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Abstract

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PARTIALLY PYROLIZED GAS-SEPARATION MEMBRANES MADE FROM BLENDS OF COPOLYETHERIMIDES AND POLYIMIDES.

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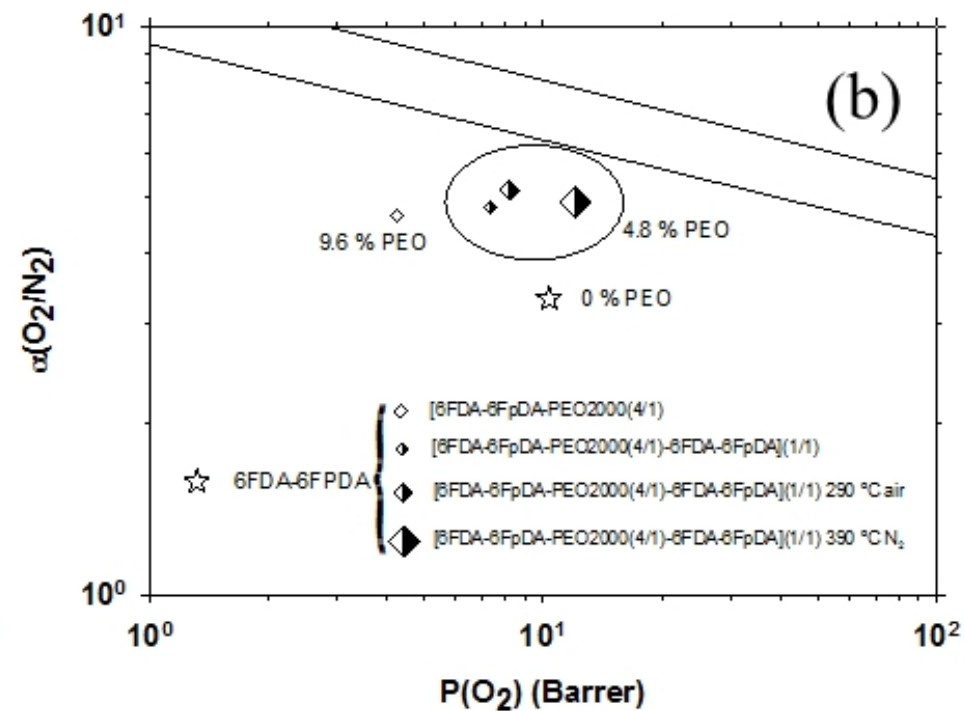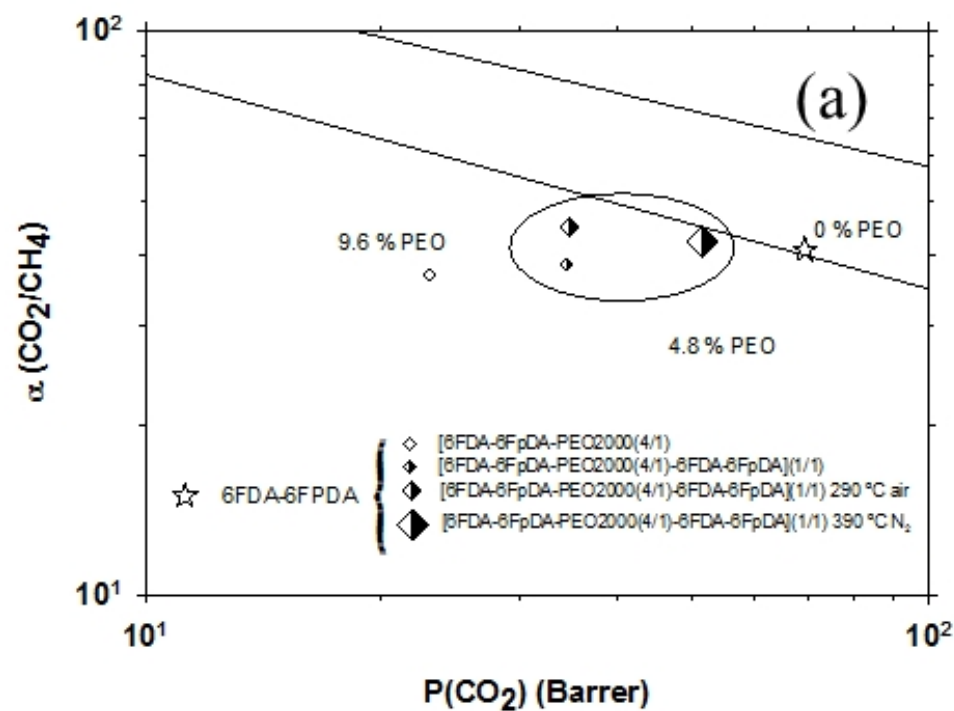[2]*Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, E-28006 Madrid, Spain.*
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1. Partial pyrolysis, PP, of polyetherimide plus homo poyimide films was reached.

