

Evaluation of CO₂ permeation through functional assembled mono-layers: Relationships between structure and transport

A. Gugliuzza^{a,*}, E. Drioli^{a,b}

^aResearch Institute on Membrane Technology, ITM-CNR, Via Pietro Bucci 17/C, I-87030 Rende, Italy

^bDepartment of Chemical Engineering and Materials, University of Calabria, Via Pietro Bucci 17/C, I-87030 Rende, Italy

Received 7 April 2005; received in revised form 20 July 2005; accepted 2 August 2005

Available online 25 August 2005

Abstract

CO₂ transport through functional assembled mono-layers was evaluated in relation to H₂O and nonpolar gases such as CH₄, O₂, N₂. Membranes based on Pebax[®]2533 were functionalised by incorporating chemical compounds containing free hydroxyl, *N*-alkyl sulphonamide, bulky benzoate groups. The effects of both the chemical nature and concentration of the modifier on the gas transport were reported, respectively. The permeability coefficients of different penetrating chemical species were compared, evidencing the higher affinity of the layers to water vapour and carbon dioxide, due to favourable interactions between polar moieties and penetrant. The condensability of the penetrant directed the permeability of the species considered and was responsible for the high solubility selectivity between H₂O and CO₂ (i.e. $P_{\text{H}_2\text{O}} = 20,330$ barrer, $D_{\text{H}_2\text{O}}/D_{\text{CO}_2} = 0.6$, $S_{\text{H}_2\text{O}}/S_{\text{CO}_2} = 11.4$ at 25 °C for Pebax/KET 50/50 w/w). An increase in polar moieties resulted in enhanced permeability and selectivity with respect to the pure polymer. In contrast, the functionalised polymer was not capable to discriminate between the smallest penetrants such as O₂ and N₂, with consequent decrease in the ideal selectivity ($P_{\text{CO}_2/\text{O}_2}$, $P_{\text{CO}_2/\text{N}_2}$). The functional layers exhibited permeability and selectivity covering broad ranges of values.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Carbon dioxide; Permeability; Pebax

1. Introduction

Many industrial applications, covering sports-wear, personal hygiene products, food, beverage, pharmaceutical packaging and separation of gas streams, need new polymer materials as precursors of layers exhibiting specific permeability and selectivity. A useful strategy for changing and improving the performance of raw materials consists of suitably incorporation of new structural and chemical elements into the polymer matrixes in order to control structure–property relationships [1–5]. One of the most flexible methods for achieving this goal is to blend different compounds, selected on the basis of their intrinsic chemical and morphological characteristics [6–8]. A proper balance between structural parameters and chemical functionalities allows aimed interactions to be designed at molecular and

supra-molecular levels, directing the mass exchange across tailored selective layers and, therefore, assuring comfortable micro-climate [9,10], prolonged freshness and stability of the packed products over longer time periods [11], and efficient vapour–gas separation [12,13]. The subject of this research work was the assessment of the chemistry–transport correlations, which govern the passage of small chemical species, such as vapours and gases, across modified matrixes. Specifically, the behaviour of CO₂ in relation to water vapour and other nonpolar gases (CH₄, O₂, N₂) was evaluated, after introducing different chemical moieties in an elastomeric block co-polyamide (Pebax[®]2533: 80PTMO/PA) [2]. Many studies, devoted to gas separations based on membrane processes, elucidated the importance to correlate the characteristics of polymers, as free volume [14], polymer chain packing and inter-segmental distance [15,16], with their transport properties, emphasising the role of the microstructure of the polymers in gas/vapour permeability and selectivity [17]. Other works were focused on the affinity of some materials, containing PEO, PTMO, PEG and moieties bearing polar ether segments, to condensable gases such as CO₂, C₂H₄ and

* Corresponding author. Tel.: +39 984 492026; fax: +39 984 402103.
E-mail address: a.gugliuzza@itm.cnr.it (A. Gugliuzza).

C₃H₈ [18–20]. This study is addressed to indicate a useful strategy for optimising and diversifying flux and selectivity of membranes based on 80PTMO, operating at low pressure and different temperature. A poly(ether-*block*-amide) (Pebax[®]2533) was blended with chemical structures compatible with the polymer segments and enabling to direct specific and selective interactions with the diffusing molecules. This last aspect is relevant, due to the necessity to establish and maintain specific micro-climate, when dense elastomeric membranes are used, in coating or packaging technologies, where relative humidity, and the O₂ and CO₂ levels have to be properly balanced and controlled. Thus, this work is aimed at illustrating the different performances, which assembled polymer layers can exhibit after modification of their physical and chemical properties. The experimental approach foresaw the use of the flux transient method [21], in order to estimate how the overall transport through membranes differently modified can be affected in terms of permeability, diffusivity and solubility. Specifically, the influence of chemical moieties, i.e. free hydroxyl groups, amphiphilic *N*-alkyl sulphonamides and sugar with hydroxyls masked by benzoate groups, on CO₂ transport was investigated as a function of the modifier content, of temperature and of condensability of all penetrating molecules considered. Permeability and selectivity of the assembled membranes covered broad ranges of values, showing in some cases performance better than that of the pure polymer.

2. Experimental

2.1. Materials and analytical methods

The procedure used for preparing dense modified membranes was described elsewhere [1]. The membrane precursor was an elastomeric poly(ether-*block*-amide) (Pebax[®]2533), while the selected chemical moieties belonged to modifiers such as triethylcitrate (TEC), *N*-ethyl-*o/p*-toluenesulphonamide (KET), and sucrose benzoate (SB). The modifier content into the polymer matrix ranged from 30 to 70 wt%. Physical and chemical properties for all membranes were detected by thermal analyses, using a Diamond Pyris DSC Perkin–Elmer Instrument. In order to establish an identical thermal history, each sample, removed from the support, was cooled down to –100 °C, heated up to 200 °C at 15 °C/min, cooled again down to –100 °C and finally heated up to 200 °C at rate of 15 °C/min. In this work the second heating runs were evaluated and compared. The weighted amount of sample for each experiment was approximately 10.5 mg.

Infrared spectra were collected directly from the sample surface at a pixel size of 6.25 × 6.25 μm over 550 × 550 μm sampling area by using Spectrum Spotlight Chemical Imaging Instrument by Perkin Elmer. FT-IR Chemical Imaging maps were extracted by comparing the spectrum

exhibiting the highest modifier content with the other ones. For all samples the scale was nearly unit. Permeation experiments to CO₂, CH₄, O₂ and N₂, by using an apparatus elsewhere described [1], were performed at 0.92 bar ranging in temperature from 25 to 55 °C. The experimental data related to the water vapour ($p/p_0=0.9$ and $T=20\text{--}35$ °C) [1] were reported in this work for comparing the performance exhibited by the assembled membranes, when contacting chemically different feeds. The results are averages of three different measurements carried out in different specimens of each sample. The experimental error was usually less than 10%. The layer thickness, measured by using a digital gauge (Carl Mhar D 7300 Esslingen a. N.), ranged from 20 to 40 μm with a deviation of ±1.5 μm. All materials were used as received.

