of Matrimid and P84 membranes (see Table 1). The contact angle of Matrimid–H40 and P84–H40 decreases for both air and glass side surfaces in comparison to the pure polymers. For Matrimid–H40 1.0 wt% the contact angle is similar for both surfaces, whereas for P84–H40 1.0 wt% the contact angle of the glass side is lower than of the top side, indicating preferred migration of H40 to the glass side of the membrane. However, for both polymers, the contact angle of both sides becomes similar at 10.0 wt% H40 but at values lower than the pure polymers.

3.2. DSC–WAXS measurements

Table 2 presents the DSC results of the membranes. It shows that the T_g of Matrimid–H40 1.0 wt% increases to 345 °C in comparison to pure Matrimid ($T_g = 333$ °C). This indicates that the Matrimid polymer chain with 1.0 wt% H40 becomes slightly more stiff and perhaps there is suppressed inter-chain packing as well as some possible conformational changes in the backbone. Perhaps as a consequence, an extra interstitial chain space is created and the free volume of the membrane

Table 1
Contact angle results of Matrimid–H40 and P84–H40 films

Sample	Contact angle (°)			
	Matrimid–H40		P84–H40	
	Air side	Glass side	Air side	Glass side
0	92	90	80	79
1.0	59	57	61	49
10.0	57	58	52	54