2. Lower temperatures are needed in air than in an inert atmosphere.

3. PP films protected against plasticization with optimal 5 to 8 % PEO contents.

4. Partial pyrolysis gave lower permeabilities burt higher selectivities.

Good selectivity versus permeability compromise.

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ABSTRACT

Herein, a new approach to achieved gas separation materials with improved resistance to plasticization, obtained by partial pyrolysis of new polyimide blends, is presented. Blends of an aromatic polyimide (formally, 6FDA-6FpDA) and aliphatic-aromatic copolyether-imides based on the same polyimide in combination with other aliphatic polyimide, having polyethylene oxide moieties, were obtained. After their synthesis and characterization, a selective elimination of the polyether by thermal treatment was carried and the obtained partially-pyrolyzed materials were tested as gas separation membranes.

For neat blends, permeability was shown to decrease when PEO content increases. This effect is due to polyethylene oxide (PEO) chains encroaching on free volume because phase segregation was minimized. When these blends were subjected to thermal treatment at relatively low temperatures in air or in N_2, it was clearly observed that all the polyether moieties were selectively eliminated from the structure, which gave rise to an increase of permeability. Higher permeabilities were obtained after a thermal treatment at 390 ºC in N_2. Degradation of PEO chains after a 290 º C treatment in air produced materials with permeability values lower than those observed under N_2. In both cases, even though PEO was selectively and wholly eliminated, permeability was not totally recovered to give the values observed for neat 6FDA-6FpDA due probably to a combination of shrinkage and crosslinking of the membrane produced during the thermal process. Crosslinking provides the materials with an increased resistance to plasticization, in particular the best improvement against plasticization proceeded from the thermal treatments at 290 ºC in air of blends.

Keywords: Gas separation, blends, polyimides, PEO, plasticization resistance

1. INTRODUCTION

During the past decades, extensive attention has been devoted to the production of membranes with high permeability and selectivity for separation processes. Robeson in 1991, tested a large number of pairs of experimental data on permeability/selectivity. As a result, he suggested a semi empirical relationship for polymers [1]. Later, he updated this limit, Robeson upper bond, in 2008 leading to a new and much more demanding empirical relationship [2], so that very few materials are able to overcome this new upper bond. However, the knowledge acquired during recent years in this field has established some basic rules to ensure that the increase of one of these two features (permeability or permselectivity) leads to a low decrease of the other one. After performing multiple studies of different membranes, it was observed that the best materials are amorphous polymers, with structures that hamper the compact packaging of the chains. This generates a high fraction of free volume and, therefore, an increase in permeability. On the other hand, these materials must be highly rigid to decrease their chain mobility what facilitates their behavior as molecular sieves generating a high selectivity.

Penetrant-induced plasticization of membranes for gas separation has been intensively studied, as far as it is a key factor that downturns the useful life and performance of gas separation membranes. Plasticization facilitates local segmental freedom and mobility of macromolecular chains. This leads to an increase of free volume because local restrictions of the polymer segments are eliminated. This increases permeability with a steeply decrease of selectivity along with an increase of softness, ductility, and a depression of glass transition temperature (Tg) [3]. In particular, CO_2 has a strong plasticizing action by causing swelling of the polymer network [4, 5]. A classical way of decreasing the plasticization of a material consists in producing crosslinking, by thermal or UV treatments of by chemical procedures. However, this crosslinking decreases the fractional free volume, what is translated in a gas separation membrane with lower permeability and higher selectivity.

