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Article

Highly Permeable Matrimid[®]/PIM-EA(H₂)-TB Blend Membrane for Gas Separation

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Abstract: The effect on the gas transport properties of Matrimid[®]5218 of blending with the polymer of intrinsic microporosity PIM-EA(H₂)-TB was studied by pure and mixed gas permeation measurements. Membranes of the two neat polymers and their 50/50 wt % blend were prepared by solution casting from a dilute solution in dichloromethane. The pure gas permeability and diffusion coefficients of H₂, He, O₂, N₂, CO₂ and CH₄ were determined by the time lag method in a traditional fixed volume gas permeation setup. Mixed gas permeability measurements with a 35/65 vol % CO₂/CH₄ mixture and a 15/85 vol % CO₂/N₂ mixture were performed on a novel variable volume setup with on-line mass spectrometric analysis of the permeate composition, with the unique feature that it is also able to determine the mixed gas diffusion coefficients. It was found that the permeability of Matrimid increased approximately 20-fold with the addition of 50 wt % PIM-EA(H₂)-TB. Mixed gas permeation measurements showed a slightly stronger pressure dependence for selectivity of separation of the CO₂/CH₄ mixture as compared to the CO₂/N₂ mixture, particularly for both the blended membrane and the pure PIM. The mixed gas selectivity was slightly higher than for pure gases, and although N₂ and CH₄ diffusion coefficients strongly increase in the presence of CO₂, their solubility is dramatically reduced as a result of competitive sorption. A full analysis is provided of the difference between the pure and mixed gas transport parameters of PIM-EA(H₂)-TB, Matrimid[®]5218 and their 50:50 wt % blend, including unique mixed gas diffusion coefficients.

Keywords: polymer blend; polymer of intrinsic microporosity; PIM-EA(H₂)-TB; Tröger's base polymer; Matrimid; gas separation; mixed gas diffusion

1. Introduction

Significant progress has been made in the development of new polymers for the fabrication of gas separation membranes. Polymers used for gas separation membranes can be either rubbers, generally characterized by a relatively low selectivity but high permeability and thus enabling a great productivity, or glassy polymers, characterized by low permeability but high gas-pair selectivity and offering a good separation efficiency. This trade-off between permeability and selectivity, first introduced [1], and updated by Robeson [2] and then by Pinna et al. [3] is typical for

polymeric membranes, and was theoretically explained by Freeman et al. [4]. An exceptional novel class of so-called polymers of intrinsic microporosity (PIMs), introduced by Budd, McKeown and co-workers [5], which combine an exceptionally high permeability with relatively high selectivities, is responsible for the large upward shift of the upper bound in recent years. PIMs owe their exceptional behaviour to extremely rigid [6] and highly contorted [7,8] polymer chains, which do not allow efficient packing and is responsible for a high free volume in these materials.

While most high performing PIMs require complex and expensive synthetic procedures, the key challenge to improve the competitiveness of membrane separations over other gas separation techniques is the fabrication of inexpensive polymer membranes, having a good trade-off between permeability and selectivity. Commercial polymers used for gas separation membranes generally have a high selectivity, but low permeability. Matrimid®5218, a commercial amorphous glassy polyimide, is one of those polymers, and improvements of its overall performance would necessarily require an increase in its permeability. One option to improve the permeability of a polymer is by blending with another polymer to combine synergistically the best properties of the two individual materials [9,10]. This is not an easy task, because due to only a very small gain in entropy, most polymers are not miscible at the molecular level. Early studies on the miscibility of Matrimid®5218 were reported by Grobelny et al. [11], and since then different polymers were blended with Matrimid, in order to increase its separation performance [12–14]. The blend of Matrimid®5218 with polyethersulfone (PES) yielded mechanically stable flat film [15] and hollow fiber [16] membranes for efficient CO₂/N₂ separation; its blend with polysulfone (PSf) enhanced the stability of Matrimid in CO₂/CH₄ binary mixtures, due to the mitigation of CO₂ plasticization [17]. While the CO₂ and CH₄ permeability of polysulfone/Matrimid®5218 blend membranes increase with the polyimide content, there is an optimum in the CO₂/CH₄ mixed gas selectivity (≈ 30) for the blend with 20% of Matrimid [18].

With their unique properties, starting with PIM-1 [19] that defined the 2008 Robeson upper bound [2], numerous new PIMs with a wide range of different chemical structures [6,20–28] and increasingly efficient gas separation performance, have moved the Robeson upper bounds further for several gas pairs [3]. Despite their high permeability, the sophisticated synthesis and high costs hinder PIMs from being the basis for large scale membrane production and industrial applications at present [29]. In addition, for demanding separations, their modest selectivity needs improvement. The idea underpinning the present work is to blend PIMs with a highly selective commercial polymer such as Matrimid®5218, in order to tailor their permeability and selectivity. In the last few years, the archetypal PIM-1 was blended with several other commercial polymers, especially with highly selective polymers such as polysulfone [30] and polyimide [31] in order to increase its selectivity. Blends of PIM-1 with polyphenylenesulfone (PPSU) and sulfonated polyphenylenesulfone (sPPSU) exhibited similar permeability of the polysulfone but enhanced selectivity compared to the neat PIM-1, with an additional anti-plasticization effect under mixture conditions [30]. Similarly, the blending of carboxylated PIM-1 (cPIM-1) with the highly selective co-polyimide P84 demonstrated increased selectivity with a simultaneous reduction of the permeability, as the amount of P84 was increased in the blend [31]. The first blend of PIM-1 with Matrimid was made by Yong et al. and they also studied the miscibility of Matrimid and Torlon with cPIM-1 [32–34]. Addition of a small quantity of Matrimid in PIM-1 improved the O₂/N₂ separation performance, while a small amount of PIM-1 in an excess of Matrimid enhanced the CO₂/CH₄ gas separation performance. Moreover, they used the PIM-1/Matrimid blend to fabricate hollow fibers, demonstrating the greater versatility of the blend for obtaining an ultrathin dense layer, potentially suitable for industrial use [35]. More recently, a novel blend membrane of PIM-1 and a Tröger's Base (TB) polymer showed lower pure gas permeability but higher ideal selectivity than that of the pristine PIM-1 membrane [36].