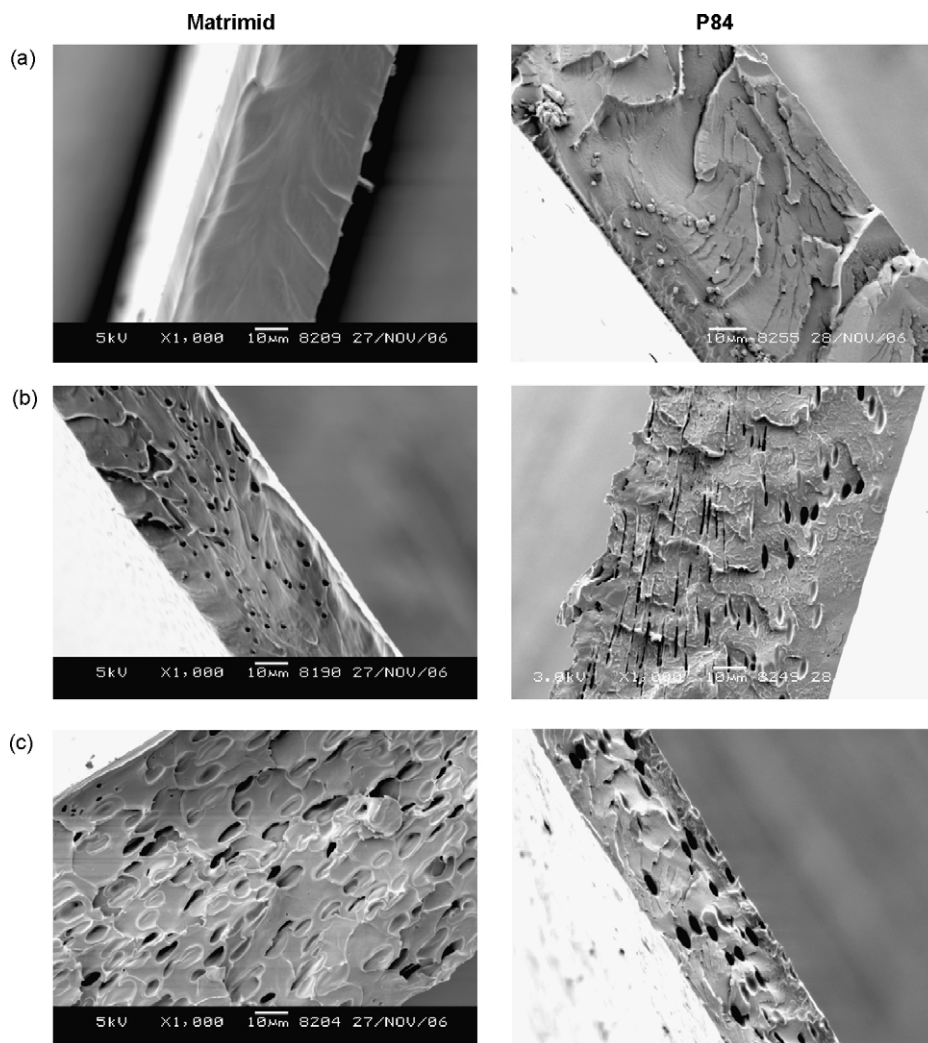


Fig. 4. SEM micrographs of cross-sections of Matrimid and P84 membranes: (a) pure polymer, (b) 1.0 wt% H40 and (c) 10.0 wt% H40.

might increase, too. Additionally, the density of Matrimid–H40 1.0 wt% decreases to 1.23 g/cm^3 in comparison to pure polymer ($\rho = 1.32 \text{ g/cm}^3$), suggesting more “open” polymer structure. For the Matrimid–H40 10.0 wt% ($T_g = 330^\circ\text{C}$) no significant change in T_g was found in comparison to pure Matrimid ($T_g = 333^\circ\text{C}$). The Matrimid–H40 10.0 wt% has two T_g at 43 and 330°C , each associated with an individual dispersion component, H40 and Matrimid, respectively (H40 has T_g at 42°C). Besides, the

density of Matrimid–H40 10.0 wt% increases to 1.41 g/cm^3 in comparison to pure polymer ($\rho = 1.32 \text{ g/cm}^3$) suggesting a more “compact” polymer structure.

The T_g of P84–H40 1.0 and 10.0 wt% membranes decreases to 289 and 277°C , respectively, in comparison to pure P84 ($T_g = 316^\circ\text{C}$). The P84–H40 10.0 wt% membrane also has two T_g (at 49 and 277°C) each associated with the individual dispersion component, H40 and P84, respectively. Additionally, the density of P84–H40 1.0 and 10.0 wt% membranes increases to 1.45 and 1.54 g/cm^3 , respectively, in comparison to pure polymer ($\rho = 1.39 \text{ g/cm}^3$), indicating more compact structure. The presence of two distinct T_g confirms the immiscibility between H40 and the polymers (Matrimid and P84), in agreement with Mulkern and Tan [5].

Finally, Fig. 6 displays WAXS spectra of pure Matrimid, P84 and H40, as well as of Matrimid–H40 and P84–H40 (1.0 and 10.0 wt%) films when the incident beam is perpendicular to the film. It seems that the presence of H40 does not cause significant changes in neither Matrimid nor P84 amorphous structure; the scattering curves are very similar from front and side view.

Table 2

DSC and density results of Matrimid and P84 with various Boltorn concentrations

Polymer	wt% H40	Density (g/cm^3)	T_g ($^\circ\text{C}$)
Matrimid	0	1.32	333
	1.0	1.23	345
	10.0	1.41	43 and 330
P84	0	1.39	316
	1.0	1.45	289
	10.0	1.54	49 and 277