Polyimides with bulky groups [6, 7] exhibit a good balance of permeability and selectivity for various gas pairs, along with high chemical resistance, thermal stability and mechanical strength, and thus they have attracted much attention since their first commercial application in separation processes [8]. In another context, Xiao et al.

revised the various strategies of molecular tailoring of polyimides in search for better membrane materials. Among them, authors outlined two of the most promising ones: synthesis of new polyimides by designing well-chosen dianhydrides and/or diamines, and use of copolymerization of polyimides with other class of polymers as, for example, those with aliphatic chains [9]. In addition, polymer blends have been used to produce gas separation membranes with excellent properties [10-15].

The objective of this work has consisted in preparing new membrane materials formed through the thermal treatment of polymer blends with the target of achieving materials with good separation features and low tendency to plasticization. Several polyimides [16, 17] have been tried as precursors for carbon molecular sieves, CMS, membranes. Polymer blends, including polyethylene oxides, PEO, [18-20] have also been used.

There is no doubt, that CMS membranes have been celebrated as very adequate for gas separation, both in terms of separation properties and stability. Our aim is to avoid mechanical damage, by increasing compatibility between the components of the blends, to reduce the pyrolysis temperature and to decrease plasticization. Thus, we will focus here on the preparation of blends of an aromatic polyimide, of high free volume, with block copolymers of aromatic-aliphatic polyimide formed by the same aromatic part but having poly ethyleneoxide groups in the main chain. The thermal treatment of these blends will produce the selective removal of the PEO, what will produce high thermal stable cross-linked materials.

The aromatic polyimide chosen is 6FDA-6FpDA which shows good gas separation properties for different gas couples, O_2/N_2 and CO_2/CH_4 for example, and has excellent thermal and mechanical features. The resulting membranes have good processability and excellent gas separation performance. However, their plasticization resistance is not very high [21].

The use of block copolymers of 6FDA-6FpDA plus PEO (PEO2000) to be employed in this work, are similar to those extensively developed and studied by Okamoto [22-27], and also by our research group . It was demonstrated with some of these copolymers that the use of a thermal treatment is able to produce a phase segregation of the aromatic and aliphatic blocks, which leads to materials with excellent capability of separation of acid gases due to the favorable interaction of these gases with

the oxygen contained in the polyethylene oxide chain [22, 24, 28-30]. Also, in these works, it was observed, by themogravimetric studies, that it was possible to selectively achieve the whole removal of the aliphatic PEO chain by thermal treatment at temperatures well below the aromatic polyimide degradation temperature. The 6FDA-6FpDA-PEO copolymer system has the advantage of not presenting phase segregation, as it was observed for other similar structures [28]. Phase segregation, due to the formation of strong charge transfer complexes (CTC), leads to low processability from organic solvents. After thermal treatments, it would lead also to non-homogeneous pore sizes. However, when aromatic diamines having electronic withdrawing moieties or bulky groups are employed, the formation of CTC is hindered and processability is clearly improved. Thus, soluble 6FDA-6FpDA-PEO can be made using the two-step polyimidation method by treatment of the precursor polyamic acid with a mixture of acetic anhydride and a tertiary base.

Herein, three copolyimides have been made by varying the composition ratio of 6FpDA and PEO 2000 (4/1, 2/1, 1/1 w/w). Afterwards, the blend of (6FDA-6FpDA-bk-6FDA-PEO2000) and 6FDA-6FpDA was obtained in different w/w ratios. These mixtures were made by mixing THF-solutions of their components. After casting, the resulting films were studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and FTIR-ATR, in order to characterize the materials and to figure out the thermal treatment needed to produce the partial pyrolysis of PEO groups. This study was also made for the (6FDA-6FpDA-bk-6FDA-PEO2000) polymers. Finally, the differences, on the final properties, of using thermal treatments under inert or oxidizing atmospheres, were investigated.