2.2. Permeation measurements

The permeability P , expressed in barrer (1 barrer = [cm³(STP)/(cm² s cmHg)] × 10^{–10}), was estimated by measuring the increase in pressure as a function of the time in a calibrated volume at the permeate side according to this relation

$$P = \frac{V22.414l}{RTAt} \ln \left(\frac{p_h - p_l}{p_h - p_{p(t)}} \right) \quad (1)$$

where V is the permeate volume (cm³), l is the membrane thickness, R is the gas constant (8.31 kJ mol^{–1} K^{–1}) and T is the absolute temperature (K), A the membrane area (cm²), t the measured time (s), p_h and $p_{p(t)}$ the downstream pressures at t_0 and t , respectively, and p_l the upstream pressure (cmHg). Each membrane was put into a flat cell thermostated at operating desired value and dried under high vacuum. A constant gas pressure was applied at the upstream side and the measurements began after closing the valve to vacuum pump. The effective membrane area was 2.14 cm². The diffusion coefficients D (cm²/s) were estimated from permeation transient according to the following equations

$$D_{1/2} = \frac{l^2}{7.2t_{1/2}} \quad D_s = \frac{l^2}{5.91t_s} \quad (2)$$

where $t_{1/2}$ is the time during which the flux rises from its initial value to one-half of its final value (i.e. steady state value), while the t_{slope} is the time where the permeability curve plotted versus the time changes its slope [1,21]. Because the transport is well described by the solution-diffusion model $P=DS$, the solubility S [cm³(STP)/(cm³_{pol} cmHg)] was derived from the relation:

$$S = \frac{P}{D_s} \quad (3)$$

Finally, the ideal selectivity $\alpha_{ij}(-)$, between two different penetrants (i and j) was expressed as ratio between the respective permeabilities

$$\alpha_{ij} = \frac{P_i}{P_j} = \left(\frac{D_i}{D_j} \right) \left(\frac{S_i}{S_j} \right) \quad (4)$$

where the terms D_i/D_j (–) and S_i/S_j (–) are the mobility and solubility selectivities, respectively.

3. Results and discussion

3.1. Compatibility between modifiers and polymer

All assembled layers have shown, on relevant length scale, a good miscibility and compatibility, as the thermal [2] and the infrared analysis [22,23] have confirmed. Fig. 1 shows the strong interactions between the systems mixed. Both the transitions related to soft (PTMO) and hard (PA) blocks of the co-polymer were shifted on higher and lower values than those measured for the pure polymer, respectively. This confirmed the migration of each modifier towards both the polymer domains. The increase in T_{m-PTMO} of the polyether segments (PTMO) was due to the increasing reduction in mobility of the polymer chains, because of hydrogen bonding of polar groups, bulky and stiff aromatic structures. The estimated T_{g-PTMO} values confirmed a good compatibility of the blended systems according to Fox equation, as reported in previous work [2]. Plasticization effects were related to the hard component (PA) of the copolyamide, the incorporated chemical moieties being free hydroxyl groups. The observation of a melting point (T_{m-PA}) depression for crystalline hard segments in relation to the pure polymer suggested the extent of inter-molecular interactions for all systems considered. Also infrared spectroscopy yielded indicative information on extent of homogeneity degree for all systems tuned. Chemical imaging analysis extracted information about the molecular

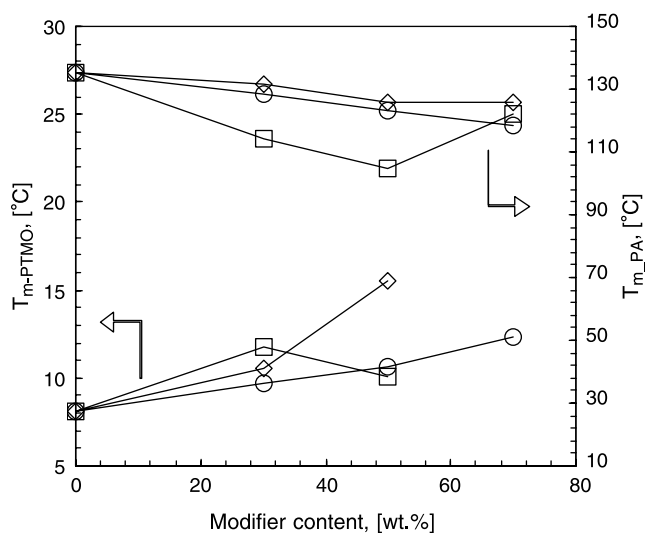


Fig. 1. Changes in T_m related to the soft and hard blocks of Pebax®2533 as a function of the modifier incorporated into the matrix: (○) TEC content, (□) KET content, (◇) SB content.

composition for all modified membranes, suggesting their substantial compatibility. Fig. 2 shows an example of Pebax membrane charged by SB at 50 wt%. The homogeneous distribution of individual chemical moieties is displayed by the coloured bi-dimensional map, exhibiting the scale nearly unit. No significant chemical differences were estimated for all membranes, the spectra collected in different sampling area being overlapped. Infrared analysis of inter-molecular interactions is the detailed subject of a further study [23].

3.2. Influence of the modifier chemistry and content

All samples were tested in the same experimental conditions to different vapour and gas permeations. In details, the behaviour of CO_2 was evaluated and compared with that of the other gaseous molecules, screening the effects of the modifier chemistry and content to the gas transport properties. Diversified trends in permeability were observed when specific chemical moieties were incorporated into the membranes at different chemical ratios. The introduction of free hydroxyl groups gave rise to a slight decrease in CO_2 permeability with respect to the pure polymer (Fig. 3(a)). The latter was remarkably affected, as the modifier containing amphiphilic sulphonamides increased up to 50 and 70 wt%, respectively (Fig. 3(b)). A sudden decrease of one order of magnitude was caused by the bulky structures of the benzoate sucrose, especially as the content was higher than 30 wt% (Fig. 3(c)). These trends were more remarkable for the other nonpolar gases, whereas rising permeability to water vapour was estimated for membranes bearing chemical polar moieties such as hydroxyl and sulphonamide groups [1]. Because the PTMO block was the 80% of the co-polymer and the operating temperature was higher than its melting point, ranging from 8.1 ± 0.3 to 15.5 ± 0.8 °C as a function of the modifier incorporated, the thermodynamic parameter played a key role in the overall transport [1,23]. Freeman et al. [20] indicated that the increase in the polymer cohesive energy density is the responsible for decreasing penetration of nonpolar gases in polar matrixes, because of the increase in energy required for open gaps sufficiently sized to allocate penetrating molecules in sorption sites. This means that the reduced permeability values of N_2 , O_2 , and CH_4 exhibited by polar matrixes were due to no favourable interactions between the nonpolar gases and polar moieties of the polymer matrixes. Differently, polarizable and polar penetrating molecules, such as CO_2 and H_2O , interacted favourably with polar matrixes, although their permeability behaviour was affected in different way by specific inter-molecular interactions, when polarity and concentration of the chemical moieties in the polymer membrane increased. Also the affinity of the polymer matrixes to quadrupolar CO_2 was the highest between all nonpolar gases. Nevertheless, London and Van der Waals interactions, that control the adhesion of this penetrating molecule onto membrane