In the present paper, we study the properties of a blend membrane based on the highly permeable PIM-EA(H₂)-TB [37–40] and the highly selective Matrimid®5218 (Figure 1). PIM-EA(H₂)-TB is a member of the new class of PIMs consisting of Tröger's Base and ethanoanthracene (EA), forming a particularly rigid polymer backbone. The equivalent polymer with methyl substituents on the

two bridgehead positions of the ethanoanthracene unit, PIM-EA-TB, was shown to have a marked size-sieving behaviour that favours the diffusion of gases with smaller kinetic diameters, and surpasses the 2008 Robeson upper bound for the O₂/N₂, H₂/CH₄ and H₂/CO₂ gas pairs [8,41]. The PIM-EA(H₂)-TB is highly selective, as the analogous PIM-EA-TB, and was recently used to increase the hydrogen permeability of polybenzimidazole by blending [40].

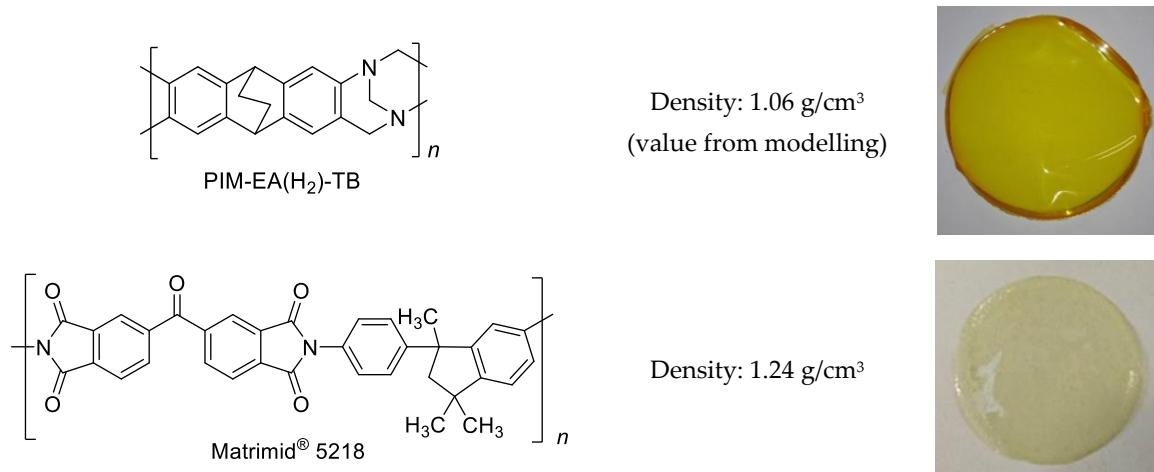


Figure 1. Structure, properties and membrane sample of PIM-EA(H₂)-TB and Matrimid. Density from Ref. [37] and [42], respectively.

The aim of this work to enhance the permeability of Matrimid by the addition of PIM-EA(H₂)-TB, and to find the desired combination of the high permeability of the PIM and the high selectivity of the polyimide. Detailed analysis of the gas transport parameters under single and mixed gas permeation conditions provides deep insight into the role of gas diffusivity and solubility in the overall transport properties of the novel Matrimid®5218/PIM-EA(H₂)-TB blend. In particular, a novel mixed gas permeation setup with the unique possibility to determine the mixed gas diffusion coefficients will provide unprecedented information on the coupling effect between CO₂ and CH₄ or CO₂ and N₂ during permeation of the respective mixtures in the neat polymers and the blend.

2. Materials and Methods

2.1. Materials

Matrimid®5218 was kindly supplied by Huntsman (Basel, Switzerland) and PIM-EA(H₂)-TB was prepared as described previously [37] and the purified polymer, isolated as a powder, was used without any further treatment.

2.2. Preparation of Matrimid®5218/PIM-EA(H₂)-TB Blend Membranes

The casting solutions of both pure polymers were prepared at a concentration of 2 wt % of the polymer in dichloromethane (DCM). Homogenous solutions were obtained under magnetic stirring overnight. The blend solution was prepared by mixing equal amounts of the two individual solutions. The blend membrane containing 50 wt % of both Matrimid®5218 and PIM-EA(H₂)-TB was prepared pouring the appropriate amount of the blend solution into a metallic casting ring of 3 cm diameter, placed on a Teflon® support. The solvent was evaporated at room temperature for 24 h, yielding optically defect-free membranes Figure 1.

2.3. Membranes Characterization

Chemical and morphological analysis of membranes were performed by scanning electron microscopy (SEM) on a Phenom Pro X desktop SEM, equipped with backscattering detector

(Phenom-World B.V., Eindhoven, The Netherlands) and infrared spectroscopy (FTIR) analyses on a Spectrum Spotlight Chemical Imaging Instrument (PerkinElmer). Single gas permeation tests were carried out at 25 °C and at a feed pressure of 1 bar, using a fixed-volume pressure increase instrument (ESSR, Geestchacht, Germany), described elsewhere [43]. Permeability coefficients, P , and diffusion coefficients, D , were determined by the time-lag method [44]. The simplest model of permeation through dense polymeric films describes permeability as the product of diffusion coefficient and solubility coefficient. Thus, the apparent solubility, S , was indirectly calculated as $S = P/D$. The ideal selectivity is the ratio of permeability of two species, $\alpha_{(A/B)} = P_A/P_B$. Mixed gas permeation tests were carried out using a custom made constant pressure/variable volume instrument, described elsewhere [45,46], equipped with a quadrupole mass filter (HPR-20 QIC Benchtop residual gas analysis system, Hiden Analytical). Measurements were carried out as a sequence of increasing and subsequently decreasing pressure steps in the range from 1–6 bar(a).

