A comparative study between single gas and mixed gas permeation of polyether-block-amide type copolymer membranes

Lidia Martínez-Izquierdo [a,b], Adelaida Perea-Cachero [a,b], Magdalena Malankowska [a,b], Carlos Téllez [a,b], Joaquín Coronas [a,b,*]

[a] Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Zaragoza 50018, Spain
[b] Chemical and Environmental Engineering Department, Universidad de Zaragoza, Zaragoza 50018, Spain

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ABSTRACT

We analyze the gas separation performance of five polyether-block-amide type copolymers (Pebax® 1657, Renew®, 2533, 3533 and 4533). These codes are composed of different hard and rubbery segments with different proportions. Dense membranes were prepared by the casting-solution method and studied by elemental, thermogravimetric and X-ray diffraction analyses, FTIR-ATR spectroscopy and single and mixed gas permeation. Codes with the best separation performance are those of polyethylene oxide as the soft phase (Pebax® 1657 and Renew®) due to the more intense interactions of this segment with CO$_2$, which increases the CO$_2$/N$_2$ solubility selectivity (17.5 and 30.5 for Pebax® 1657 and Renew®, respectively) and hence the CO$_2$/N$_2$ separation selectivity of the membrane (36 and 37 for Pebax® 1657 and Renew®, respectively, obtained from mixed gas permeation). It is also noticeable that the proportion of the soft phase in the copolymer determines the permeability of CO$_2$. It was found that the codes with a greater soft/hard segment ratio (Pebax® 2533 and 3533) have also a greater permeability value (239 and 220 Barrer for Pebax® 2533 and 3533, respectively, measured by mixed gas permeation). Pebax® Renew® was the polymer with the best separation performance with CO$_2$ permeabilities of 167 and 164 Barrer and CO$_2$/N$_2$ selectivities of 41 and 37, measured by single and mixed gas permeation, respectively. The comparison between the single and mixture gas permeation results revealed a relatively good correspondence between both for most of the Pebax® codes tuned by the solubility and diffusion properties of the polymers.

1. Introduction

The processes applied to obtain the majority of the current energy forms (electricity, fuel or gas) result in CO$_2$ emissions to the atmosphere. CO$_2$ holds a major share in causing global warming and its impact can now be seen on the world panorama affecting not only the climate but also the economy simultaneously having important social implications. The treatment of post-combustion flue streams as well as exhausts from cement and stainless steel factories, focused on separating CO$_2$ from N$_2$, is one of the possible remediation approaches for decreasing the CO$_2$ concentration in the corresponding outlet streams [1,2], particularly efficient when carried out with membrane technology [3]. This CO$_2$/N$_2$ separation, properly carried out at industrial scale thanks to the energetic and economic advantages of the membrane technology, would allow the decrease of the CO$_2$ concentration in the atmosphere alleviating the current climatic situation.

Membranes can provide an eco-friendly and low energy consumption alternative to traditional separation techniques [4,5]. They are characterized by low requirement of weight and space, process flexibility and simplicity, good mechanical complexity and low cost of implementation and operation, to name a few. Even though membrane separation is a very attractive technology, it shows some limitations, especially for the gas separation application. The inherent trade-off between permeability and selectivity reported by Robeson in 1991 and 2008 remains the biggest challenge in developing polymeric membranes. Polymers with high permeability usually exhibit low selectivity and vice versa [6,7]. One approach to overcome such limitation is to combine the flexibility of polymers such as polyethylene oxide (PEO) with the mechanical stability of hard or crystalline polymers like polyamide (PA), polyimides (PI) and polystyrene (PS). Among the many polymers studied, polyether-block-amide (PEBA) copolymers are considered some of the most promising materials [8–13]. PEBA copolymers, commercialized

under the trademark of Pebax®, are a series of novel thermoplastic elastomers comprised of rigid polyamide blocks (PA) and flexible polyether (PE) segments which are glassy and rubbery at room temperature, respectively [14].

In the membrane gas separation process, gas molecules are transported through due to the partial pressure difference between the feed and permeate sides. In a nonporous membrane, gas mixtures are fractionated in virtue of the differences in solubility and diffusivity of the mixture components through the polymer. Such transport is described by the solution-diffusion mechanism, which dominates the gas separation application [15]. Based on the solution-diffusion mechanism, the permeability of gases in polymeric membranes depends on their gas sorption and diffusion intrinsic properties. On the one hand, diffusion is a kinetic phenomenon related to the velocity of the gaseous permeant that passes through the membrane under a concentration gradient. On the other hand, sorption is a thermodynamic phenomenon where the usually reversible interactions between the membrane material and the gaseous permeants determine the sorption interaction.

In this work, we aim at studying how the segment nature and the proportion of each of them (PE/PA) within five different Pebax® codes affect the solubility, diffusivity and permeability parameters and hence the CO_2/N_2 gas separation performance of the membranes. Moreover, the intention of this study is also to compare two well established methods for the gas separation performance estimation from single and mixed gas permeation experiments. Single gas permeation measurements allow estimating the solution and diffusion parameters, whereas mixed gas permeation constitute a more realistic approach to the evaluation of the separation ability of the membrane. Further investigation was carried out by measuring the gas separation performance at different operational temperatures to calculate the apparent activation energy of permeation. Membranes have also been characterized in terms of thermal stability and crystallinity by thermogravimetric and X-ray diffraction analyses, respectively. Some other works have reported the preparation and CO_2 separation performance of Pebax® type copolymers[16–19]; however, as far as we are concerned, such a complete study has never been reported in the open literature before, and it is our belief that it could be useful to select the appropriate polymer for gas separation applications concerning the CO_2/N_2 post-combustion mixture. In addition, the results gathered here will allow to gain insight into the use of single gas permeability measurements as a means to predict the gas separation performance of a certain membrane material.

2. Materials and methods

2.1. Materials

Five different Pebax® codes were analyzed (Table 1). All codes in the form of pellets were kindly provided by Arkema, France. As seen in

Table 1
Properties of the Pebax® type copolymers studied in this work. The theoretical content of flexible segment was given by the supplier, while the measured content of flexible segment was obtained in this work from elemental analysis.