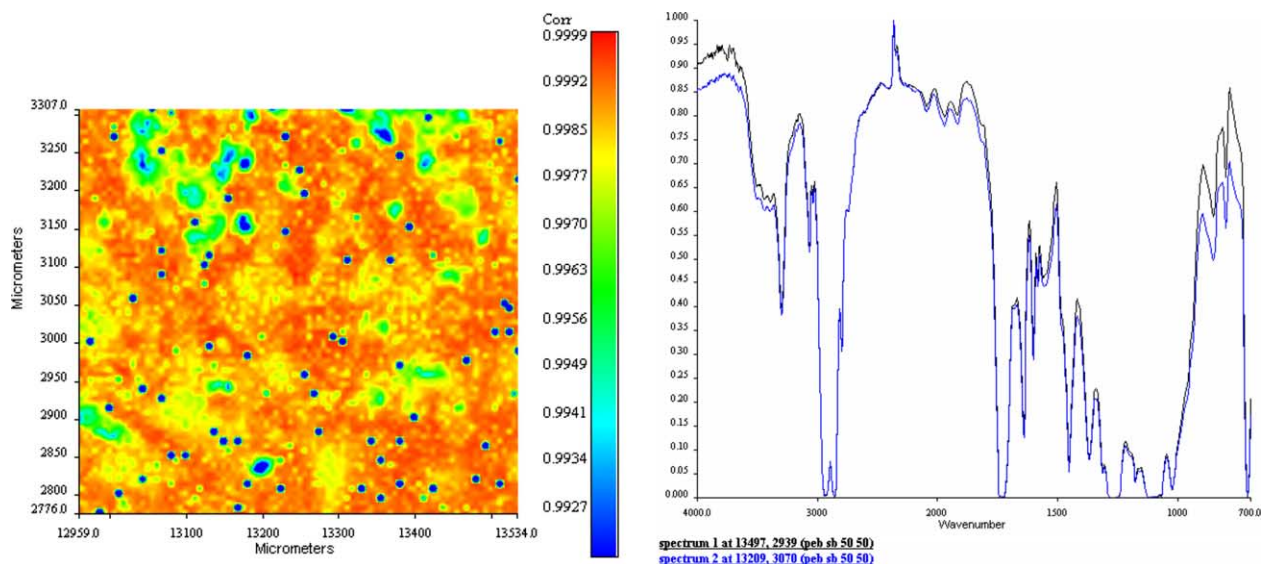


Fig. 2. FT-IR spectra and chemical imaging map for the Pebax/SB membrane at 50/50 w/w.

surfaces and, then, its dissolution into the polymer matrixes [23], were less favoured than Lewis's acid–base interactions [1,2], that are responsible for the rising water vapour solubility and, therefore, for higher permeability of water vapour versus carbon dioxide. The overshadowing solubility selectivity between H₂O/CO₂ can be explained in details analysing the interactions between gas molecules and polymer matrix [23]. So, CO₂ solubility values for all modified membranes, except for those containing a large amount of SB, were generally higher than those estimated for the pure polymer (Table 1). The slightly lower solubility values of membranes containing TEC and KET at 70 wt%, with respect to those containing a lower content, could presumably be ascribed to adjacent polar groups interacting between themselves rather than with CO₂. The diffusivity behaviour of CO₂ was comparable with that observed for the permeability (Fig. 4(a)–(c)), evidencing remarkable effects on the decrease in rotational freedom of the polymer segment chains. This could be due to hydrogen bonding between polar groups and the increased stiffness and bulkiness of the aromatic structures of the modifiers. For

Table 1
Estimated solubility values of CO₂ at 35 °C and 0.92 bar in all functional assembled membranes

Modifier	Content (wt%)	S _{CO₂} [cm ³ (STP)/(cm ³ _{pol} cmHg)]
–	0	0.039
KET	30	0.047
	50	0.056
	70	0.039
	70	0.048
TEC	30	0.048
	50	0.058
	70	0.044
SB	30	0.040
	50	0.029
	70	0.017

membranes containing TEC at 70 wt% and KET, at 30 wt% the estimated diffusion coefficients were comparable with those of the pure polymer, whereas in the other cases they were lower of one or two orders of magnitude. The incorporation of functional bulky modifiers into the polymer matrix has two effects: it is responsible for the destruction of the packing density of crystalline domains in the block copolymer, but also it causes a decreasing rotational freedom of the segment chains. The H-bonding formation between donors and acceptors as well as the inter-segmental agglomeration of the modifiers, especially at higher content, produce a rising amorphous character and slow down the free volume fluctuations. Differential scanning calorimetry, by monitoring position and magnitude of glass transition temperatures and endothermic melting in events for the crystallinity, yielded indicative information on the extent of these two phenomena [2]. Consequently, the stiff and bulky structure of some modifiers as well as the higher cohesive energy of the modified polymer matrixes prevented segmental mobility, slowing down the diffusivity. Despite the large CO₂ solubility, the kinetic parameter overshadowed the thermodynamic one during CO₂ transport, as suggested by the linear correlation found between permeability and diffusivity (Fig. 5).