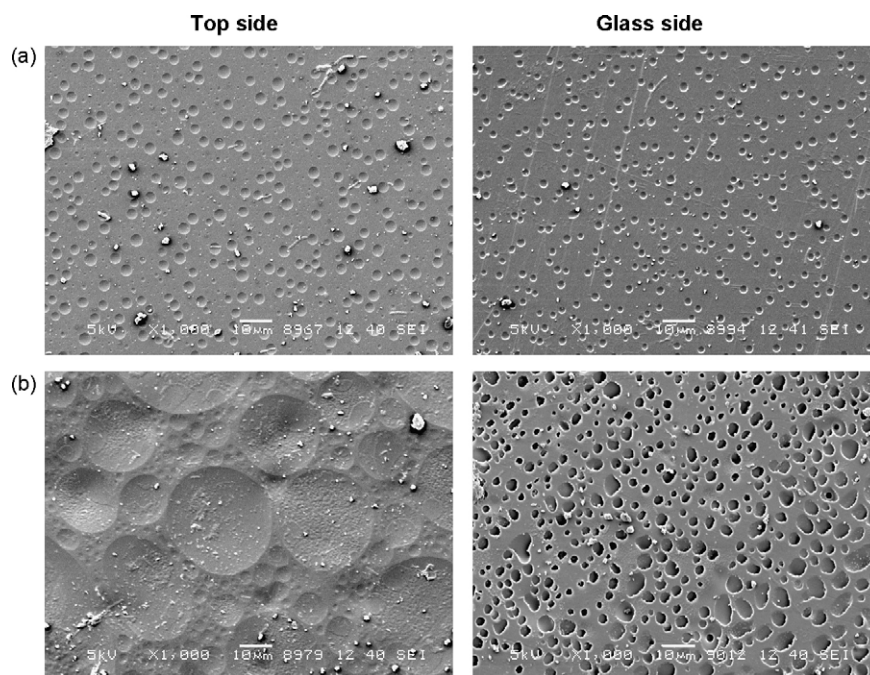


Fig. 5. SEM micrographs of (a) Matrimid-H40 1.0 wt%, and (b) P84-H40 1.0 wt% membranes after “washing” with H₂O.