3. Results and Discussion

3.1. Chemical and Morphological Characterization

The chemical interaction between Matrimid®5218 and PIM-EA(H₂)-TB was studied by means of FTIR-ATR. The IR-spectrum for neat Matrimid®5218, neat PIM-EA(H₂)-TB and for the blend were shown in Figure 2. The distinctive imide peaks of Matrimid®5218 appear at 1712 for C=O stretching and at 1361 cm⁻¹ for C-N stretching, these peaks are also found in the spectrum of the blend. The characteristic peaks of PIM-EA(H₂)-TB are the CH₂ asymmetric stretch vibrations of the ethanoanthracene (EA) unit at 2960 cm⁻¹ and the scissoring vibrations at 1420 cm⁻¹. The water peak (3370 cm⁻¹) in the neat PIM-EA(H₂)-TB and in the blend demonstrate the relatively hydroscopic nature of TB-PIMs [23]. The good compatibility of Matrimid®5218 and PIM-EA(H₂)-TB was also deduced from the high optical transparency of the film and high mechanical resistance. The cross-sectional SEM image shows very few separate domains (less than 1% of the area) confirming the excellent miscibility between PIM-EA(H₂)-TB and Matrimid (Figure 2).

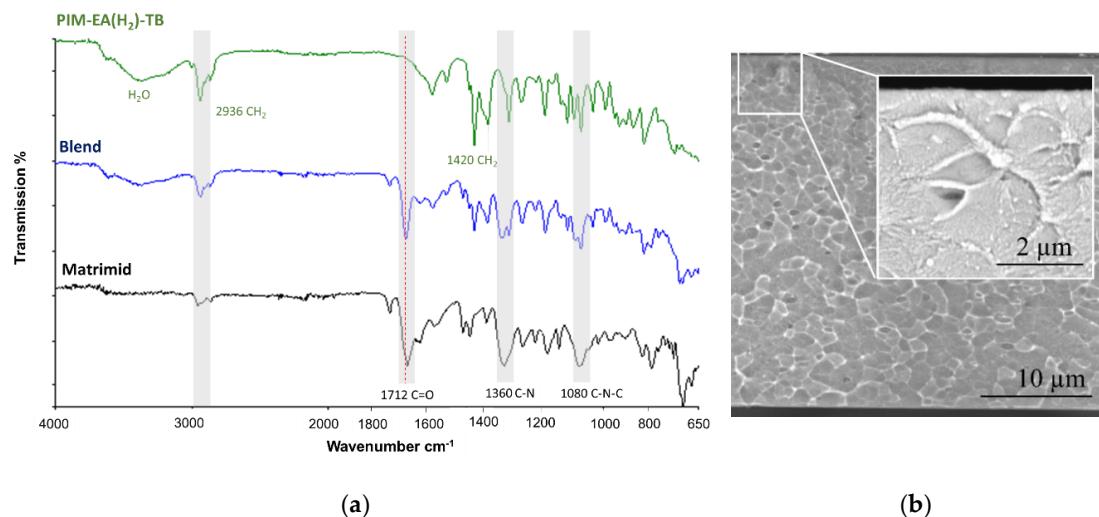


Figure 2. (a) ATR-FTIR spectra of the Matrimid®5218/PIM-EA(H₂)-TB blend and neat polymer membranes, and (b) SEM cross-sectional image of the Matrimid®5218/PIM-EA(H₂)-TB blend membrane at a magnification of 8000 \times and 30,000 \times at an accelerating voltage of 10 kV.

3.2. Pure Gas Transport Properties

Single gas permeation measurements were carried out in the order He, H₂, O₂, N₂, CH₄ and CO₂ at 25 °C on time-stabilized membranes [47]. Figure 3 shows a plot of the gas transport parameters of 30 days aged PIM and blend membranes, and a >1 year aged Matrimid membrane as a function

of the membrane composition. The quantitative values are reported in Table 1. The experimental results highlight the different behaviour of Matrimid®5218 and PIM-EA(H₂)-TB. For all gases, the pure gas permeability (Figure 3a), diffusivity (Figure 3c) and solubility (Figure 3e) are all higher in the Matrimid®5218/PIM-EA(H₂)-TB blend than in neat Matrimid membrane, thanks to the higher free volume of the PIM.