Pebax® code	Rigid segment of polyamide (PA)	Flexible segment of polyether (PE)	Theoretical flexible segment (wt %)	Measured flexible segment (wt %)	Ref.
1657	PA6	PEO	60	59	[20, 21]
2533	PA12	PTMO	80	84	[22, 23]
3533	PA12	PTMO	70	77	[24, 25]
4533	PA12	PTMO	–	55	
Renew® 30R51	PA11	PEO	–	81	

Table 1, three of the five codes (2533, 3533, and 4533) are constituted by the same segments, which are present in different proportions, whereas Pebax® 1657 and a new code based on renewable sources (Pebax® Renew® 30R51) are comprised by the same soft phase but a different hard segment. The chemical structures of the hard and soft segments constituting these copolymers, as well as the molecular weight of their repeated unit are depicted in Fig. 1 1. These codes also have different mechanical and water absorption properties, which could be decisive when selecting a polymer for its application in gas separation. In the case of Pebax® 4533, the proportion of flexible segment within the polymer is still unknown from the supplier. However, the greater tensile modulus value suggests that this code is constituted by a greater proportion of hard segment than its analogs (2533 and 3533), probably comparable to that of Pebax® 1657. Similarly, the Renew® code would have a higher percentage of soft phase than Pebax® 1657. This is in agreement with the results obtained by elemental analysis, measuring the content of C, N and H (Table 1).

Solvents, absolute ethanol, 1-propanol and 1-butanol were purchased from Gilca, Labbox and Scharlab, Spain, respectively. All gases used for the gas permeation tests were of research-grade (>99.9 % pure) and supplied by Abelló Linde S.A, Spain. All gases, polymers, and solvents were used as received.

2.2. Membrane preparation

All membranes were prepared by the casting-solution method. Pebax® 1657 was dissolved in a mixture of ethanol and water (70/30 (v/v)) [26] and Pebax® 2533 in absolute ethanol [27,28]. Both were dissolved under reflux for 2 h. Pebax® 3533, 4533 and Renew®, were dissolved in a mixture of 1-propanol and 1-butanol (3/1 (v/v)) under reflux for 3 h [24]. Once dissolved and cooled down to room temperature, all casting solutions (3 wt%) were poured onto glass Petri dishes and left to evaporate in a solvent saturated atmosphere for 48 h. Membranes prepared in this way (40–50 µm thick) were peeled off from the Petri dish and tested for gas permeation.

2.3. Membrane characterization

The percentages of soft and hard segments within the Pebax® copolymers matrices were estimated from data obtained by elemental analysis in a Perkin Elmer II 2400 CHNS elemental analyzer. Scanning electron microscopy (SEM) images of the membranes were obtained using an Inspect F50 model scanning electron microscope (FEI) operated at 10 kV. Cross-sections of membranes were prepared by freeze-fracturing after immersion in liquid N_2 and subsequently coated with Pd. Thermogravimetry (TGA) and differential thermogravimetry (DTG) analyses were carried out using Mettler Toledo TGA/STDA 851e. Small pieces of membranes (~ 3 mg) placed in 70 µL alumina pans were heated under airflow (40 cm^3(STP) min^{-1}) from 35 to 700 ºC at a heating rate of 10 ºC min^{-1}. Membranes were also characterized by X-ray diffraction (XRD) using a Panalytical Empyrean equipment with CuKα radiation (λ = 0.154 nm), over the 2·θ angle range of 5º to 40º at a scan rate of 0.03º s^{-1}. Finally, Fourier transform infrared spectroscopy (FTIR-ATR) was performed with a Bruker Vertex 70 FTIR spectrometer equipped with a DTGS detector and a Golden Gate diamond ATR accessory. The spectra were recorded by averaging 40 scans in the wavenumber range of 4000–600 cm^{-1} at a resolution of 4 cm^{-1}.

2.4. Gas permeation tests

2.4.1. Mixed gas separation tests

Membranes were cut in circles and placed in a module consisting of two stainless steel pieces and a 316L stainless steel macro-porous disk support (Mott Co.) with a 20 µm nominal pore size. Membranes, 2.12 cm^2 in area, were gripped inside the module with Viton o-rings. To control the temperature of the experiment (in the 25–50 ºC range), the
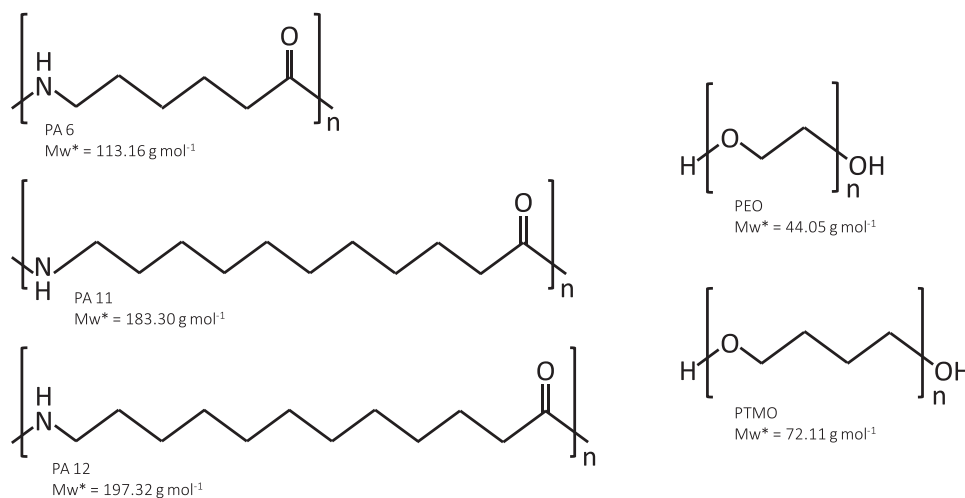
Fig. 1. Chemical structures and their molecular weights of the hard and soft segments of the Pebax® copolymers studied in this work.

permeation module was placed in a UNE 200 Memmert oven. The gas separation measurements were carried out by feeding the post-combustion gaseous mixture of CO_2/N_2 (15/85, both in cm^3(STP) min^{-1}) to the feed side at an operating pressure of 3 bar (i.e., the CO_2 partial pressure in the feed was 0.45 bar) to favor CO_2 permeation. Gas flows were controlled by two mass-flow controllers (Alicat Scientific, MC-100CCM-D). The permeate side of the membrane was swept at atmospheric pressure (~ 1 bar) with a 2 cm^3(STP) min^{-1} of He (Alicat Scientific, MC-5CCM-D). Concentrations of N_2 and CO_2 in the permeate side were analyzed online by an Agilent 3000 A micro-gas chromatograph. Permeability was calculated in Barrer (1 Barrer = 10^{-10} cm^3(STP) cm cm^{-2} s^{-1} $cmHg^{-1}$) once the steady-state of the exit stream was reached (after at least 2 h). The CO_2/N_2 separation selectivity was calculated as the ratio of the corresponding permeabilities. A scheme of the mixed gas separation setup is shown in Fig. S1.