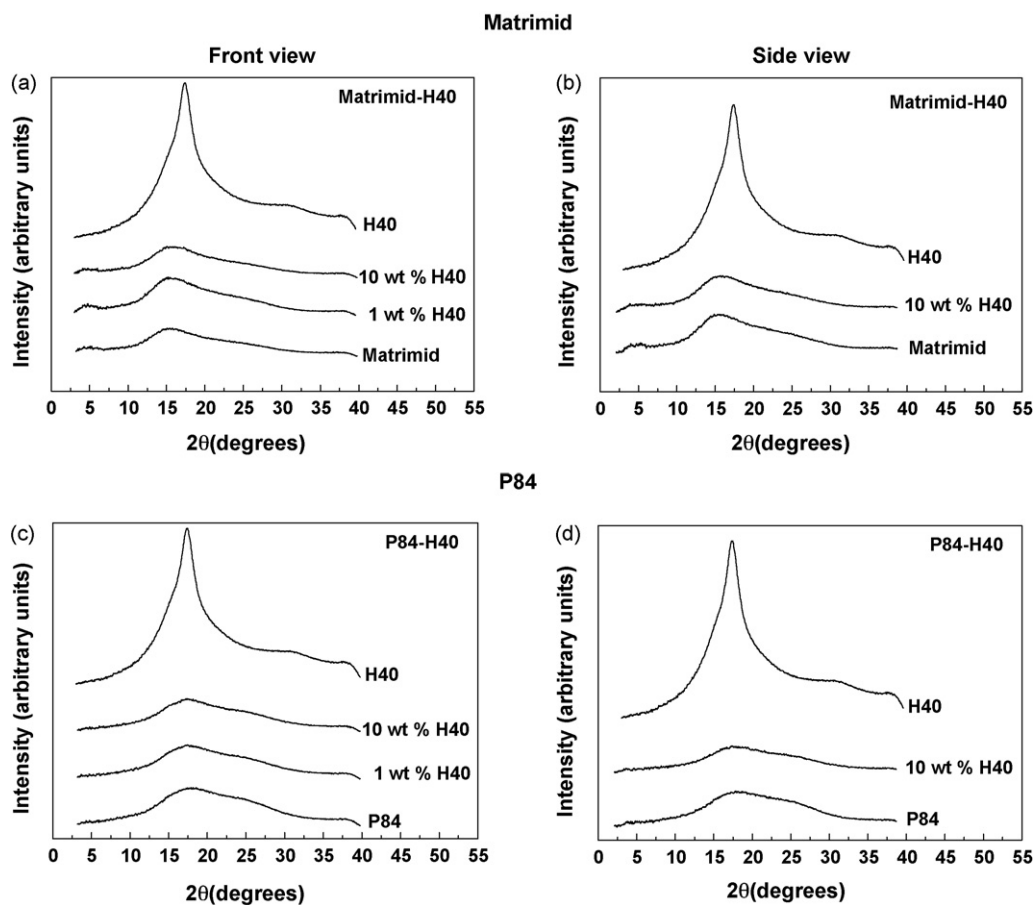


Fig. 6. Scattering intensity as a function of the scattering angle for: (a) pure H40, Matrimid-H40 with 1.0 and 10.0 wt% H40—from front, (b) pure H40, Matrimid-H40 with 10.0 wt% H40—from side, (c) pure H40, P84-H40 with 1.0 and 10.0 wt% H40—from front, and (d) pure H40, P84-H40 with 10.0 wt% H40—from side.

Table 3
Permeability and ideal gas selectivity of Matrimid–H40 membranes

wt% H40 in Matrimid	Permeability (barrer)			Ideal selectivity		
	N ₂	O ₂	CO ₂	P _{O₂} /P _{N₂}	P _{CO₂} /P _{N₂}	P _{CO₂} /P _{O₂}
0	0.15 ± 0.03	1.02 ± 0.09	5.20 ± 0.40	6.8 ± 2.0	34.7 ± 9.6	5.1 ± 0.8
1.0	0.64 ± 0.04	1.31 ± 0.08	5.25 ± 0.62	2.0 ± 0.3	8.2 ± 1.5	4.0 ± 0.7
5.0	0.11 ± 0.03	0.70 ± 0.04	3.29 ± 0.20	6.4 ± 2.1	29.9 ± 10.0	4.7 ± 0.6
10.0	0.09 ± 0.02	0.61 ± 0.04	2.85 ± 0.25	6.8 ± 1.9	31.7 ± 9.8	4.7 ± 0.7

Feed pressure: 3.5 bar, $T = 35^\circ\text{C}$.

3.3. Gas permeability and gas sorption

Fig. 7 shows the gas permeability of Matrimid–H40 and P84–H40 in comparison to the pure polymer membranes measured at 35°C and 3.5 bar feed pressure. The permeability values for N₂, O₂ and CO₂ of pure Matrimid are in agreement with literature [14]. The N₂ permeability through Matrimid–H40 1.0 wt% membranes increases considerably (more than 4 times) compared to the permeability of the pure Matrimid whereas the permeability increases slightly for O₂ (28%) and stays more or less constant for CO₂ (Fig. 7a and Table 3). With increasing H40

content (5.0 and 10.0 wt%) the permeability of Matrimid–H40 decreases and becomes lower than pure Matrimid. Table 3 presents the ideal gas selectivity at 3.5 bar feed pressure corresponding to the average of two different membrane samples. For Matrimid–H40 1.0 wt% membrane, it decreases significantly in comparison to pure Matrimid due to increase of N₂ permeability, whereas the selectivity of Matrimid–H40 5.0 and 10.0 wt% membranes stays almost constant within the experimental error of our measurements.

The permeability coefficient of P84 for all gases (N₂, O₂ and CO₂) decreases with increasing Boltorn content compared to the pure polymer (Fig. 7b and Table 4). The ideal gas selectivity of P84–H40 generally stays constant with increasing concentration of Boltorn and is comparable with pure P84. Due to low N₂ permeability through the membrane, the experimental error leads to a wide range of selectivity values. Therefore, the ideal gas selectivities of P84 are not presented here.

The DSC, density and SEM results give some insights into the changes of the membrane structure due to the incorporation of H40. Perhaps, the introduction of 1.0 wt% H40 to Matrimid enhances the free volume (as found for PPO [8]) and the mobility of N₂ and O₂ gas molecules increases. The permeability of N₂ (the biggest gas molecule, in diameter) increases the most; indicating that probably the free volume introduced in the polymer is rather big and therefore leads to a substantial loss in selectivity. The lower density of the Matrimid–H40 1 wt% membrane seems to support this hypothesis. For Matrimid–H40 10.0 wt% membrane phase separation occurs (two T_g) and probably there is decrease in free volume, indicated by the higher density (see Table 2). Therefore, the permeability for all three gasses decreases. Similar conclusions can be drawn for the P84–H40 10 wt% membranes, too. This behavior is similar to that found for PPO–Boltorn membranes [8]. There, the gas permeability has a maximum at 1 wt% Boltorn and then decreases at higher concentrations. The main difference between the results of