3.3. Influence of temperature and penetrant chemistry

Fig. 6 shows temperature dependence of the permeability to different penetrating species, H₂O, CO₂, CH₄, O₂ and N₂, for all functionalised membranes in the Arrhenius type plots, exhibiting linear increase in flux when operating temperature is raised. Similar behaviour was also observed for the diffusion coefficients. For each set of functional layers the fluxes of the five diffusing molecules were compared and water vapour resulted much more permeable

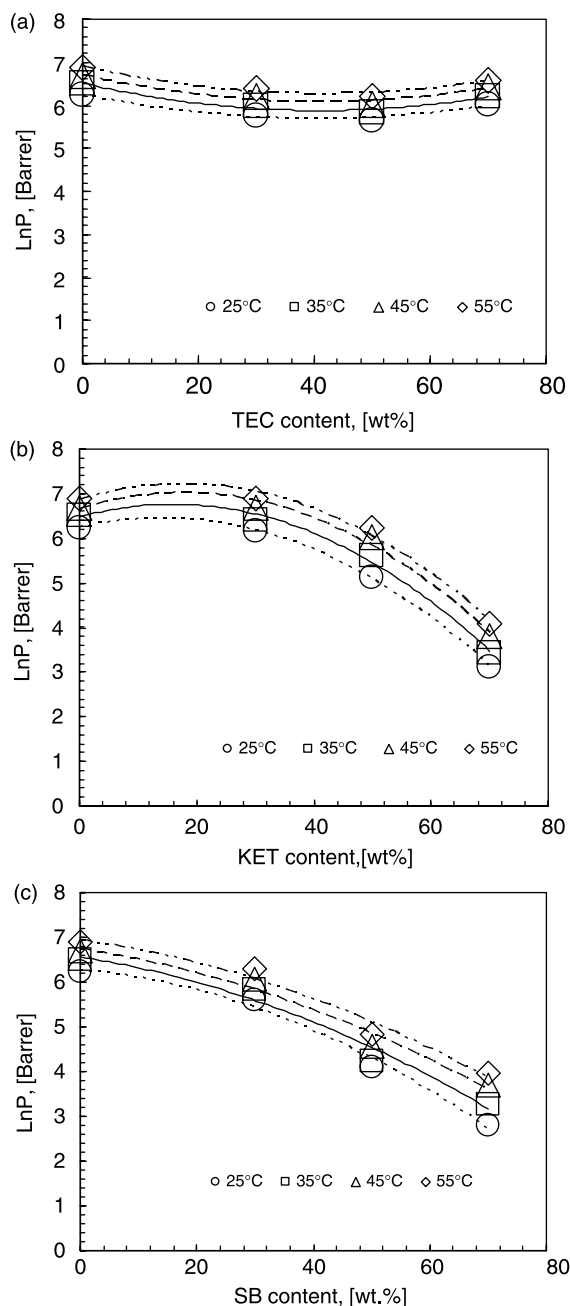


Fig. 3. CO₂ permeability as a function of weight percent modifier. The permeability coefficients were measured at 0.92 bar, ranging from 25 to 55 °C: (a) TEC content, (b) KET content, (c) SB content.

than CO₂ and than the other nonpolar gases. Specifically, the membranes of Pebax/TEC, containing free hydroxyl groups, exhibited permeability according to this sequence: H₂O \gg CO₂ \gg CH₄ > O₂ > N₂. Also membranes of Pebax/KET and Pebax/SB, with chemical moieties such as amphiphilic sulphonamide and benzoate groups, respectively, were responsible for a decrease in permeability in the following order: H₂O \gg CO₂ > CH₄ \approx O₂ > N₂. The order of these sequences was mainly due to the different condensability of the penetrant species [24], as shown in Fig. 7, the penetrants with higher critical temperature being more

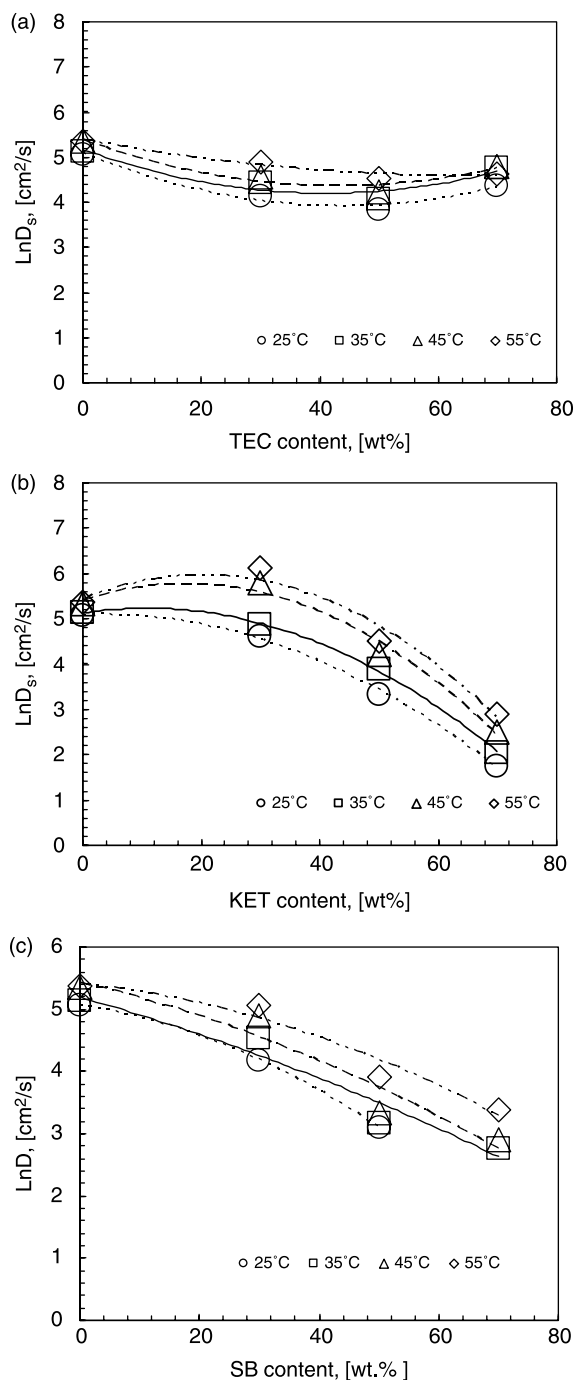


Fig. 4. CO₂ diffusivity versus weight percent modifier, measured at 0.92 bar from 25 to 55 °C: (a) TEC content, (b) KET content, (c) SB content.

condensable and, therefore, more soluble, especially in membranes bearing groups with high polarity degree (–OH, –SO₂NH–, –OC(=O)–). Nonetheless, the different critical volume of the penetrants, combined with structural changes induced by bulky modifiers, was in some cases responsible for a decrease in selectivity. Membranes incorporating KET and SB, for example, exhibited comparable permeability to CH₄ and O₂, probably for the concomitant and conflicting effects of both the critical temperature and volume (i.e.

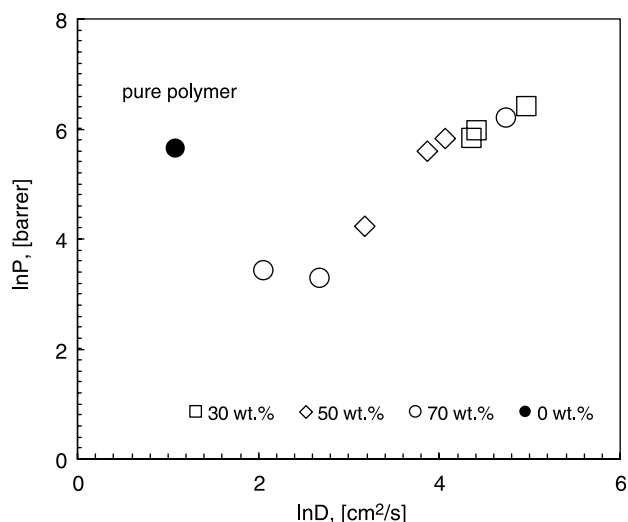


Fig. 5. CO₂ permeability versus diffusivity at 35 °C for pure Pebax[®]2533 and all modified membranes.