As a final point, an exhaustive study of the gas separation properties of the starting materials, along with those of the partially pyrolized materials, has been performed. This gas separation study has been extended to the determination of the plasticization resistance for the thermally treated membranes.

2. EXPERIMENTAL

2.1. Chemicals

2-2´-bis (4-aminophenyl) hexafluoropropane (6FpDA) was obtained from Chriskev (Kansas, USA) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride

(6FDA) was obtained through Apollo Scientific (London, UK). Both monomers were purified by sublimation under high vacuum before use. Bis (2-aminopropyl) poly(ethylene oxide) 2000 (Jeffamine ED 2003, named in this paper for simplicity sake as PEO2000), with a molecular weight of 1942 g/mol was kindly donated by Huntsman (The Netherlands). PEO-2000 was used after vacuum drying in an oven for 5 h at 60 °C.

Anhydrous *N*-methyl-2 pyrrolidone (NMP) and *N, N´*-dimethylacetamide (DMAc) were obtained from Aldrich (Missouri, USA). Anhydrous pyridine (Py), 4,4-dimethylaminopyridine (DMAP) and high-purity trimethylchlorosilane (TMSCl) were also purchased from Aldrich. Solvents and other commercial reagents such as acetic anhydride and pyridine were obtained from Aldrich and used as received.

2.2. Polymer synthesis

6FDA-6FpDA polyimide was made using the following procedure: In a three necked flask of 500 mL mechanically stirred under nitrogen atmosphere, 30 mmol (10.03 g) of 6FpDA and 25 ml of anhydrous DMAc were mixed. Once the monomer was dissolved, the solution was introduced into an ice-water bath with 60 mmol of chlorotrimethylsilane (TMSCl), 60 mmol of pyridine, and (6 mmol) of 4,4 '-dimethylaminopyridine (DMAP). Subsequently, 30 mmol (13.33 g) of 6FDA were added. The mixture was allowed to react at room temperature for approximately 12 hours. After this time, 120 mmol of acetic anhydride, and 120 mmol of pyridine were added on to produce the cyclo-imidization of the polyamic acid to the final polyimide. This mixture was kept under mechanical stirring at room temperature for 6h and then at 60 °C during 45min. Afterwards, the solution was precipitated onto water and washed several times in a water-ethanol (1:1) mixture to remove traces of solvents and reagents. Polymer fibers were dried at 180 ºC, overnight under vacuum.

Furthermore, the synthesis of aromatic-aliphatic copolyimides 6FDA-6FpDA-PEO2000, was made by using the same methodology employed for 6FDA-6FpDA in which only the ratio (w/w) of 6FpDA and PEO2000 was varied. Polymerizations were carried out in 3-neck-flasks of 100 ml, equipped with a mechanical stirring, under an inert atmosphere of N_2. First off, x g, of previously dried PEO2000 (1g = 0.5149 mmol) were added and dissolved in 5 ml of NMP. When the monomer was completely dissolved, the required amount of the diamine 6FpDA was added. Thus, to obtain the

6FpDA/PEO2000 y/x (w/w), y g of 6FpDA (1g = 2.992 mmol) were added. Once the diamines were dissolved, the reaction was immersed in an ice-water bath and a stoichiometric amount of dianhydride 6FDA (equimolar to the sum of both the diamines) was added. After 12 hours of reaction, the chemical cyclization of the polyamic acid was performed as explained previously for the aromatic polyimide 6FDA-6FpDA. Afterwards, the chemically formed polyimides were precipitated into water and thoroughly washed in water and in ethanol-water 1/2 mixtures. After washing, the polymer was dried at 60 ° C for 12 h, then at 120 ° C under vacuum for 1 h, and finally at 180 ° C under vacuum for 6 h.

Finally, the blends w/w proportions were prepared by dissolving the required ratio (m/n) of the copolymer and the aromatic homopolymer at 10 weight % (w/v) THF. Table I shows the PEO weight % content for all the compositions. A scheme of the synthesis route is shown in Figure 1.