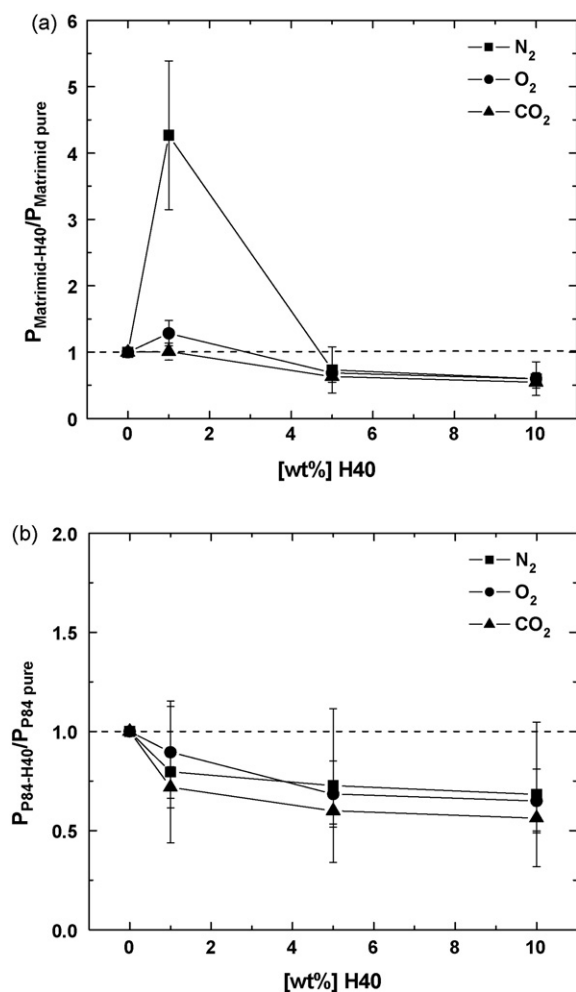


Fig. 7. Permeability of (a) Matrimid–H40 and (b) P84–H40 for N₂ (■), O₂ (●) and CO₂ (▲) normalized with the permeability of pure polymer versus the wt% H40 content (feed pressure: 3.5 bar at 35°C).

Table 4
Permeability and ideal gas selectivity of P84–H40 membranes

wt% H40 in P84	Permeability (barrer)		
	N ₂	O ₂	CO ₂
0	0.05 ± 0.01	0.57 ± 0.08	1.67 ± 0.10
1.0	0.04 ± 0.01	0.51 ± 0.06	1.20 ± 0.10
5.0	0.03 ± 0.01	0.39 ± 0.04	1.00 ± 0.05
10.0	0.03 ± 0.01	0.37 ± 0.04	0.94 ± 0.05

Feed pressure: 3.5 bar, $T = 35^\circ\text{C}$.