99.2 cm³ mol⁻¹ and 191.05 K for CH₄, 73.4 cm³ mol⁻¹ and 154.6 K for O₂). As the steric hindrance of these modifiers was larger and larger, the amorphous character of the systems increased [2]. In the membranes the modifiers also grouped together in form of clusters had different mobility in comparison to that of the polymer matrix,

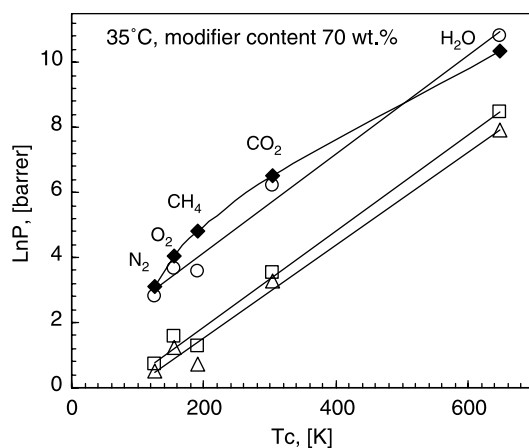


Fig. 7. Estimated permeability as a function of the critical temperature at 35 °C for: (◆) Pebax[®]2533 (100), (○) Pebax/TEC (30/70), (□) Pebax/KET (30/70), (△) Pebax/SB (30/70).

especially at high modifier content. Presumably, at the interstices the diffusion of the smallest penetrant molecule was facilitated in comparison to the gases of bigger dimension and interacting with the fillers. As a consequence, the highest condensability and the biggest size of CH₄ produced a lower permeability than that estimated for H₂O and CO₂ and in the same order of magnitude of O₂.

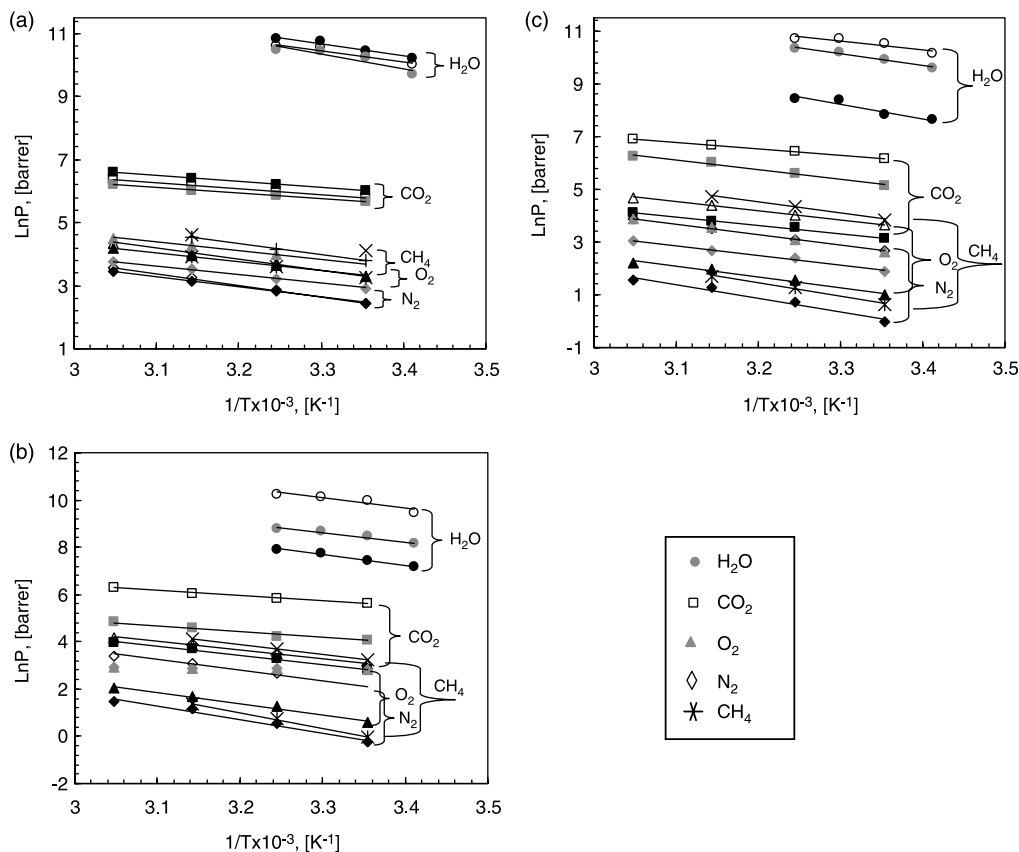


Fig. 6. Temperature dependence of permeability to H₂O (20–35 °C, $p/p_0=0.9$), CO₂, CH₄, O₂ and N₂ (25–55 °C, 0.92 bar) for all functionalised assembled membranes: (a) for TEC series, (b) KET series, (c) SB series. Weight percent modifier for each series: unfilled symbols, 30 wt%; grey-filled symbols, 50 wt%; filled symbols, 70 wt%.

Finally, the systems, considered in this work, exhibit structural features enough complicated, considering that they are mixtures of hard-segment-rich hard domains, of soft-segment-rich segment matrix and of relative inter-phases, and they undergo markedly changes when charged by poly-functional and bulky modifiers. With this regards, computational studies, still in progress, are leading to a deep understanding of the structures and dynamics for the assembled membranes investigated in this work, yielding indicative information on geometry, inter-segmental mixing and free volume characterising the systems of interest.