Table I.PEO percentages of blends.

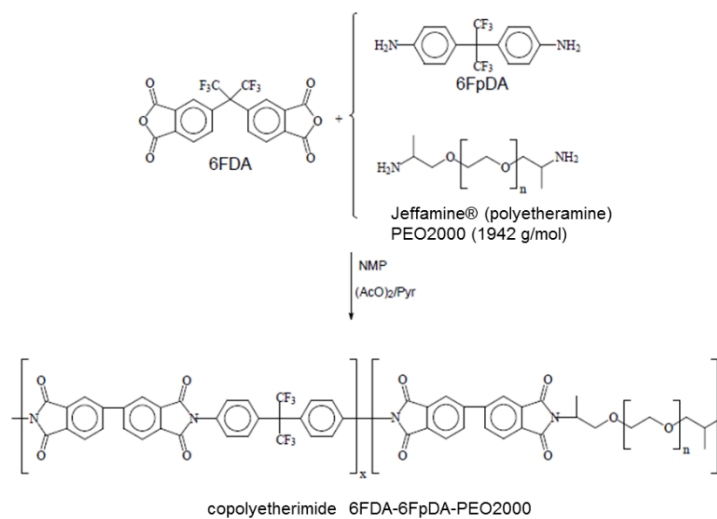| MEMBRANES 6FDA-6FpDA-PEO2000(x/y)-6FDA-6FpDA](m/n)	PEO2000 content % (w/w)
6FDA-6FpDA-PEO2000(4/1)-6FDA-6FpDA](1/2)	3.3
6FDA-6FpDA-PEO2000(4/1)-6FDA-6FpDA](1/1)	4.8
6FDA-6FpDA-PEO2000(2/1)-6FDA-6FpDA](1/1)	8.7
6FDA-6FpDA-PEO2000(1/1)-6FDA-6FpDA](1/1)	14.6

Fig. 1. Scheme of the synthesis of 6FDA-6FpDA-PEO2000 copolyetherimides.

2.3. Preparation of films

Films for homopolymer, copolymers and blends were prepared from 10 % (w/v) solutions, using THF as a solvent.

All polymer solutions were filtered through a Symta® fiber-glass filter having of 3.1μm pore size, and cast onto a levelled glass at 30 ºC. Subsequently, most of solvent was evaporated by keeping the membrane at 30 ºC for 12h. Homogeneous films having 40 and 60 μm thickness were obtained.

Afterwards, the formed films were subjected to the following thermal protocol in a vacuum oven: 60 °C for 1h, 80 °C for 30 min, 120 °C for 1h, 150 °C 30 min and 180 °C 1h. Finally, two thermal treatments were selected (after performing isothermal TGA) for the whole elimination of PEO of the precursor membranes: 290 ºC under air atmosphere for 30 minutes or 390 ºC under nitrogen atmosphere for 30 minutes.

2.4. Characterization Methods

The inherent viscosity (η_{inh}) of each polymer was obtained by measuring the time of falling along a capillary using solutions in NMP at a concentration of polymer of 0.5 g/dL. The measurements were performed with an Ubbelhode viscometer in a thermostatic bath at 25 ° C. Inherent viscosity is defined by the following equation:

$$\eta_{inh} = \frac{\ln \frac{t}{t_0}}{c} \qquad\qquad (1)$$

where t is the time of fall of the polymer solution through the capillary, t_0 is the time of fall of the solvent and c the concentration of the polymer solution.

The Fourier transform infrared spectra (FTIR) of polymer films were recorded using an attenuated total reflection device (ATR). Measurements were performed by a Perkin Elmer Spectrum One FT-IR (Perkin Elmer, Waltham, Massachusetts, U.S.), apparatus mounting the Universal ATR sampling accessory module. IR spectra were the average of 16 scans recorded in the spectral range of 4000–650 cm^{-1} with a 4 cm^{-1} resolution.