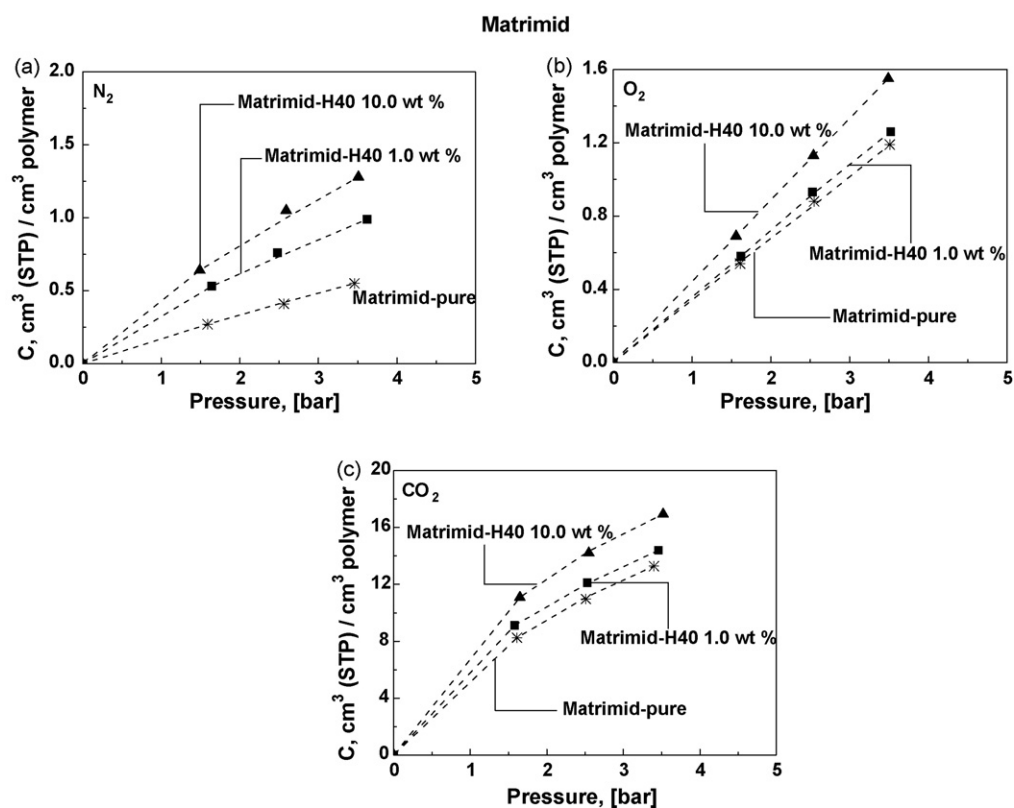


Fig. 8. Sorption isotherms $T = 35^\circ\text{C}$ for (a) N_2 , (b) O_2 , and (c) CO_2 of Matrimid–H40 with 1.0 wt% H40 (■) and 10.0 wt% H40 (▲) in comparison to pure Matrimid (*). The dotted lines represent fitting of the data according to the dual mode sorption model.