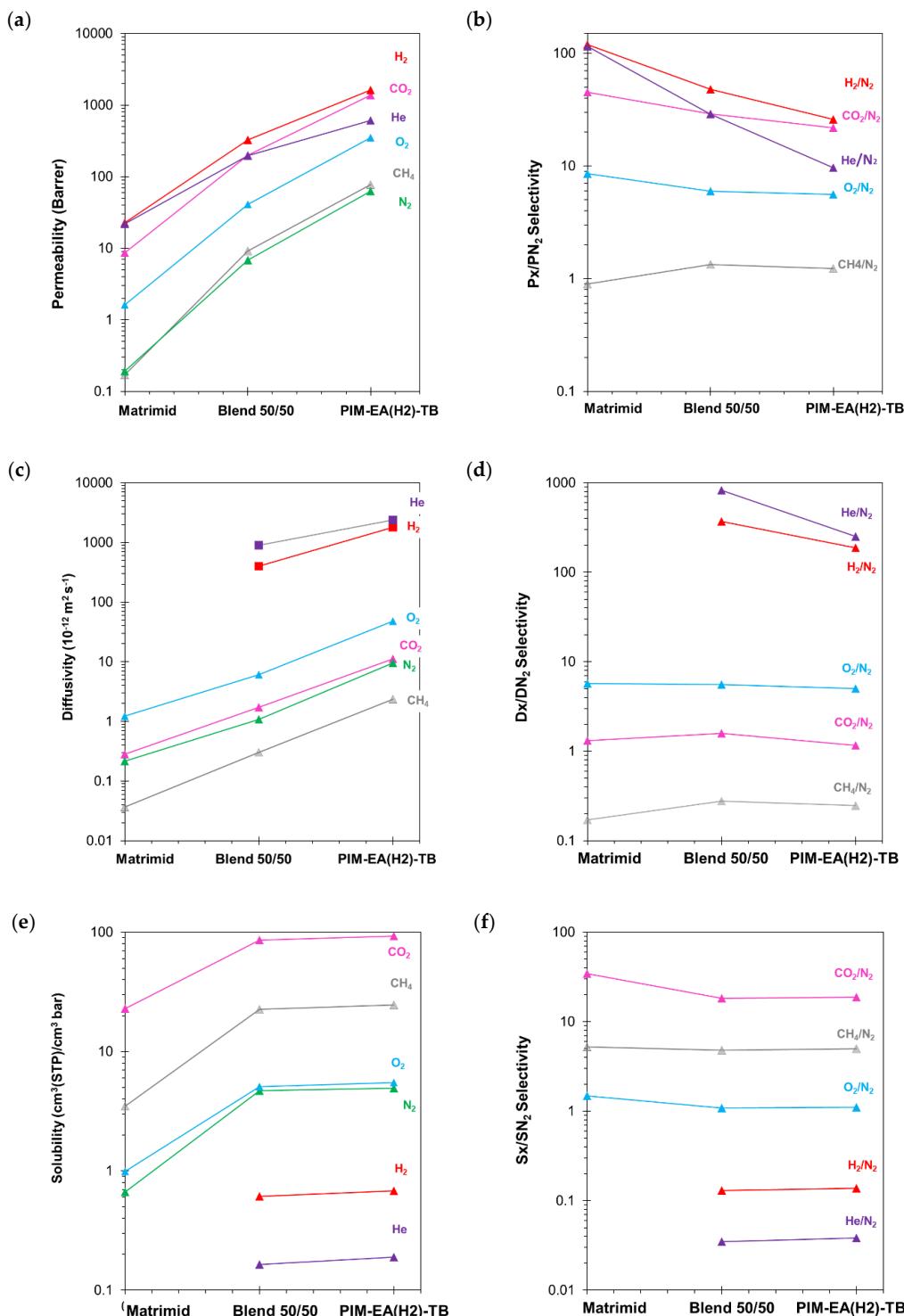


Figure 3. (a) Permeability, (c) diffusivity and (e) solubility coefficients with their respective selectivities (b,d,f) of Matrimid® (100%); Matrimid®5218/PIM-EA(H₂)-TB blend and PIM-EA(H₂)-TB (100%). The lines are indicated as a guide to the eye.

Table 1. Experimental data of single gas permeation in the neat polymers and the Matrimid®5218/PIM-EA(H₂)-TB blend membrane.

Membrane	Permeability (Barrer)						Selectivity (Px/Py)						
	N ₂	CH ₄	O ₂	He	H ₂	CO ₂	H ₂ /N ₂	He/N ₂	O ₂ /N ₂	CH ₄ /N ₂	O ₂ /CH ₄	CO ₂ /CH ₄	CO ₂ /N ₂
Matrimid	0.19	0.17	1.63	21.9	22.8	8.62	120	115	8.54	0.90	9.54	50.6	45.3
Blend	6.83	9.14	41.0	197	328	198	48.0	28.8	6.00	1.34	4.48	21.6	29.0
PIM-EA(H ₂)-TB	62.8	77.6	350	606	1630	1380	25.9	9.64	5.57	1.23	4.51	17.7	21.9
Diffusivity (10 ⁻¹² m ² /s)													
Membrane	N ₂	CH ₄	O ₂	He	H ₂	CO ₂	H ₂ /N ₂	He/N ₂	O ₂ /N ₂	CH ₄ /N ₂	O ₂ /CH ₄	CO ₂ /CH ₄	CO ₂ /N ₂
Matrimid	0.21	0.04	1.23			0.28			5.74	0.17	33.6	7.69	1.31
Blend	1.09	0.30	6.04	900	403	1.73	370	826	5.54	0.28	19.9	5.71	1.59
PIM-EA(H ₂)-TB	9.6	2.36	47.9	2400	1790	11.2	187	251	5.01	0.25	20.3	4.72	1.17
Solubility (cm ³ (STP)/cm ³ bar)													
Membrane	N ₂	CH ₄	O ₂	He	H ₂	CO ₂	H ₂ /N ₂	He/N ₂	O ₂ /N ₂	CH ₄ /N ₂	O ₂ /CH ₄	CO ₂ /CH ₄	CO ₂ /N ₂
Matrimid	0.67	3.49	0.99			22.9			1.49	5.24	0.28	6.58	34.4
Blend	4.70	22.6	5.08	0.16	0.61	85.7	0.13	0.03	1.08	4.81	0.22	3.79	18.2
PIM-EA(H ₂)-TB	4.93	24.6	5.47	0.19	0.68	92.5	0.14	0.04	1.11	5.00	0.22	3.76	18.8

1 Barrer = 10⁻¹⁰ cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹.

The gas permeability and diffusivity are greater for the neat PIM, while there is little difference in solubility between the blend and the neat PIM. The effect of composition is largest for diffusivity, which increases about two orders of magnitude from Matrimid to PIM, whereas the solubility increases less than an order of magnitude. The time lag of H₂ and He is too short to be measured accurately in the relatively thin neat Matrimid®5218 membrane, and thus the related diffusion coefficient and solubility of this membrane could not be determined. The combined effect of S and D is reflected in an exceptionally high permeability of the neat PIM membrane, with an approximately three orders of magnitude higher N₂ and CH₄ permeability compared to the Matrimid membrane. On the other hand, the selectivity is generally higher in Matrimid®5218 (Figure 3b and Table 1), especially for gas pairs with very different kinetic diameters, like H₂/N₂, He/N₂, mainly as a result of the much higher diffusion selectivity (Figure 3d). The O₂/N₂ selectivity is higher in Matrimid®5218 due to a slightly higher diffusion selectivity and solubility selectivity, whereas the higher CO₂/N₂ selectivity in Matrimid®5218 must be ascribed mainly to the higher solubility selectivity (Figure 3e).