2.4.2. Single gas separation tests. Time lag experiments

Time lag experiments were carried out at different temperatures using a constant volume/pressure instrument (Fig. S2) built by our group. In the time-lag method, dense membranes are placed in a stainless steel membrane cell with two separated compartments (feed and permeate sides). The downstream reservoir (permeate side) consists of 3/8″ stainless steel tubing to minimize resistance. Two membrane cells are available with different diameters: 3.2 and 4.5 cm. Circular membranes were inserted in the stainless steel module similar to the one described above. The inlet pressure of the feed gas can reach a value of up to 6 bar. The feed or upstream pressure is measured by a Wika A-10 pressure transducer (PT1, absolute pressure range of 0–10 bar). The downstream pressure is measured by a Pfeiffer TPR 271 Pirani gauge (PT2, pressure range of $5 \cdot 10^{-4}$-10^3 mbar). The resolution of both pressure transducers is 1 % of reading. The inlet tubing to the membrane module, the membrane module, and the downstream compartment are placed in an oven (Memmert UN55) to control the temperature. To ensure that the feed gas is at the desired temperature, a loop made of stainless steel tubing was mounted inside the oven before the membrane cell. Evacuation is performed by a rotary vane pump (vacuum level down to $5 \cdot 10^{-4}$ mbar).

Circular membranes with an effective area of 5.7 cm^2 (3.2 cm in diameter) were used. All the measurements were performed at 25, 35, and 50 ºC with a feed pressure of 3 bar. The order of gases was first N_2 and second CO_2. The leak rate was determined for each membrane after the first measurement. The maximum leak rate was two orders of magnitude lower than the lowest permeation flux. Before every experiment, the membranes were evacuated (10^{-3} mbar) at both sides for at least 10 times the time lag (θ_d) to remove any gas traces from the

membrane surface and from the rig. The experiments started when the membranes were exposed to the feed gas. The downstream pressure (p_d) was recorded during all the test. Experiments were performed for 10 times the time lag at least. To fulfill the boundary conditions of the time lag method and obtain an effective stationary state of flux, the downstream pressure should be much lower than the upstream pressure, so that the maximum downstream pressure was fixed at 0.1 % of the upstream pressure [29]. Once this value was reached, the experiment was finished. Permeability (P) was calculated using the slope of the p_d-t curve in the stationary region. The diffusion coefficient (D) was estimated through the time lag method and the solubility coefficient (S) was obtained from P and D [30,31]. A more detailed explanation of the time lag method can be found in Fig. S3. The equations used for each calculation (D, P and S parameters) are also collected in the SI file.

3. Results

3.1. Membrane characterization

Dense polymeric membranes made of 5 different Pebax® codes (Table 1) have been prepared by the casting-solution method. As aforementioned, dense membranes usually follow the solution-diffusion mechanism of permeation [32], which assumes that gas species are separated due to their distinct solubility and diffusivity through the membrane [33]. The non-porous character of the prepared membranes has been confirmed by cross-sectional SEM images shown in Fig. S4.

Further characterization was carried out by testing the thermal stability of the membranes. TGA and DTG analyses are represented in Fig. 2a and b, respectively. As shown in these figures, even if all the membranes start degrading at above 300 ºC, a slight difference in the thermal stability can be observed for the codes which are constituted by the same segments (Pebax® 2533, 3533, and 4533). Such differences deal with the ratio between the rigid segment of polyamide and the flexible segment. The greater proportion of the hard block (PA) in Pebax® 4533 code provokes a higher resistance to temperature, whereas the major proportion of flexible PTMO in Pebax® 2533 code increases the polymer chain mobility and therefore accelerates the thermal degradation of the polymer. In any event, PEBA type membranes generally work at low temperature, the highest operating temperature reported being in the 65–70 ºC range [16]. The differences in the nature of the segments, as well as the proportions of each one within the copolymer, can also be observed in Fig. 2c, corresponding to the XRD patterns of the membranes. The codes constituted by PA12 and PTMO (2533, 3533, and 4533) show three characteristic peaks at 5.7º, 11.1º, and 22.3º consistent with both, the PA12 and PTMO segments [34]. The
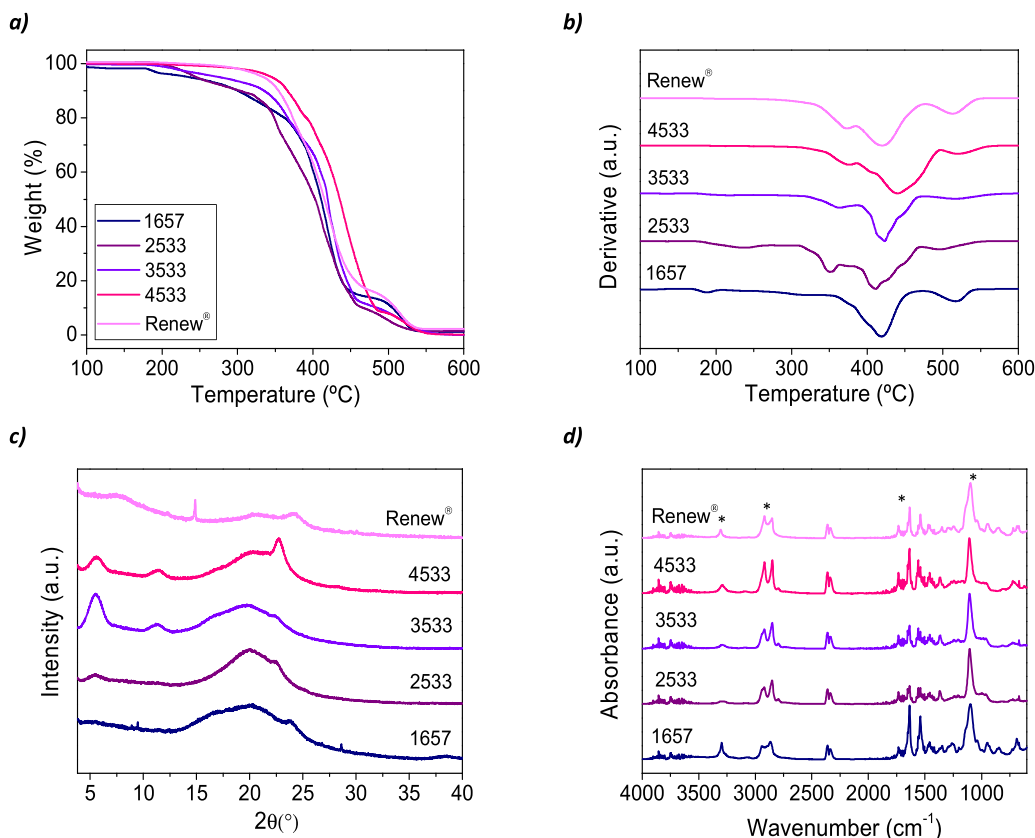
Fig. 2. Thermal properties: TGA (a), DTG (b) and XRD patterns (c) and ATR-FTIR spectra of the membranes (d).