3.4. Ideal selectivity

Concerning the membrane affinity to penetrating molecules, the highest condensability of the water vapour was responsible for the high permeability ratio between water vapour and carbon dioxide. By comparing the combination of solubility and diffusivity coefficients for these penetrants to the overall permeability, the solubility overshadowed the diffusivity. Really, the diffusion coefficient values measured for the carbon dioxide were slightly higher than those estimated for the water vapour, but the solubility values were remarkably larger for the water vapour. This is reflected by the predominant solubility selectivity with respect to the diffusivity selectivity, as shown in Fig. 8(a) and (b). Generally, the solubility selectivity has enhanced as the modifier content and, therefore, the accessible polar moieties increased. In KET series, due mainly to the bulky aromatic structure and partial double-bond character of the amide linkage, the overall stiffness of the systems mixed gave rise to the reduction of the rotational freedom, as well displayed by the rising diffusivity selectivity with the modifier content. Nonetheless, in all cases the predominant solubility selectivity between water vapour and carbon dioxide was reflected on the permeability selectivity (Fig. 9(a)). Furthermore, the membrane functionalization has optimized the ideal selectivity of the pure polymer. Diversifying the chemical moieties and their content in the polymer matrix, the majority of the membranes were much more permeable and selective to the water vapour, especially those functionalised by TEC (30–70 wt%), KET (30–50 wt%) and SB (30 wt%). Similarly, in the case of CO₂ and CH₄ permeability and selectivity were optimised, specifically for Pebax/TEC (30/70) and Pebax/SB (70/30) (Fig. 9(b)). For the other modified membranes an increase in selectivity resulted in a decrease in permeability. As a whole, the functional assembled layers exhibited higher selectivity values, maintaining comparable permeability values with the pure polymer at the different operating temperatures (Fig. 9(a) and (b)). In contrast, high CO₂/N₂ selectivity was only exhibited by the membrane containing TEC at 70 wt%. The selectivity of the membranes charged by KET and SB at 30 wt% was comparable with that estimated for the pure polymer, though a decrease in permeability was observed. In the

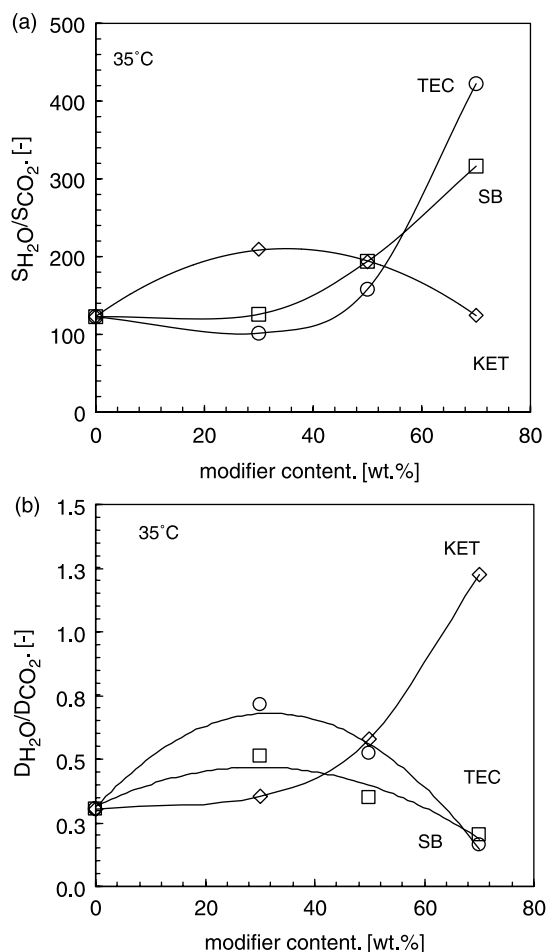


Fig. 8. Estimated (a) solubility selectivity and (b) diffusivity selectivity with increasing modifier content between water vapour and carbon dioxide at 35 °C. (○) Pebax/TEC, (◇) Pebax/KET, (□) Pebax/SB.

others cases the permeability and selectivity values were much lower than those estimated for the pure Pebax (Fig. 9(c)). The reason for this could be due to the different size of the diffusing molecules, enabling to influence the permeability in larger measure than the condensability, as mentioned above. Despite N₂ condensability is lower than that of the carbon dioxide, the nitrogen gets also a smaller critical volume (89.9 and 93.9 cm³ mol⁻¹ for N₂ and CO₂, respectively). This can facilitate the diffusivity through the polymer matrix, affecting the membrane capability to discriminate among small-sized penetrating molecules. Furthermore, the incorporation of bulky and stiff structures into the polymer matrixes destroys the packing of the polymer chains [2], producing amorphous morphologies, which could facilitate the passage of small sized penetrants. This effect appears still more evident when the modifiers are KET and SB at high content and the penetrating molecule is the oxygen ($V_c = 73.4$ cm³ mol⁻¹). The highest CO₂/O₂ selectivity was exhibited by Pebax/TEC (30/70); the membranes charged by TEC, SB at 30 wt% and KET at 30–50 wt% exhibited slightly lower selectivity, but also much lower permeability than the pure Pebax (Fig. 9(d)).