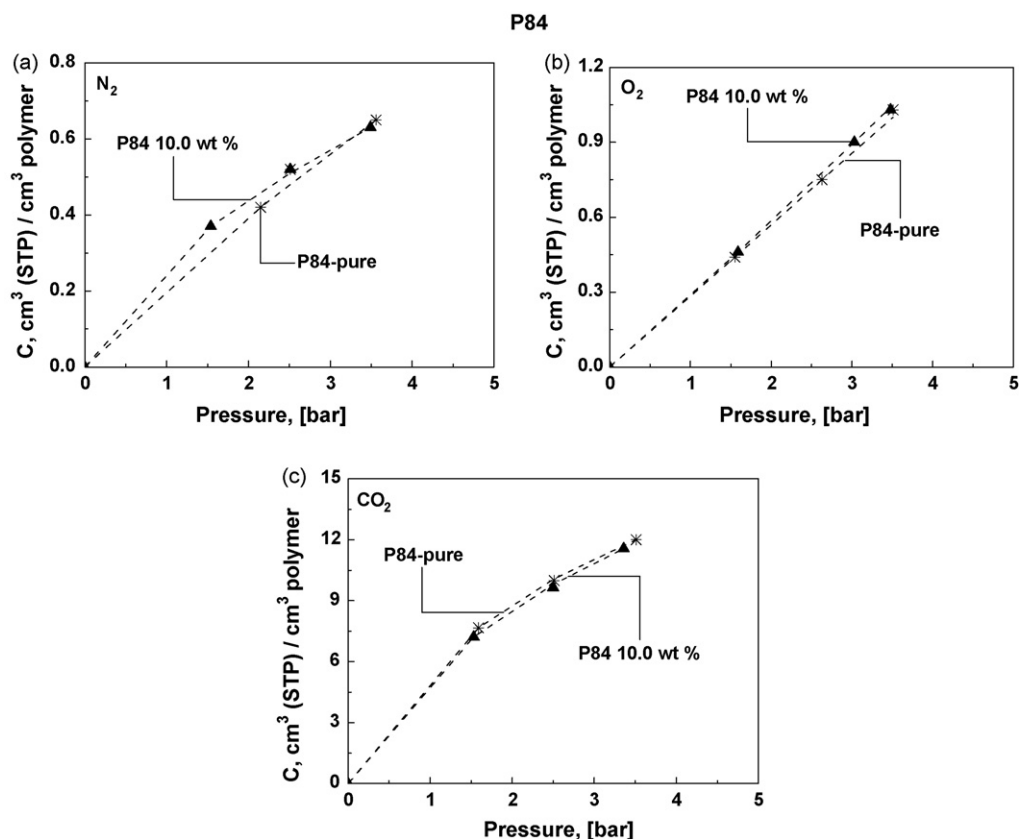


Fig. 9. Sorption isotherms at $T = 35^\circ\text{C}$ for (a) N_2 , (b) O_2 , and (c) CO_2 of P84–H40 with 10.0 wt% H40 (▲) in comparison to pure P84 (*). The dotted lines represent fitting of the data according to the dual mode sorption model.

Table 5
Gas permeability, solubility, and diffusivity of pure Matrimid and Matrimid–H40 films

wt% H40 in Matrimid	N ₂				O ₂				CO ₂			
	<i>P</i>	<i>S</i>	<i>D</i> ^a	<i>D</i> ^b	<i>P</i>	<i>S</i>	<i>D</i> ^a	<i>D</i> ^b	<i>P</i>	<i>S</i>	<i>D</i> ^a	<i>D</i> ^b
0	0.15	2.13	0.70	0.75	1.02	4.52	2.26	2.35	5.20	51.30	1.01	1.10
1.0	0.64	3.65	1.75	1.86	1.31	4.81	2.72	2.84	5.25	53.80	0.97	1.05
10.0	0.09	3.98	0.23	0.29	0.61	5.89	1.03	1.09	2.85	64.18	0.44	0.51

Feed pressure: 3.5 bar, $T = 35^\circ\text{C}$, $P = (\text{barrer})$, $S = 10^{-3} \text{ cm}^3 (\text{STP})/\text{cm}^3 \text{ cmHg}$, $D = 10^{-8} \text{ cm}^2/\text{s}$.

^a Calculated from the P/S ratio.

^b Calculated from the sorption kinetics.

Table 6
Gas permeability, solubility, and diffusivity of pure P84 and P84–H40 films

wt% H40 in P84	N ₂				O ₂				CO ₂			
	<i>P</i>	<i>S</i>	<i>D</i> ^a	<i>D</i> ^b	<i>P</i>	<i>S</i>	<i>D</i> ^a	<i>D</i> ^b	<i>P</i>	<i>S</i>	<i>D</i> ^a	<i>D</i> ^b
0	0.05	2.43	0.20	0.24	0.57	3.80	1.50	1.49	1.67	45.52	0.37	0.34
10.0	0.03	2.39	0.13	0.15	0.37	3.95	0.94	0.90	0.94	44.87	0.21	0.18

Feed pressure: 3.5 bar, $T = 35^\circ\text{C}$, $P = (\text{barrer})$, $S = 10^{-3} \text{ cm}^3 (\text{STP})/\text{cm}^3 \text{ cmHg}$, $D = 10^{-8} \text{ cm}^2/\text{s}$.

^a Calculated from the P/S ratio.

^b Calculated from the sorption kinetics.

Matrimid and PPO is the gas selectivity. Whereas the selectivity for the modified PPO membranes stays constant, the selectivity of modified Matrimid membranes decreases significantly. This indicates the creation of non-selective free volume in the case of Matrimid.