The solubility tests were carried out by weighting 10 mg of polymer in different test tubes and adding, to each one, 1 mL of the specific solvent. If the polymer was not soluble in the solvent, solutions were heated at the boiling temperature of the corresponding solvent. The solvents used were: *N, N'*-dimethylacetamide (DMA), N-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), chloroform (CH_3Cl), ethanol, pyridine (Py), acetone and toluene.

Tensile properties were measured in an MTS Synergie 200 (MTS, Eden Prairie, Minnesota, US) testing machine equipped with a 100 N load cell. Rectangular test pieces of 3.5 mm width and 25 mm length were cut from films. A crosshead speed of 5 mm/min was used. Strain was measured from crosshead separation and referred to 10 mm initial length. At least six samples were tested for each copolymer at room temperature.

Thermogravimetric analysis of the polymers were carried out in a thermobalance TA-Q500 (TA instruments-Water Corp. Milford, Massachusetts, US), in samples of about 5-10 mg, under a nitrogen flow of 40 mL/min, from 40 to 800 °C by using the high resolution (HiRes) mode.

DSC experiments were conducted in a differential scanning calorimeter TA-DSC Q2000 (TA instruments-Water Corp. Milford, Massachusetts, US), analyzing about 5-10 mg of polymer films under N_2 atmosphere with a heating rate of 10° C / min. The first scan was used to homogenize the thermal history of the sample and ensure the

removal of residual stresses that may have arisen during the stages of precipitation and purification of the polymer. Tg was determined in the second heating cycle, from the middle point of the resulting peaks. In addition, a High Pressure DSC 1 from Mettler Toledo (Mettler Toledo, Greifensee, Switzerland) was used to study the *in-situ* thermal transition of samples at high pressure (up to 20 bar) in a CO_2 atmosphere.

The gas separation properties measurements were performed in a permeator device at 30 °C and a feed pressure of 3 bar, using a barometric method. Permeability, diffusivity and solubility were obtained by the time-lag method [31].

3. RESULTS AND DISCUSSION

3.1. Inherent viscosity, Solubility and Mechanical Properties

Inherent viscosities for the homo polyimide and copolyetherimides are shown in Table II. The obtained values of inherent viscosity ensured the formation of high molecular weigth for these polymers [32].

Table II. Results of viscosity.

POLYMERS	PEO2000 content % (w/w)	ηinh (dL/g)
6FDA-6FpDA	0	0.63
6FDA-6FpDA-PEO2000 (1/1) 180ºC	29.1	0.33
6FDA-6FpDA-PEO2000 (2/1) 180ºC	17.4	0.45
6FDA-6FpDA-PEO2000 (4/1) 180ºC	9.6	0.50

The results of solubility of the polymers in various solvents are shown in Table III. These polymers exhibited an excellent solubility in polar aprotic media and even chloroform, tetrahydrofuran and pyridine, solvents in which the polyimides are generally insoluble. The higher the PEO2000 content the greater the difficulty of the polymer to be dissolved, particularly for amide-based solvents (DMAc and NMP). In conclusion, it can be stated that the combination of the structure of PEO2000 along with the use of diamine 6FpDA enabled these polymers to be processed into films by using low boiling point solvents. It is interesting to note that polymer mixtures with 6FDA-6FpDA and PEO copolymers produced totally clear and homogeneous solutions and

films, in all proportions. Copolymers and polymer blends, after heating, showed very low solubility leaving important amounts of insoluble polymer, due probably to the partial crosslinking process that occurred during the partial pyrolysis.

Table III. Solubility of polymers in different solvents.

POLYMERS	Solvents						
	EtOH	DMAc	NMP	THF	CHCl$_3$	Py	Toluene
6FDA-6FpDA	-	++	++	++	++	++	-
6FDA-6FpDA-PEO2000(1/1) 180ºC	+-	++	++	++	++	++	-
6FDA-6FpDA-PEO2000(2/1) 180ºC	+-	++	++	++	++	++	-
6FDA-6FpDA-PEO2000(4/1) 180ºC	+-	++	++	++	++	++	-

+ + : Soluble in cold, + : soluble in hot, - : insoluble; + - : insoluble or polymer only swollen in the solvent.