differences in the peak intensities found for these codes are due to the proportion of each segment within the polymer. A property of Pebax® type copolymers is their semicrystalline nature [35], which is related to both the amorphous PTMO and the crystalline PA12 segments. As shown in Fig. 2c, the increment in the hard segment (PA12) proportion is associated with an increase in the intensity of the crystalline peaks. Although all peaks can be appreciated in the three XRD patterns (2533, 3533 and 4533 codes), in that corresponding to the 3533 code the 5.7° and 11.1° intensities are higher than in the 2533 code, while in the XRD pattern corresponding to the 4533 code the three peaks, including that at 22.3° associated to the hard PA [36], appear to be intense. This suggests that the crystallinity increases as the PA12/PTMO ratio increases, which could be a crucial parameter affecting the gas separation performance of the membranes. The XRD pattern corresponding to Pebax® 1657 shows two characteristic peaks at 20.0° and 23.8° 2θ values, also corresponding to the soft and hard phases of the copolymer, the PEO and the PA6, respectively [37,38]. In the case of the renewable source code (Pebax® Renew® 30R51), three weak and broader peaks at ca. 7.6°, 20.4° and 24.2° 2θ values appear in the XRD pattern, the two first related to the PEO and the last to the PA11 segments [39].

The FTIR-ATR spectra of the Pebax® membranes are shown in Fig. 2d. In this figure, different bands associated with both the polyamide and the polyether segments can be appreciated. In spite of the different nature of each segment, it can be seen that the bands appear at the same wavenumber values. Regarding the hard segments (PA6, PA11 and PA12), the band at 1640 cm^{-1} corresponds to the vibrations of the H-N-C=O group [40], and the band at 3298 cm^{-1} to the –N-H- linkages [36]. Vibrations corresponding to the soft segments (PEO and PTMO) are visible in the bands at 2925 and 1100 cm^{-1}, assigned to the stretching and bending vibrations of the aliphatic C-H group and the stretching vibration of the C-O-C ether group, respectively, in accordance with the literature [41,42].

3.2. Single and mixture gas permeation at room temperature

A comparison was accomplished between the two well established methods for the estimation of the gas separation performance of membranes, single gas permeation using the time lag method and mixture separation assisted by a gas chromatograph. In both cases, the errors shown along the paper were obtained from the repetition of permeation measurements with at least 2-3 different membrane samples prepared in the same conditions. Single gas permeation experiments, carried out using a constant volume/pressure instrument, are regarded as an ideal separation test, whereas mixed gas separation considering a binary mixture in a specific proportion is closer to a real situation. However, the single gas permeation measurements allow the characterization of the membranes in terms of solubility, diffusivity and permeability parameters. This can be of interest to perform some mathematical modeling or to understand the effect of the membrane composition and operation conditions on the separation parameters of solubility and diffusivity. Conversely, the mixed gas separation only gives information about the permeability and selectivity of the membranes when they are exposed to a mixture of gases which, however, undoubtedly has a practical interest as already commented. As seen in Fig. 3 and collected in Tables S1 and S2, there are remarkable differences in the gas separation performance of the five different membrane polymers. As expected, these differences are mainly related to the nature of the segments as well as their proportion in the corresponding copolymer. Pebax® block copolymers have recently emerged as potentially interesting materials since it is possible to combine the properties of two different polymers into one obtaining a customized polymeric material, what is of particular interest in the membrane field. In fact, the final copolymer made of hard and soft phases would provide a relatively high CO$_2$ permselectivity in CO$_2$/nonpolar gas separations (for example in CO$_2$/N$_2$ separations, among others [16]). The polyether segment has a strong affinity to CO$_2$ due to the dipole-quadrupole interactions between this molecule and the polyether
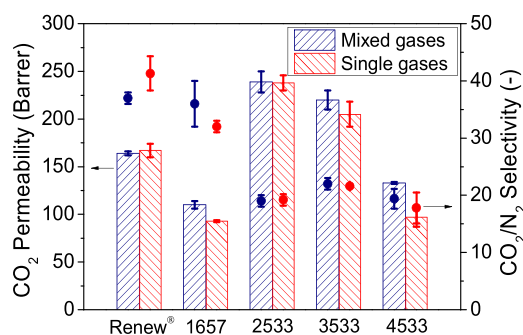
Fig. 3. Gas separation performance of Pebax® type copolymer membranes measured with mixed and single gases at 3 bar feed pressure and 35 °C.

chains, whereas the polyamide block mainly provides mechanical stability [43]. Also in Pebax®, the rigid segment of the polyamide is much less permeable than the soft polyether [38]. Therefore, it is expected that the higher the proportion of the soft segment, the higher the CO_2 solubility and permeability values.