The blend membrane with 50 wt% of each polymer exhibits intermediate properties with respect to the two individual polymers, with a roughly linear trend in permeability on a logarithmic scale. This trend suggests that the two polymers have good compatibility and form a homogeneous blend, because Robeson [48] anticipated that the permeability, P_b, of a homogeneous polymer blend can be expressed as:

$$\ln P_b = \phi_1 \ln P_1 + \phi_2 \ln P_2 \quad (1)$$

where ϕ_1 and ϕ_2 are the volume fractions of the two polymers in the blend, and P₁ and P₂ are their respective permeabilities. The minor deviations of the experimental data from linearity are likely due to the use of the weight fraction (Figure 3) instead of volume fraction (Equation (1)). The volume fraction of the PIM, which has a lower density than Matrimid®5218, is higher than the weight fraction. To some extent, the nonlinearity may also be due to slight differences in the degree of physical ageing in the three samples, typically observed for PIMs but less in common glassy polymers with lower free volume.

3.3. Mixed Gas Transport Properties

3.3.1. Mixed Gas Permeability

The membrane performance for two relevant industrial separations was investigated via mixed gas permeability measurements on the pristine Matrimid®5218, PIM-EA(H₂)-TB and on the Matrimid®5218/PIM-EA(H₂)-TB blend (See Appendix A Table A1). Measurements were performed from 1 to 6 bar(a) with two binary gas mixtures of CO₂/CH₄ (35:65 vol %) and CO₂/N₂ (15:85 vol %),

in order to simulate the biomethane purification process from biogas and CO₂ capture from flue gas, respectively (Figure 4, Table 2).

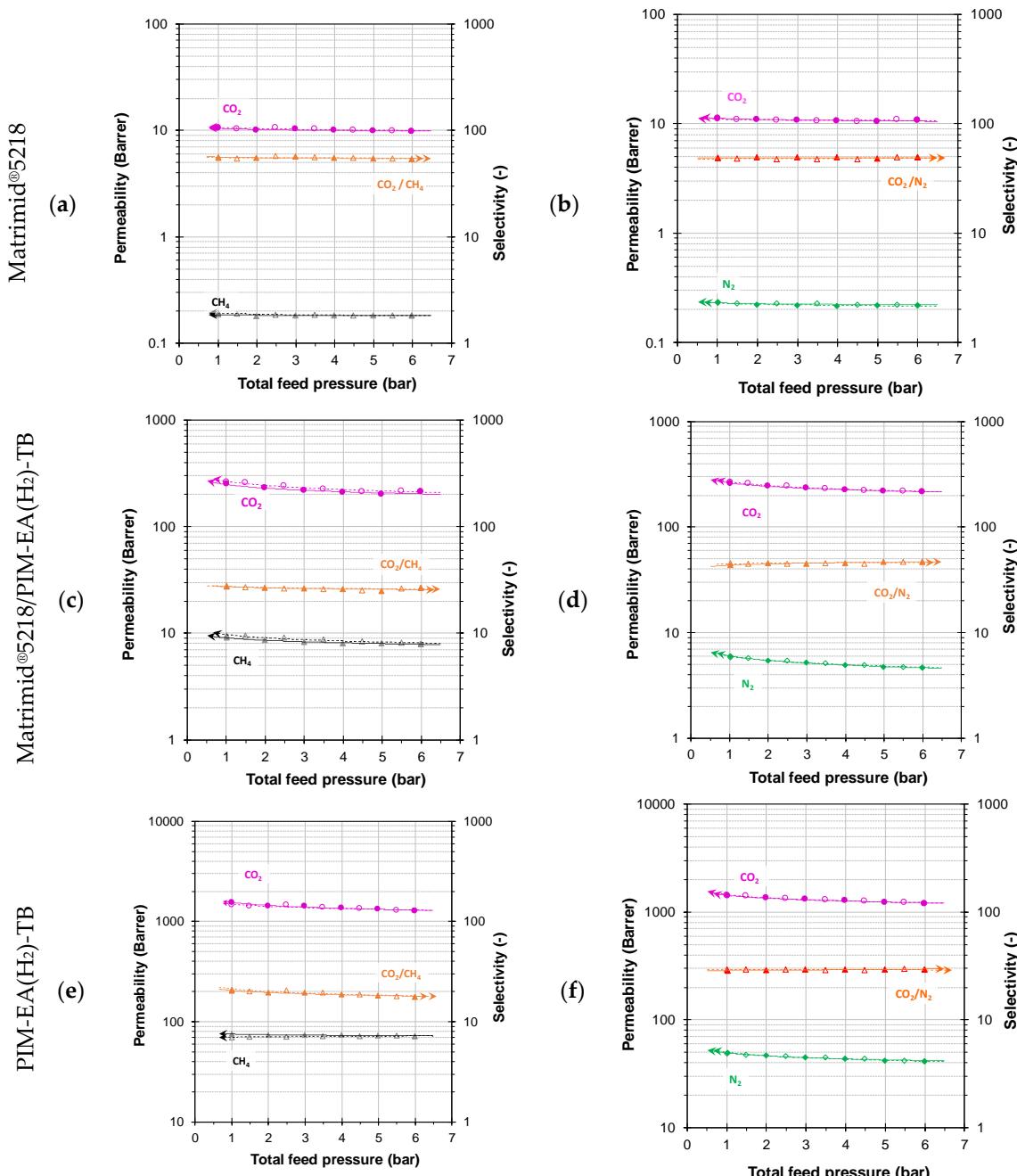


Figure 4. (a,c,e) Pressure dependence of CO₂ and CH₄ permeabilities and CO₂/CH₄ selectivity using the binary mixture of CO₂/CH₄ (35:65 vol %) for neat polymers and Matrimid®5218/PIM-EA(H₂)-TB blend membranes. (b,d,f) Pressure dependence of CO₂ and N₂ permeabilities and CO₂/N₂ selectivity in binary mixtures CO₂/N₂ (15:85 vol %); Closed symbols are used for the stepwise increase of the pressure and open symbols for the subsequent stepwise decrease of the pressure.