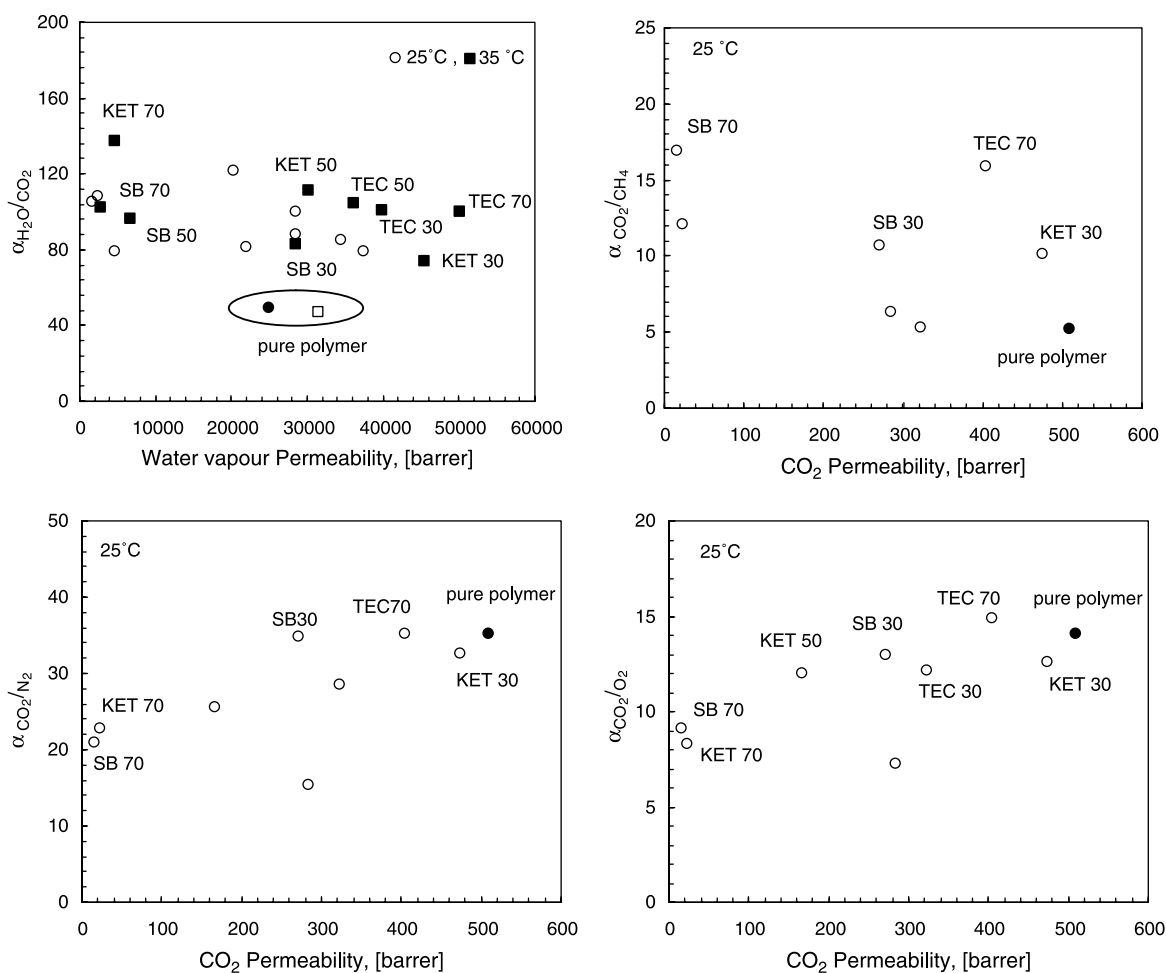


Fig. 9. Estimated ideal selectivity (P_i/P_j) of CO_2 in relation to water vapour at 25 and 35 °C and the other nonpolar gases at 25 °C in all functional membranes: (●, □) Pure polymer, (○, ■) functional assembled layers. Ideal selectivity/permeability plots: (a) $P_{\text{H}_2\text{O}}/P_{\text{CO}_2}$ versus $P_{\text{H}_2\text{O}}$, (b) $P_{\text{CO}_2}/P_{\text{CH}_4}$ versus P_{CO_2} , (c) $P_{\text{CO}_2}/P_{\text{N}_2}$ versus P_{CO_2} , (d) $P_{\text{CO}_2}/P_{\text{O}_2}$ versus P_{CO_2} .

Nonetheless, from a comparison with data reported in literature (Table 2), the experimental results confirmed the good performance in terms of permeability and selectivity of the membranes considered in this work, since high permeability was combined with high selectivity. CO_2 permeability, CO_2/N_2 and CO_2/O_2 selectivities for all of the functional layers were remarkably higher than that exhibited by some rubbers and polymers containing PTMO [25,26]. Higher permeability and selectivity values were also estimated with respect to some amorphous glassy poly (arylene ether)s [16], whereas comparable values were obtained with some hybrid films based on Pebax MX1657 [27]. As a result, the incorporation of new chemical functionalities into the polymer matrix allowed getting broad ranges of selectivity and permeability values to be properly combined as a function of the specific application. This is an advantage, if we consider that some applications such as packaging require a strict control of the gas levels (i.e. O_2 and CO_2) within confined spaces. In this case, for example, optimal O_2 and CO_2 concentrations are to be maintained, since injuriously low O_2 or high CO_2 levels

could reduce significantly the shelf-life of packed products, due to induction of fermentative metabolisms or growth of bacteria. The possibility to diversify and balance permeability and selectivity of one protective layer offers the opportunity to select properly the performance, which better may satisfy the industrial requirements.

4. Conclusions

Membranes based on Pebax[®] 2533 were functionalised by incorporating additional chemical moieties such as free hydroxyls, amphiphilic sulphonamides, and benzoate groups. The permeation of CO_2 in relation to water vapour and to other nonpolar gases was estimated through these functional mono-layers. The effects of the modifiers on CO_2 permeability, diffusivity and solubility were elucidated in comparison with data related to the water vapour. The influence of the condensability of the penetrating species was responsible for the much higher permeability of water vapour and of carbon dioxide. Favourable Lewis' acid–base

Table 2
Permeability and selectivity in rubbery, glassy and semi-crystalline polymers

Polymer	P_{CO_2} (barrer)	$\alpha_{\text{CO}_2/\text{N}_2}$ (–)	$\alpha_{\text{CO}_2/\text{O}_2}$ (–)	Ref.	Polymer ^a	$P_{\text{H}_2\text{O}}$ (barrer)	P_{CO_2} (barrer)	$\alpha_{\text{H}_2\text{O}/\text{CO}_2}$ (–)	$\alpha_{\text{CO}_2/\text{N}_2}$ (–)	$\alpha_{\text{CO}_2/\text{O}_2}$ (–)
Natural rubber ^b	120	16.3	–	[25]	PEBAX 100	25,030	500	49.2	35.0	14.0
Butyl rubber ^b	4.7	16.0	–	[25]	PEBAX /KET 70/30	37,500	480	79.0	35.5	12.6
Polybutadiene ^b	127	21.0	–	[25]	PEBAX /KET 50/50	20,330	167	121.7	25.6	12.0
Ter-Bpa ^c	30.3	16.6	4.28	[16]	PEBAX /KET 30/70	2455	23	108.1	22.9	8.3
Ter-6fbpa ^c	37.3	13.5	3.88	[16]	PEBAX /TEC 70/30	28,500	320	88.4	28.6	12.2
Ter-Fluorene ^c	41.2	15.2	4.01	[16]	PEBAX /TEC 50/50	28,560	285	100.3	15.4	7.3
PUU(PDMS0.9K1) ^d	984	7.6	3.3	[26]	PEBAX /TEC 30/70	34,440	400	85.1	35.2	14.9
PU(PTMO) ^d	64	20.6	10.7	[26]	PEBAX /SB 70/30	21,960	270	81.0	34.8	13.0
PUU(PTMO/ PDMS) ^d	82	24.8	8.1	[26]	PEBAX /SB 50/50	4730	60	79.3	–	–
Pebax/TEOS ^e 80/20	51	37.7	17.00	[27]	PEBAX /SB 30/70	1720	16	105.0	21.0	9.0
Pebax/TEOS ^e 60/40	18	22.5	13.85	[27]						
Pebax/TiOP ^e 80/20	37	52.9	23.13	[27]						
Pebax/TiOP ^e 60/40	44	48.9	14.19	[27]						

^a The data were at: 25 °C and 0.92 bar (PEBAX[®]2533-membranes used in this work).

^b The data were at: 25 °C and 0.967 bar.

^c The data were at: 35 °C and 1 atm.

^d The data were at: 30 °C and 1 atm.