The renewable source (Renew®) and Pebax® 1657 codes are both composed of the same soft phase (PEO) but with a different hard segment (PA11 and PA6, respectively). As seen in Fig. 3, the permeability of CO_2 is higher in the Renew® code than in the 1657 code, no matter the method used for the estimation of this parameter: 164 ± 2 and 167 ± 7 Barrer vs. 110 ± 4 and 93 ± 1 Barrer for the Renew® and the 1657 codes, respectively, corresponding the first value to mixed gas and the second to single gas permeation. This phenomenon can be related to the different proportions of the polyether in the copolymer, favoring Pebax® Renew® (81 wt% PEO, see Table 1) over Pebax® 1657 (59 wt% PEO). It is also worth mentioning that the nature of the polyamide phase (longer PA11 for the Renew®, shorter PA6 for the 1657) can be involved in the higher or lower permeation of gases. Polyamides are named based on their chain length and usually the higher the chain length, the worse the chain packing efficiency, which means a higher free volume and thus a superior gas diffusion [44]. The diffusion and solubility parameters measured by the time lag method are plotted in Fig. 4a and b, respectively, and collected in Table S3. As expected, the Renew® code has a greater diffusivity value ($12.9 \cdot 10^{-7}$ cm^{-2} s^{-1}) than the 1657 code ($7.3 \cdot 10^{-7}$ cm^{-2} s^{-1}) due to the PA chain length. Furthermore, the CO_2 solubility is also slightly higher in the renewable source code ($131 \cdot 10^{-4}$ cm^3(STP) cm^{-3} cmHg^{-1}) than in the 1657 code ($127 \cdot 10^{-4}$ cm^3(STP) cm^{-3} cmHg^{-1}) due to the higher PE/PA ratio (4.3 vs 1.4, respectively). As already explained, the permeability parameter depends on both the solubility and diffusivity values, being directly proportional to them (i.e., $P = D \cdot S$). Hence, the higher the diffusivity and solubility, the higher the permeability. As shown in Table S4, the CO_2/N_2 ideal selectivity is somehow greater in the case of the Renew®

code membranes (ca. 37–51 at 25–50 °C) than for the Pebax® 1657 membranes (ca. 26–37) what can be justified by the higher PE/PA ratio for the former polymer.

The same behavior is shown for the codes made of PA12 and PTMO. First, in general, it is worth mentioning that copolymers with PEO (monomer with molecular weight of 44.05 g·mol^{-1}) are less permeable and have smaller diffusivities than those with PTMO (monomer with molecular weight of 72.11 g·mol^{-1}), what is explained due to the fact that the smaller PEO with a higher mobility than larger, cyclic PTMO would pack more densely with PA segments. In this case, for the 2533, 3533 and 4533 series, the permeability increases as the percentage of PTMO increases (from 84 to 55 wt%, see Table 1). This is related to both higher solubility and diffusivity values, which produced the best performance of code 2533. In fact, the highest CO_2 solubility for code 2533 is due to the greatest PTMO/PA12 ratio (5.3), which means stronger interactions of the PTMO block with the CO_2 molecule. Moreover, the highest proportion of PTMO in Pebax® 2533 (84 wt%) code than in the 3533 (77 wt%) and 4533 (55 wt%) codes would hinder the chain rearrangement worsening the packing efficiency of the PA segments, which would be translated into an increase in the free volume, and thus in the CO_2 diffusivity in addition to the soft nature of the PTMO that favors diffusion as compared to the rigid PA12. Besides, the diffusivity of N_2 is also accelerated due to the chain packing, which limits the CO_2/N_2 selectivity of Pebax® 2533 to values below 20, this code being the one with the lowest selectivity (19 ± 1 for both, mixed and single gases at 35 °C).

From Fig. 4a and b it is also possible to deduce which mechanism, solution or diffusion, is prevailing in each membrane and which would be the main responsible for the final separation performance. Such information can be analyzed from the diffusivity and solubility selectivities. As seen in these figures and in Table S3, for all codes the predominating mechanism is based on the high solubility of CO_2 in the polymer. This is an expected behavior since the soft phase of the Pebax® type copolymers has a strong affinity towards CO_2, as aforementioned. It is Pebax® Renew® which holds the greatest solubility selectivity value (30.5 ± 5.6), whereas the rest of the codes have similar solubility selectivity values, ranging from 14.7 ± 1.1 (2533) to 19.4 ± 4.6 (3533). Despite the similar solubility selectivity value of Pebax® 1657 (17.5 ± 0.1) and the codes composed of PA12 and PTMO, the diffusion of CO_2 through Pebax® 1657 is more favored in comparison to that of N_2. This difference is what gives Pebax® 1657 higher CO_2/N_2 ideal/separation selectivity values (32.0/37.0) as compared to Pebax® 2533 (19.0/19.1), 3533 (22.0/21.5) and 4533 (18.0/20.9), as shown in Fig. 3 and Tables S4 and S5 at the same temperature of 35 °C.