The Matrimid®5218 membrane showed very weak pressure-dependence of permeability and selectivity for both gas pairs, CO₂/CH₄ and CO₂/N₂ in the given pressure range. It does not show significant hysteresis between the pressure increase steps and the pressure decrease steps, which means that neither substantial physical ageing, nor CO₂ induced dilation of the polymer takes place. On the other hand, for the Matrimid®5218/PIM-EA(H₂)-TB blend and the neat PIM-EA(H₂)-TB

membranes, the CO₂ permeability decreases as function of the feed pressure for both gas mixtures. This is typical for polymers with distinct dual mode behaviour, which is indeed very common for PIMs [49]. The N₂ permeability decreases in a similar fashion as a function of pressure, and thus the CO₂/N₂ selectivity is virtually constant in all three samples. In the blend and the pure PIM, the methane permeability is slightly less pressure-dependent than that of CO₂, and therefore the CO₂/CH₄ selectivity decreases in these two membranes. The stronger effect of CO₂ on methane than on nitrogen is likely due to its higher concentration (35 vol %) in the CO₂/CH₄ mixture, compared to 15 vol % in the CO₂/N₂ mixture. All membranes were aged for at least a month before the measurements, so that further ageing during the experiments should not be expected. Only neat PIM-EA(H₂)-TB showed a slightly lower permeability in the pressure decrease steps, but the difference was hardly more than the experimental error, so may not be necessarily attributed to physical ageing. On the contrary, the Matrimid®5218/PIM-EA(H₂)-TB blend showed weak hysteresis for CO₂ and CH₄, with slightly higher permeability of both gases in the pressure decrease steps. This suggests a slight dilatation of the polymer matrix and/or removal of trace amounts of residual solvent at elevated CO₂ partial pressures.

Table 2. Comparison of the pure and mixed gas permeability of the neat Matrimid®5218, PIM-EA(H₂)-TB and their blend membrane as measured in the mixed gas setup. Feed gas: binary mixture CO₂/CH₄ (35/65 vol %) and binary mixture CO₂/N₂ (15/85 vol %) at 1 bar.

		Permeability (Barrer)			Px/Py Selectivity (—)	
		CO ₂	CH ₄	N ₂	CO ₂ /CH ₄	CO ₂ /N ₂
Matrimid®5218	Pure gas	10.4	0.20	0.24	52	43.3
	Mix (CO ₂ /CH ₄)	10.5	0.19	-	55	-
	Mix (CO ₂ /N ₂)	11.3	-	0.23	-	49.1
Blend	Pure gas	198	9.1	6.83	21.66	28.99
	Mix (CO ₂ /CH ₄)	250	9.09	-	27.49	-
	Mix (CO ₂ /N ₂)	260	-	6.00	-	43.37
PIM-EA(H ₂)-TB	Pure gas	1391	62.6	53.1	22.22	26.20
	Mix (CO ₂ /CH ₄)	1527	76.1	-	20.07	-
	Mix (CO ₂ /N ₂)	1445	-	49.4	-	29.25

3.3.2. Mixed Gas Diffusion and Solubility

As described recently, a unique feature of our mixed gas permeation setup with on-line mass-spectrometric analysis of the permeate composition is that it allows the determination of, not only, the permeability but also the diffusion coefficients of the individual gases in the mixture [45,46]. The results for the three membranes are given in Table 3. The diffusion coefficient is determined by a time lag method for gas mixtures [45], and the solubility is approximated indirectly as $S = P/D$. The most obvious result for the blend and PIM membrane is that, while the CH₄ and N₂ permeability change relatively little in the mixture (Table 2), their diffusion coefficients increase substantially and since the change in diffusion coefficient of CO₂ is much smaller, the diffusion selectivity decreases significantly. The gas solubility shows exactly the opposite trend: the CH₄ and N₂ solubility decrease in the presence of CO₂. This provides clear evidence of competitive sorption by CO₂ at the expense of the less condensable gases.

Table 3. Comparison of the pure and mixed gas diffusivity and solubility of the neat Matrimid®5218, PIM-EA(H₂)-TB, and their blend membrane as measured in the mixed gas setup. Feed gas: binary mixture CO₂/CH₄ (35/65 vol %) and binary mixture CO₂/N₂ (15/85 vol %) at 1 bar.

		Diffusivity (10 ⁻¹² m ² s ⁻¹)			Dx/Dy Selectivity (-)	
		CO ₂	CH ₄	N ₂	CO ₂ /CH ₄	CO ₂ /N ₂
Matrimid®5218	Pure gas	0.35	0.05	0.28	7.04	1.24
	Mix (CO ₂ /CH ₄)	0.29	0.06	-	5.12	-
	Mix (CO ₂ /N ₂)	0.24	-	0.30	-	0.80
Blend	Pure gas	2.36	0.46	1.58	5.71	1.59
	Mix (CO ₂ /CH ₄)	2.10	0.66	-	3.18	-
	Mix (CO ₂ /N ₂)	1.40	-	2.11	-	0.61
PIM-EA(H ₂)-TB	Pure gas	10.7	2.31	9.22	4.63	1.16
	Mix (CO ₂ /CH ₄)	10.6	3.61	-	2.94	-
	Mix (CO ₂ /N ₂)	7.14	-	10.5	-	0.68
		Solubility (cm ³ (STP) cm ⁻³ bar ⁻¹)			Sx/Sy Selectivity (-)	
		CO ₂	CH ₄	N ₂	CO ₂ /CH ₄	CO ₂ /N ₂
Matrimid®5218	Pure gas	22.2	3.00	0.64	7.39	34.8
	Mix (CO ₂ /CH ₄)	27.0	2.50	-	10.8	-
	Mix (CO ₂ /N ₂)	34.9	-	0.57	-	61.5
Blend	Pure gas	85.8	22.6	4.70	3.79	18.3
	Mix (CO ₂ /CH ₄)	89.2	10.3	-	8.66	-
	Mix (CO ₂ /N ₂)	138	-	1.94	-	71.0
PIM-EA(H ₂)-TB	Pure gas	97.5	20.3	4.32	4.80	22.3
	Mix (CO ₂ /CH ₄)	109	15.7	-	6.91	-
	Mix (CO ₂ /N ₂)	148	-	3.53	-	42.0