^e The data were at: 25 °C and 4 bar (PEBAX[®]MX1657).

and polar–quadrupole interactions promoted the dissolution of the penetrant molecules in the polymer matrixes, though the first ones predominated on the second ones [23], especially as polar moieties were incorporated into the membranes. With this regards, the solubility selectivity, overshadowing the diffusivity one, was consistent with the additional polar moieties that, combined with the ether linkages of the polymer, promoted an increase in membrane affinity to more condensable species. Specifically, the functional layers exhibited H₂O permeability and H₂O/CO₂ selectivity much higher than those measured for the pure polymer. Similarly, the membrane functionalization was responsible for the high CO₂ permeability compared to that measured for CH₄ and for the increase in CO₂/CH₄ selectivity. The low critical volume of penetrating species such as N₂ and O₂ affected the selectivity of CO₂ with respect to these molecules, especially at high content in KET and SB. Probably different amorphous morphologies affected the discriminate character of the membranes, enhancing the passage of the smallest diffusing molecules. As a result, the chemical functionalization of polymeric membranes plays a key role in controlling the performance of membranes, which can find application in different industrial fields. Broad ranges of selectivity and permeability values can be obtained and combined in order to match properly the requirements from specific applicative technologies.

Acknowledgements

The authors gratefully acknowledge the support of this work, realised within the framework of STRP NMP3-CT-

2005-013644 MULTIMATDESIGN funded by the European Community.

References

- [1] Gugliuzza A, Drioli E. New performance of a modified poly(amide-12-*b*-ethyleneoxide). *Polymer* 2003;44(7):2149–57.
- [2] Gugliuzza A, Drioli E. Role of additives in the water vapor transport through block co-poly(amide/ether) membranes: effects on surface and bulk polymer properties. *Eur Polym J* 2004;40(10):2381–9.
- [3] Nagai K, Freeman BD, Cannon A, Allcock HR. Gas permeability of poly(bis-trifluoroethoxyphosphazene) and blends with adamantane amino/trifluoroethoxy (50/50) polyphosphazene. *J Membr Sci* 2000; 172:167–76.
- [4] Hu CC, Wang YC, Lib CL, Leeb KR, Chen YC, Lai JY. Relationship between polymer structure and gas transport properties in a series of fluorine-containing aromatic polyamide membranes for oxygen enrichment. *Desalination* 2002;144:103–8.
- [5] McDowell CC, Partin JM, Freeman BD, McNeely GW. Acetone solubility and diffusivity in poly(ethylene terephthalate) modified with low levels of 2,6-naphthalene dicarboxylic acid, isophthalic acid, and 2,5-bis-(4-carboxyphenyl)-1,3,4-oxadiazole. *J Membr Sci* 1999; 163:39–49.
- [6] Rezac ME, Sorensen ET, Beckham HW. Transport properties of crosslinkable polyimide blends. *J Membr Sci* 1997;136:249–59.
- [7] Rezac ME, Schöberl B. Transport and thermal properties of poly(ether imide)/acetylene-terminated monomer blends. *J Membr Sci* 1999; 156:211–22.
- [8] Su TM, Ball IJ, Conklin JA, Huang SC, Larson RK, Nguyen SL, et al. Polyaniline/polyimide blends for pervaporation and gas separation studies. *Synth Met* 1997;84:801–2.
- [9] Gugliuzza A, Clarizia G, Golemme G, Drioli E. New breathable and waterproof coatings for textiles: effect of an aliphatic polyurethane on the formation of PEEK-WC porous membranes. *Eur Polym J* 2002;38: 235–42.
- [10] Gebben B. A water vapour-permeable membrane from block copolymers of poly(butylenes terephthalate) and polyethylene oxide. *J Membr Sci* 1996;113:323–9.

- [11] Del Nobile MA, Buonocore GG, Palmieri L, Aldi A, Acierno A. Moisture transport properties of polyamides copolymers intended for food packaging applications. *J Food Eng* 2002;53:287–93.
- [12] Metz SJ, van de Ven WJC, Potreck J, Mulder MHV, Wessling M. Transport of water vapor and inert gas mixtures through highly selective and highly permeable polymer membranes. *J Membr Sci* 2005;251:29–41.
- [13] Jia L, Xu XF, Zhang HJ, Xu JP. Permeation of nitrogen and water vapor through sulfonated polyetherethersulfone membrane. *J Polym Sci, Polym Phys Ed* 1997;35:2133–40.
- [14] Wang ZF, Wang B, Qia N, Ding XM, Hu JL. Free volume and water vapor permeability properties in polyurethane membranes studied by positrons. *Mater Chem Phys* 2004;88:212–6.
- [15] Sheth JP, Xu J, Wilkes GL. Solid state structure–property behavior of semicrystalline poly(ether-*block*-amide) PEBAX[®] thermoplastic elastomers. *Polymer* 2003;44:743–56.
- [16] Banerjee S, Maier G, Dannenberg C, Spinger J. Gas permeabilities of novel poly(arylene ether)s with terphenyl unit in the main chain. *J Membr Sci* 2004;119:63–71.
- [17] García-Ayuso G, Salvarezza R, Martínez-Duart JM, Sánchez O, Vázquez L. Relationship between the microstructure and the water permeability of transparent gas barrier coatings. *Surf Coat Technol* 1998;100–101:459–62.
- [18] Lin H, Freeman BD. Gas solubility, diffusivity and permeability in poly(ethylene oxide). *J Membr Sci* 2004;239:105–17.
- [19] Hirayama Y, Tanihara N, Kusuki Y, Kase Y, Haraya K, Okamoto K. Permeation properties to hydrocarbons, perfluorocarbons and chlorofluorocarbons of cross-linked membranes of polymethacrylates with poly(ethylene oxide) and perfluorononyl moieties. *J Membr Sci* 1999;163:373–81.
- [20] Bondar VI, Freeman BD, Pinnau I. Gas sorption and characterization of poly(ether-*b*-amide) segmented block copolymers. *J Polym Sci, Part B: Polym Phys* 1999;37:2463–75.
- [21] Watson JM, Payne PA. A study of organic compound pervaporation through silicon rubber. *J Membr Sci* 1990;49:171.
- [22] Gugliuzza A, Drioli E. Water vapor and carbon dioxide permeation through block co-polyamide-based membranes: relationships between structure and transport, proceeding of the Euromembrane Congress, Hamburg, Germany 2004.
- [23] Gugliuzza A, Fabiano R, Garavaglia MG, Spisso A, Drioli E. Study of the surface character as responsible for controlling interfacial forces at membrane-feed interface. Submitted for publication.
- [24] Weast RC (editor), *Handbook of chemistry and physics*, 64th ed. Florida: CRC Press; 1983–1984.
- [25] Van Amerongen GJ. Influence of structure of elastomers on their permeability to gases. *J Polym Sci* 1949;3:307–32.
- [26] Ho BP, Choon KK, Young ML. Gas separation properties of polysiloxane/polyether mixed soft segment urethane urea membranes. *J Membr Sci* 2002;204:257–69.
- [27] Zoppi RA, das Neves S, Nunes SP. Hybrid films of poly(ethylene oxide-*b*-amide-6) containing sol-gel silicon or titanium oxide as inorganic fillers: effect of morphology and mechanical properties on gas permeability. *Polymer* 2000;41:5461–70.