The decrease of gas permeability for Matrimid containing higher concentration of H40 (5.0 and 10.0 wt%) can probably be attributed to the increased inter-segmental mobility of the polymer chain, clustering of H40, and reduced free volume due to the space filling by H40, comparable with the findings for PAMAM in 6FDA [16]. Perhaps, due to a large number of peripheral hydroxyl groups the H40 may have strong intermolecular interaction. Therefore, at high concentrations in Matrimid, they form aggregates that partly migrate to the membrane surface. This phenomenon leads to phase separation and loss of free volume and therefore to decrease in gas permeability. However, the ideal selectivity generally stays constant. Similar effects were also found for P84–H40 at all H40 concentrations (1.0, 5.0 and 10.0 wt%).

Figs. 8 and 9 present the sorption isotherms of CO₂, N₂ and O₂ through Matrimid–H40 and P84–H40 in comparison to pure polymers, at 35°C . The sorption isotherms are fitted by the dual mode sorption model [17]. For O₂ and CO₂ the difference in sorption between the Matrimid–H40 1.0 and 10.0 wt% is not big and they are both slightly higher than the pure Matrimid. However, for N₂ the sorption is somewhat higher for Matrimid–H40 10.0 wt% (Fig. 8a). The sorption of CO₂, N₂ and O₂ of P84–H40 10.0 wt% are very similar to the pure P84 (Fig. 9).

The sorption isotherms are necessary to deconvolute the permeability into its solubility and diffusivity contributions. Tables 5 and 6 report the permeability, solubility and diffusivity coefficients of N₂, O₂ and CO₂ gases in Matrimid–H40 and P84–H40 membrane, respectively, at 35°C and 3.5 bar feed pressure. The solubility coefficient, S , was estimated from the

gas sorption measurements and the diffusion coefficient, D , was calculated from the P/S ratio. To confirm the validity of this calculation, the diffusion coefficient D was also calculated from the sorption kinetics assuming Fickian sorption kinetics. The values of D found by both methods are generally in good agreement (see Tables 5 and 6).

For the Matrimid–H40 1.0 wt% membrane the increase of N₂ and O₂ permeability in comparison to pure Matrimid seems to be due to the increase of both S and D . However, for N₂, the D increases the most ($\sim 150\%$), whereas for O₂, it increases only 20%. For CO₂ however, the diffusion and solubility coefficients are rather comparable, therefore the permeability stays constant. The increase of D for N₂ and O₂ can be result of suppressed inter-chain packing associated with higher free volume. The lower increase of D for O₂ is probably due to its smaller gas molecule diameter in comparison to N₂. This difference in enhancement between gases results to loss of ideal selectivity (see Table 3). For Matrimid–H40 10.0 wt%, the solubility for N₂, O₂ and CO₂ increases in comparison to pure Matrimid, but the decrease of permeability should be attributed to decrease of D (Table 5). The N₂, O₂ and CO₂ solubility coefficients are about the same for P84–H40 10.0 wt% and P84 pure membranes (see Table 6). The decrease of N₂, O₂ and CO₂ permeability for the 10.0 wt% H40 membrane should be mostly attributed to decrease of D .

The decrease of gas permeability through Matrimid–H40 and P84–H40 10.0 wt% is perhaps result of phase separation (shown by SEM and DSC) and the formation of more compact structure (shown by density measurements).

4. Conclusions

The N₂ and O₂ gas permeability of Matrimid–H40 1.0 wt% membranes increases in comparison to pure Matrimid, while it stays more or less constant for CO₂. Therefore, the ideal

gas selectivity decreases. The increase in N₂ permeability at low concentration of H40 is probably due to the increase of free volume by the introduction of H40 into the matrix. This affects mostly the permeability of the bigger molecule, N₂ and has less influence on the permeability of the smaller O₂ and CO₂ gases. In contrary, this phenomenon seems to be absent in P84–H40 1.0 wt% where the permeability for all gases decreases in comparison to pure P84, while the selectivity stays constant.

The decrease of gas permeability for Matrimid and P84 membranes containing higher concentration of H40 (5.0 and 10.0 wt%) can probably be attributed to the increased inter-segmental mobility of the polymer chain, clustering of H40 and phase separation between the polymer and H40. Nevertheless, the ideal selectivity generally stays constant.

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