3.4. Robeson Plots and Comparison with Literature Blend-Data

The gas permeability data of neat Matrimid®5218, PIM-EA(H₂)-TB, and the blended membrane are plotted in the Robeson diagrams for CO₂/N₂, CO₂/CH₄, O₂/N₂ and H₂/CH₄ (Figure 5). From Matrimid®5218 to the blend and to pure PIM-EA(H₂)-TB, the diagrams show a strong increase in the pure gas permeability, accompanied by a modest decrease in ideal selectivity, as a common trend for all gas pairs. Literature data of pure Matrimid and other PIM/Matrimid blend membranes for CO₂/N₂ and CO₂/CH₄ separation are plotted for reference. Most of the data of our samples lie inside the data cloud near its top range. The cloud of Matrimid data derives from the different measurement conditions, membrane preparation and conditioning.

Only the CO₂/N₂ selectivity of the neat PIM and the blend lie significantly higher than the cloud and these samples are positioned much closer to the most recent upper bound than Matrimid. Especially for CO₂/N₂, with PCO₂ = 198 Barrer and α CO₂/N₂ = 29, the Matrimid®5218/PIM-EA(H₂)-TB blend presents a better trade-off between permeability and selectivity compared to other Matrimid®5218/PIM (50:50) blends reported in the literature, such as PIM-1/Matrimid (PCO₂ = 155 Barrer; α CO₂/N₂ = 27) and cPIM-1/Matrimid (PCO₂ = 145 Barrer; α CO₂/N₂ = 24) [32,34]. Of note is that the Matrimid permeability was increased approximately 20-fold by the addition of 50 wt % of PIM-EA(H₂)-TB. This offers the potential for the preparation of asymmetric or thin film composite membranes with much higher permeability, without compromising selectivity too much.

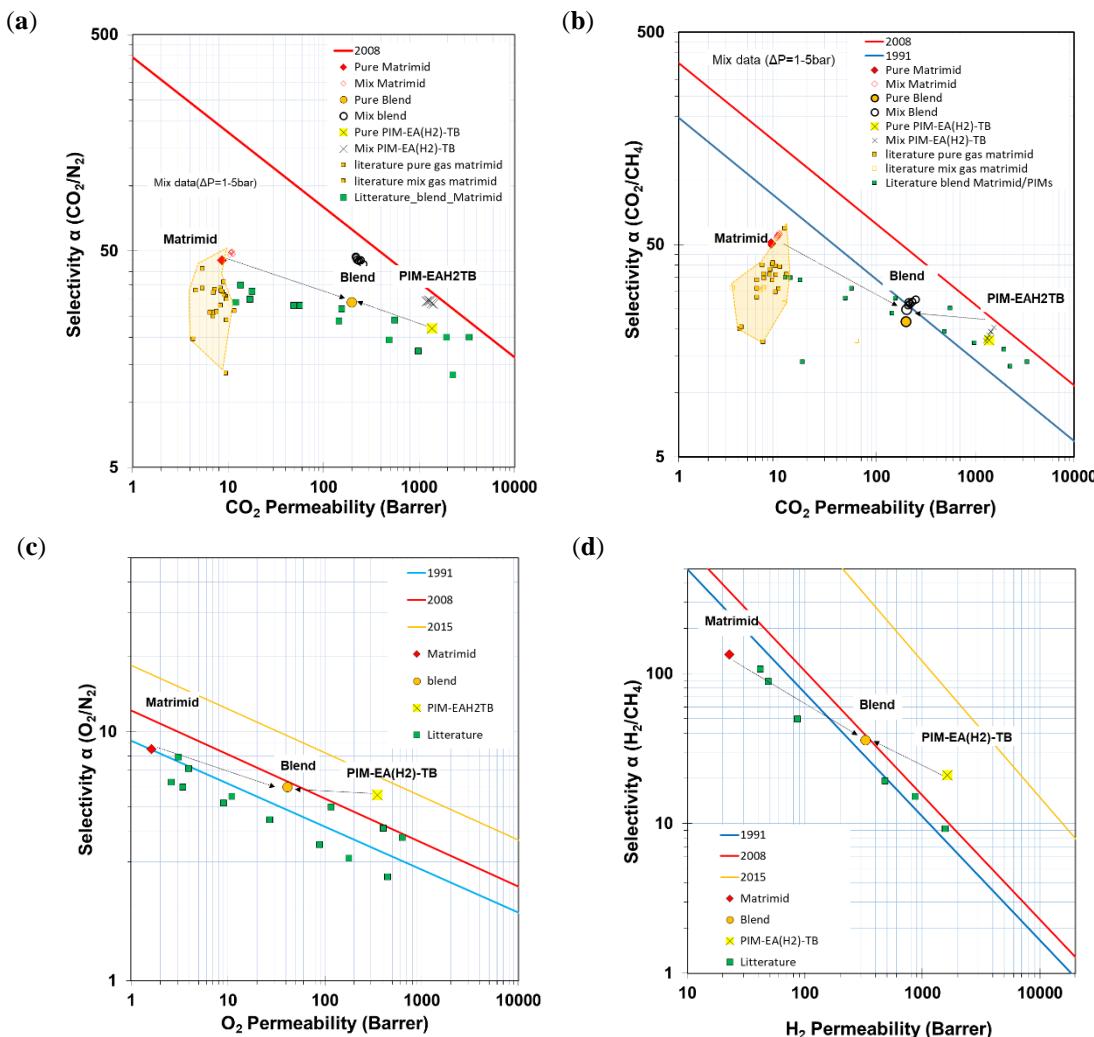


Figure 5. Robeson's plots of ♦ neat Matrimid®5218, X PIM-EA(H₂)-TB and Matrimid®5218/PIM blend membranes for CO₂/N₂ (a), CO₂/CH₄ (b), O₂/N₂ (c) and H₂/CH₄ (d) gas pairs (pure gas filled symbols and Mixed gas open symbols). Reference data for other matrimid-based blends (■) and other PIM-based blends (■) are plotted for comparison.