3.3. Gas permeation as a function of temperature

Further characterization was carried out by measuring the gas separation performance of the membranes at different operational tem-
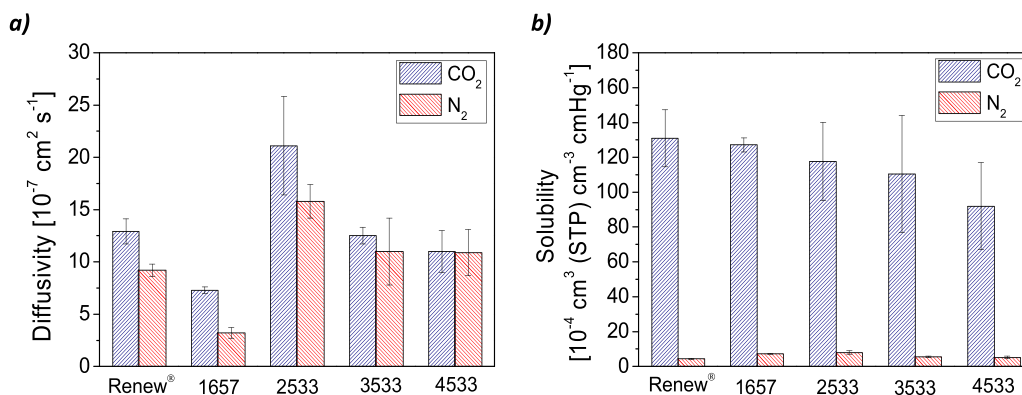

Fig. 4. Diffusivity (a) and solubility (b) parameters measured by the time lag method at 35 °C.

peratures (25, 35 and 50 ºC). The maximum temperature of 50 ºC was chosen since hysteresis effects as a function of temperature have been found in the CO_2 permeability with similar types of membrane co-polymers when the temperature reached 70 ºC [19]. This can be related to some non-reversible phase separation favored by the polyether segregation from its blend with the amorphous copolymer having in mind that melting points of PEO and PTMO are ca. 14 and 53 ºC, respectively [26,45]. In any event, an increase in temperature leads to a higher chain mobility and a decrease of solubility, which means higher permeability of permeants and thus lower CO_2/N_2 selectivity (Fig. 5a-d). As seen in Fig. 5a and c, the relationship between permeability and temperature is usually linear and follows the Arrhenius equation (Eq. 1) [46]:

$$P = P_0 \bullet e^{\left(\frac{-E_p}{R \bullet T}\right)} \tag{1}$$

where P is the permeability of permeants (CO_2 and N_2 in this work) in Barrer, P_0 is the pre-exponential factor (Barrer), E_p is the apparent activation energy of permeation in J mol^{-1}, R is the ideal gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature in K. Therefore, with the data obtained at different temperatures (Tables S4 and S5) and plotting the gas permeability vs. the inverse of the temperature, it was possible to obtain the apparent activation energy of permeation from the slope of the linear regression, as follows (Eq. 2):

$$\ln P = \ln P_0 - E_p \bullet \frac{1}{R \bullet T} \tag{2}$$

Based on this equation, higher E_p values indicate more activation with temperature. In this sense the E_p parameters were calculated from mixed and single gas permeations results. The values obtained for CO_2 and N_2 are collected in Table 2 and compared with data obtained from the literature. As shown in this table, the E_p values ranged from 13.3 to

Table 2

Apparent activation energies of permeation. Comparison between mixed and single gas permeation.

Pebax® code	Single gases, E_p (kJ mol^{-1})		Mixed gases, E_p (kJ mol^{-1})		Ref.
	CO_2	N_2	CO_2	N_2	
1657	13.3	30.4			[19]
1657			14.9	28.0	[26]
1657	18.6	32.0			[47]
1657	14.6	33.6			[38]
2533	16.7	27.2			[47]
2533	18.2	31.0			[48]
2533	18.5–18.6	33.2–34.6			[49]
1074	13.4	30.3			[46]
3533			14.2	29.6	[24]
Renew®	15.6	26.0	13.0	21.8	This work
1657	18.0	29.3	15.0	27.6	This work
2533	13.3	27.7	14.8	25.6	This work
3533	19.8	29.3	15.0	22.2	This work
4533	16.7	28.6	13.3	22.7	This work

19.8 kJ mol^{-1} for CO_2 and from 26.0 to 29.3 kJ mol^{-1} for N_2 when obtained from single gas permeability measurements, and from 13.0 to 15.0 kJ mol^{-1} for CO_2 and from 21.8 to 27.6 kJ mol^{-1} for N_2 in the case of mixed gas separation. These values are also in agreement with the data found in the literature for Pebax® type copolymers [19,24,26, 46–48]. It is worth mentioning that, in general, the E_p values measured by single gas permeation are higher than those measured by mixed gas separation. Higher activation energy corresponds to a higher slope in the Arrhenius equation. This means that the variation of temperature causes larger changes in the permeability of the membranes measured by single gas permeation. This could be explained by taking into account the presence of nitrogen in the mixed gas separation, hindering the
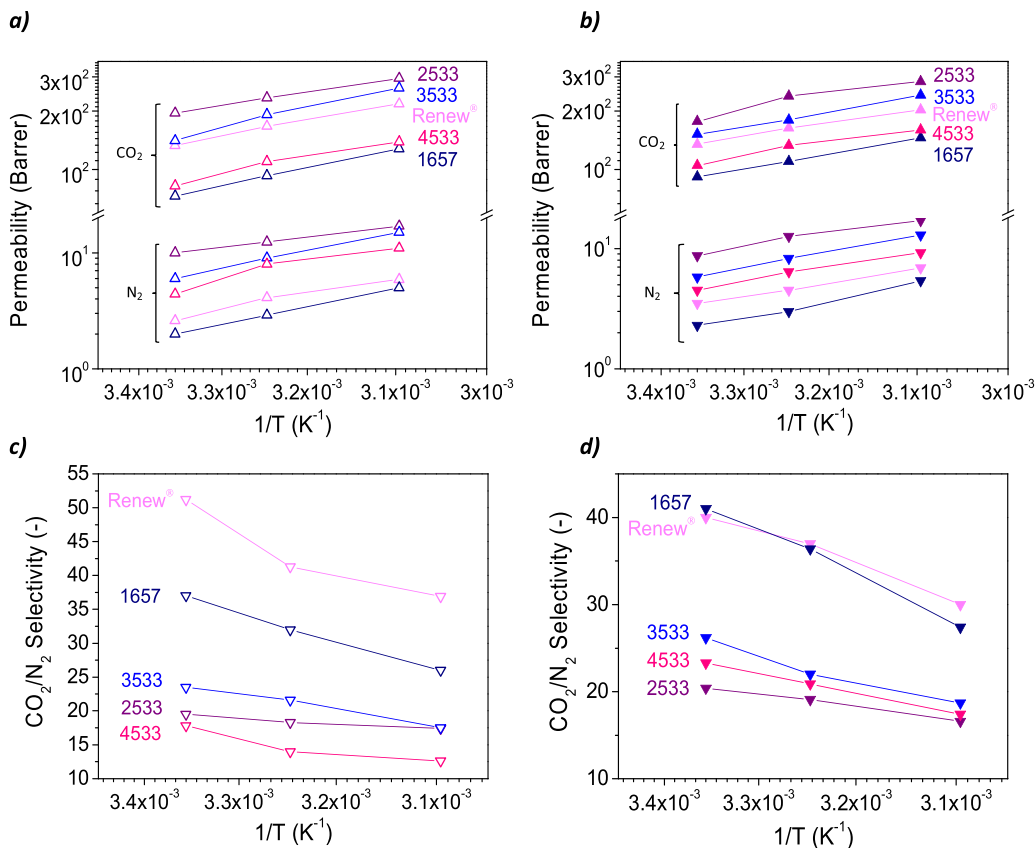