4. Conclusions

The pure and mixed gas permeation measurements of neat polymer of intrinsic microporosity PIM-EA(H₂)-TB, Matrimid®5218 and their 50/50 wt % blend demonstrated that the permeability of Matrimid®5218 can be increased dramatically by the addition of the PIM whilst maintaining a reasonably high selectivity. Mixed gas permeation experiments reveal a comparable CO₂ permeability and a slightly higher selectivity than the ideal one for the CO₂/CH₄ and CO₂/N₂ gas pairs, and addition of the PIM moves the performance of Matrimid®5218 closer to the Robeson upper bound for these gas pairs. Interestingly, in spite of the slightly higher mixed gas permselectivity, the mixed gas diffusion selectivity is significantly lower than the ideal diffusion selectivity. This indicates that the presence of CO₂ favours the diffusion of the slower gases N₂ and CH₄, but that the effect of competitive sorption, which reduces their solubility, dominates the overall performance of the membranes. All membranes show a moderate to weak decrease in either the permeability or the selectivity for the CO₂/CH₄ and CO₂/N₂ gas pairs with increasing pressure, typical for dual mode sorption behaviour. The very strong effect of PIM-EA(H₂)-TB offers the possibility to tailor the permeability of Matrimid®5218 over a wide range and opens perspectives for making high permeability thin film composite membranes with the mechanical resistance of Matrimid and PIM-like permeabilities.

Author Contributions: E.E. and I.M. conceived, designed and performed the membrane preparation and characterization experiments under the supervision of J.C.J., R.M.-E., M.C. and N.B.M. conceived, synthesized and provided the polymer PIM-EA(H₂)-TB. E.E., I.M. and A.F. conceived, designed and performed the single gas permeation experiments under the supervision of J.C.J., M.M. conceived, designed and performed the mixed gas permeation experiments under the supervision of J.C.J., All authors analyzed the data and wrote the manuscript with similar effort.

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Appendix A. Mixed Gas Permeation Data

Table A1. Mixed gas permeabilities and selectivity for Matrimid, Matrimid®5218/PIM-EA(H₂)-TB blend and PIM-EA(H₂)-TB membranes using the binary mixture CO₂/CH₄ (35/65) vol % and the binary mixture CO₂/N₂ (15/85) vol %.

	Pressure	P _i (Barrer)		Selectivity (–)	Pressure	P _i (Barrer)		Selectivity (–)
	(bar(a))	CH ₄	CO ₂	CO ₂ /CH ₄	(bar(a))	N ₂	CO ₂	CO ₂ /N ₂
Matrimid	1	0.19	10.5	55.7	1	0.23	11.3	48.5
	2	0.18	10.0	55.6	2	0.22	11.0	49.8
	3	0.18	10.3	56.7	3	0.22	10.8	49.3
	4	0.18	10.1	55.3	4	0.22	10.7	49.3
	5	0.18	9.9	54.0	5	0.22	10.4	48.0
	6	0.18	9.8	53.6	6	0.22	10.8	49.4
	5.5	0.18	9.9	54.3	5.5	0.22	10.9	49.5
	4.5	0.18	10.1	55.3	4.5	0.22	10.5	47.3
	3.5	0.18	10.3	56.3	3.5	0.23	10.7	47.1
	2.5	0.19	10.6	57.2	2.5	0.23	10.8	47.7
	1.5	0.19	10.4	54.4	1.5	0.23	11.0	48.3
	1	0.19	10.6	55.2	1	0.23	11.1	48.5
Matrimid®5218/PIM-EA(H ₂)-TB blend	Pressure	P _i (Barrer)		Selectivity (–)	Pressure	P _i (Barrer)		Selectivity (–)
	(bar(a))	CH ₄	CO ₂	CO ₂ /CH ₄	(bar(a))	N ₂	CO ₂	CO ₂ /N ₂
	1	9.09	250	27.5	1	6.0	260	43.5
	2	8.59	231	26.8	2	5.4	246	45.3
	3	8.29	217	26.2	3	5.2	236	45.0
	4	8.09	210	25.9	4	5.0	225	45.6
	5	8.08	200	24.8	5	4.7	219	46.6
	6	7.91	212	26.8	6	4.6	217	47.0
	5.5	8.16	215	26.4	5.5	4.7	219	46.7
	4.5	8.46	213	25.2	4.5	4.9	224	45.2
	3.5	8.70	226	26.0	3.5	5.2	233	45.3
	2.5	9.09	240	26.4	2.5	5.4	244	45.2
	1.5	9.48	257	27.1	1.5	5.7	258	45.0
	1	9.46	263	27.8	1	5.8	265	45.5
PIM-EA(H ₂)-TB	Pressure	P _i (Barrer)		Selectivity (–)	Pressure	P _i (Barrer)		Selectivity (–)
	(bar(a))	CH ₄	CO ₂	CO ₂ /CH ₄	(bar(a))	N ₂	CO ₂	CO ₂ /N ₂
	1	75.7	1540	20.3	1	49.6	1410	28.4
	2	73.4	1430	19.5	2	47.1	1350	28.7
	3	73.7	1430	19.4	3	44.8	1320	29.4
	4	73.4	1370	18.7	4	43.4	1280	29.5
	5	72.6	1320	18.2	5	42.0	1230	29.4
	6	72.1	1270	17.6	6	41.1	1200	29.2
	5.5	72.2	1290	17.8	5.5	41.6	1230	29.5
	4.5	71.6	1340	18.8	4.5	43.7	1260	28.8
	3.5	71.6	1390	19.4	3.5	44.9	1290	28.8
	2.5	71.1	1460	20.6	2.5	46.1	1340	29.1
	1.5	71.1	1430	20.2	1.5	47.7	1410	29.5
	1	69.5	1460	21.0	1	48.6	1430	29.4

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