Fig. 5. Gas permeation of membranes measured at different temperatures: (a) and (b) correspond to single gas permeation (time lag), (c) and (d) correspond to the mixed gas separation.

permeation of CO_2 and thus decreasing its activation with temperature. Furthermore, this effect can be due to the competitive sorption of CO_2 and N_2 molecules. Finally, activation energies are greater for N_2 than for CO_2 in line with the fact that with increasing temperature the most soluble CO_2 reduces its concentration in the membrane facilitating the N_2 transport and decreasing the separation selectivity.

To conclude this part, the permeability and selectivity data obtained with both methods have been plotted together with the Robeson upper bound [7] and they are depicted in Fig. 6. With this figure it is possible to compare all the codes in terms of their efficiency for CO_2/N_2 gas separation performance. A good membrane for gas separation will be that surpassing the Robeson limit. Therefore, the polymer closer to that limit can be consider to be the best for the separation of the gases studied. In this case, Pebax® Renew® can be considered the code with the best performance in gas separation, whereas Pebax® 4533 would be the one with the worst separation performance, no matter the method used for its determination. It is also worth mentioning that the data sets of permeability and selectivity obtained in this work are in agreement with the values found in the literature for some of these codes [19,24,26, 47–49].

3.4. Comparison between single and mixture gas permeation

Besides the comparison done in Fig. 6, Fig. 7 plots CO_2 and N_2 permeabilities and CO_2/N_2 selectivities obtained under gas mixture conditions as a function of their respective single gas permeability values, for all the Pebax codes and temperatures. Fig. 7a depicts a relatively good lineal correlation for CO_2 permeabilities. However, at about 150 Barrer of CO_2 single gas permeability the CO_2 mixture permeability tends to be smaller than the expected value (the equal). This can be due to the fact that a large CO_2 permeability (e.g., obtained by increasing the temperature) runs parallel to a low CO_2/N_2 separation selectivity, what means more N_2 in the membrane hindering the CO_2 permeability in the mixture. In case of N_2 permeability, most of the points tend to be closer to the diagonal. This, together with the fact that the relative error must be larger for this molecule (due to the lower permeability values as compared to those of CO_2), allows to infer that both single and mixture permeability differences can be considered within the experimental error. The question for the CO_2/N_2 selectivity is not that clear. The expected trend would be larger separation selectivities than ideal selectivities due to the fact that the more soluble CO_2 hinders the N_2 diffusion when operating at mixture conditions. A trend can be envisaged in this sense with most of the points in Fig. 7c placed above the diagonal. Nevertheless, Pebax® Renew® shows ideal selectivities clearly larger
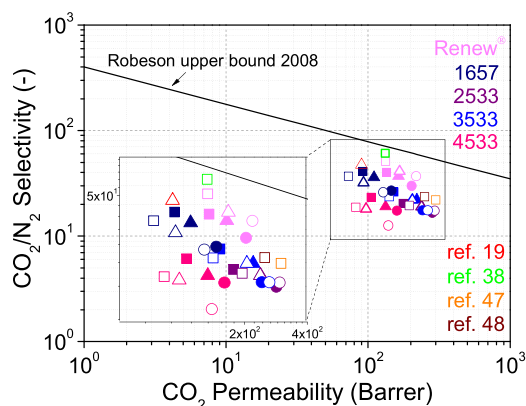

Fig. 7. CO_2 and N_2 permeabilities (a, b) and CO_2/N_2 selectivities (c) obtained under gas mixture conditions as a function of their respective single gas permeability values, for all the Pebax® codes and temperatures. Values taken from Tables S4 and S5. Variation lines are also plotted.

than the corresponding separation selectivities obtained from the mixture studies. This can be related to the large CO_2/N_2 solubility selectivity that this polymer exhibits compared to the other codes (see Fig. 4b). Moreover, it should be noted that in the experiments with single gases the CO_2 pressure is 3 bar, while in the mixture the CO_2 partial pressure is 0.45 bar. This means that in polymers such as Pebax® Renew®, which bases its separation on the selectivity by solubility in a prominent way with respect to the other polymers (Fig. 4b), the selectivity is greater with the pressure due to the greater solubility of CO_2. On the other hand, polymers such as Pebax® 1657 with a notable separation component in terms of diffusion selectivity with respect to the other polymers (Fig. 4a) or the Pebax® 4533 polymer with the lowest CO_2 solubility (Table S3) are clearly found above the diagonal.

These plots demonstrate that, at least in case of the Pebax® codes studied there is a relatively good correlation between single gas permeability results and mixture separation results, the former providing, with the exception of the Renew® code, a conservative estimation of the membrane separation selectivity. It should be noted

Fig. 6. Robeson type graphic comparing the gas permeation results of the membranes prepared in this work with other data found in the literature at different temperatures: 25 ℃ (squares), 35 ℃ (triangles) and 50 ℃ (circles). Empty scatters correspond to the data obtained by time lag and filled scatters to mixed gas permeation. The inset shows in more detail the permeability-selectivity results.
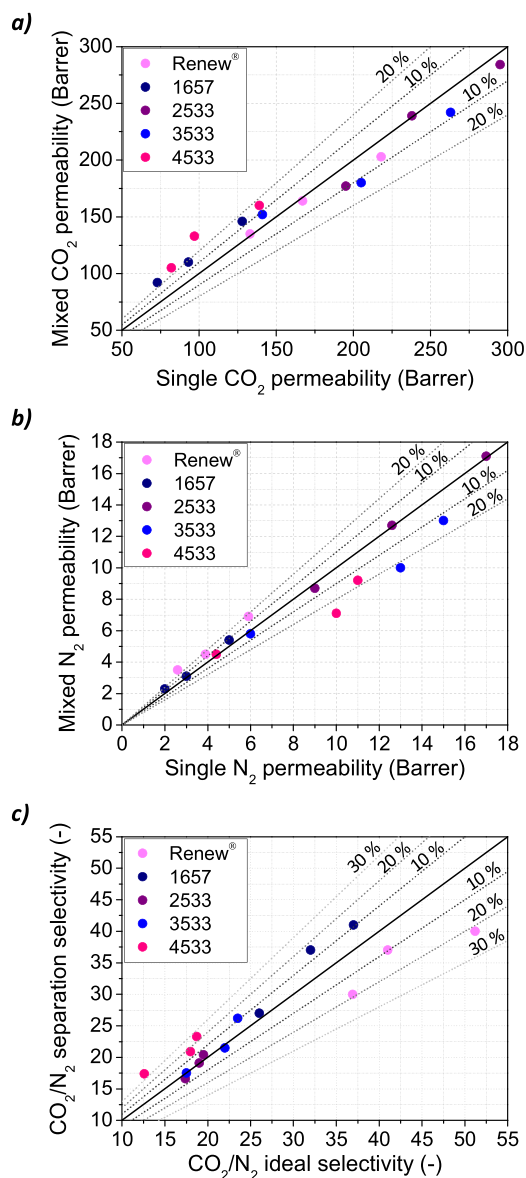
that although greater differences between single gas and mixed gas separations could be expected depending on the working conditions (e. g., CO_2 partial pressure) [50], the good correlation found in this study is probably due to the relatively low concentration of CO_2 (15 %) in the feed stream during the mixed gas separation tests. In any event, every gas permeation technique has its typical operation conditions (e.g., use of pure gases in case of time lag, while 10–15 % mixture CO_2 concentration when emulating post-combustion separation conditions). Our results suggest that the application of a simple and cheaper measurement technique (i.e., single gas permeation testing) as characterization of the membrane separation performance can be appropriate in most of the cases. However, for either non-very studied polymers or new membrane polymers it can be prudent the permeation study under more realistic conditions feeding a gas mixture to the membrane.

4. Conclusions

Pebax® type copolymers are composed of polyamide (PA) and polyether (PE) segments. In the market, there is a great variety of codes that differ in the nature and proportion of each segment within the copolymer. The gas separation performance of five different Pebax® type membranes was analyzed by single and mixed gas permeation. Single gas permeation, using the constant volume/pressure method (time lag), leads to the estimation of ideal selectivities, whereas mixed gas separation is closer to a real situation and allows the calculation of separation selectivities. In dense polymeric membranes, gases follow the solution-diffusion mechanism. Once the gas is in contact with one side of the membrane, it is solubilized and diffuses through the membrane until it reaches the other side and is desorbed. Therefore, the permeability of dense membranes directly depends on the solubility and diffusivity of the gas. These parameters can only be estimated by the time lag method (single gas). Moreover, the composition, thermal stability and crystallinity of the membranes, investigated by elemental, TGA and XRD analyses, can be correlated to their gas separation performance. Although all membranes have similar thermal stability, the greater proportion of soft phase (PE) leads to a slight decrease in the degradation temperature. Moreover, the membranes with greater PE/PA ratio are also those with higher CO_2 permeability (Pebax® 2533, 3533 and Renew®). The nature of the hard segment (PA) was also found to have an effect on the performance of the membrane. Polyamides are named based on their chain length, and this parameter has an effect on the packing efficiency. Usually, the higher the chain length, the worse the packing efficiency, which leads to higher free volumes and gas permeabilities. Besides, the lower CO_2/N_2 selectivity values of the codes made of PA12 (2533, 3533 and 3533) can also be related to the worst packing efficiency of these polymers. Conversely, the renewable source code (Pebax® Renew®), in spite of being composed of PA11, which has a similar chain length than PA12, holds the best CO_2/N_2 selectivity value (37 and 41, for mixed and single gas, respectively). This can be related to the nature of the PE segment. While Pebax® Renew® is composed of PEO, the others (2533, 3533 and 4533) are composed of PTMO and the interactions between these segments and the CO_2 are different. The solubility of CO_2 is higher in the case of the Renew® code favoring its CO_2/N_2 selectivity.

Additional characterization was carried out by measuring the single and mixed gas permeation performance at different temperatures. These allowed the calculation of the apparent activation energy of permeation for CO_2 and N_2. As expected, the apparent activation energy was higher for N_2, the gas with lower solubility. Besides, the CO_2 activation energy calculated by single gas separation was slightly higher than that obtained by mixed gas separation, which can be related to the presence of N_2 in the mixture. Moreover, the values obtained in this study were in agreement with those found in the literature for this type of polymers.

Finally, comparing the gas separation results obtained with both, single and mixture gas permeation, where the CO_2 partial pressure is different affecting the permeation, it was found that there is a relatively

good correlation between single gas permeability and mixture separation results for the Pebax® codes. Being acceptable, the correlation between the ideal selectivity and the mixture selectivity is tuned by the solubility and diffusion properties of the polymers. This suggests that the application of a simple and cheaper measurement technique (i.e., single gas permeation testing) as characterization of the membrane separation performance can be appropriate in most of the cases.

Credit authorship contribution statement

Lidia Martínez-Izquierdo: conceptualization, methodology, validation, formal analysis, investigation, writing-original draft, review, visualization. **Adelaida Perea-Cachero**: conceptualization, methodology, validation, formal analysis, investigation, writing-original draft, review, visualization, supervision. **Magdalena Malankowska**: conceptualization, verification, writing-original draft, review, supervision. **Carlos T é llez**: conceptualization, verification, writing-original draft, review, funding, supervision. **Joaquín Coronas**: conceptualization, verification, writing-original draft, review, funding, supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2022.108324.

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