Because molecular weights were high enough as to give relatively high viscosities, the corresponding films had good mechanical properties. In effect, mechanical measurements confirmed that all the polymer films showed high tensile strengths, greater than 50 MPa, mechanical modules over 1GPa, and moderate elongations, which were directly correlated to the amount of PEO present in the structure.

3.2. ATR-FTIR

ATR-FTIR was used to characterize the membranes and their evolution as a function of the thermal treatment used to their partial pyrolysis. Figure 2 shows the FTIR-ATR spectra of 6FDA-6FpDA membrane (blue) along with the polymer 6FDA-6FpDA-co-6FDA-PEO2000 1/1.

It can be seen that both the spectra are very similar, differing only in the peaks associated with PEO2000. In effect, both the spectra show the typical peaks of associated imide groups at: 1780 cm^{-1} (asymmetric vibration of C = O), at 1720 cm^{-1} (symmetric vibration of C = O group), 1360 cm^{-1} (asymmetric vibration of C-N group) and 720 cm^{-1} (imide ring strain). In the case of the co-polymer with PEO groups, the most characteristic bands should be positioned at 1100 cm^{-1} (stretching band C-O-C) and at 840 cm^{-1} (band bending C-O group). Nevertheless, these bands overlapped with part of the aromatic ones and it was clearly difficult to determine them. It is worth to

note that there are not practically any bands in the 3250 cm^{-1} and 2500 cm^{-1} areas, what determined that cycloimidation was good enough to produce almost complete conversion to polyimide.

Intense bands at 2924 and 2854 cm^{-1}, that can be associated to the CH stretching of methylene group of PEO, were seen for the copolyimides. A superposition of the FTIR spectra of the three copolymers shows that the intensity of these bands is proportional to the amount of PEO present in the copolymer; what can be used to determine the degree of PEO removal. Moreover, a superposition of the thermally treated spectra of all blends, both for the sample thermally treated in N$_2$ at 390 ° C as for that treated in air at 290 ºC, showed that, in both cases, the complete elimination of PEO was attained.
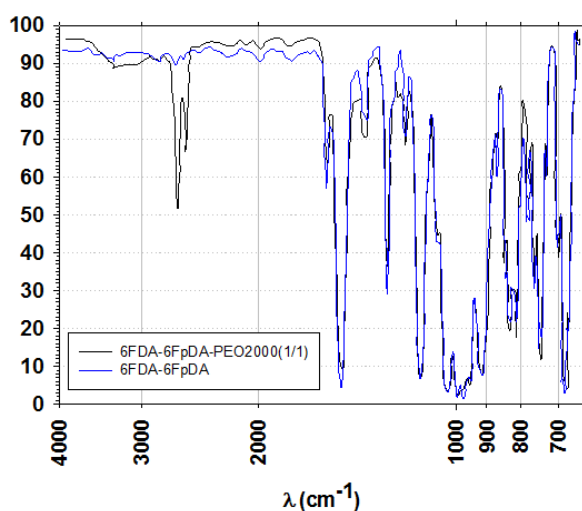
Fig. 2. FTIR of some films: (black) coplyetherimide 6FDA-6FpDA-PEO2000(1/1); (blue) 6FDA-6FpDA.

3.3. Thermo-gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

In Figure 3-a, TGA results are shown for the 6FDA-6FpDA polyimide. This polyimide, widely studied in the literature, has a very high (525 °C) onset degradation temperature T$_d$ and a high carbon residue at 800 ° C (53%). In the graph, the small weight loss at 350 ° C can be associated with the solvent loss that occurs when the polymer Tg is exceeded. Therefore, films were heated to 330 °C in an inert (nitrogen)

atmosphere to remove the residual solvent. After this treatment the polymer did not show that loss, leading to the same values of T_d and similar carbonaceous residues.

Figure 3-b shows the thermograms, together with their derivatives, for the three PEO copolymers obtained in this work.
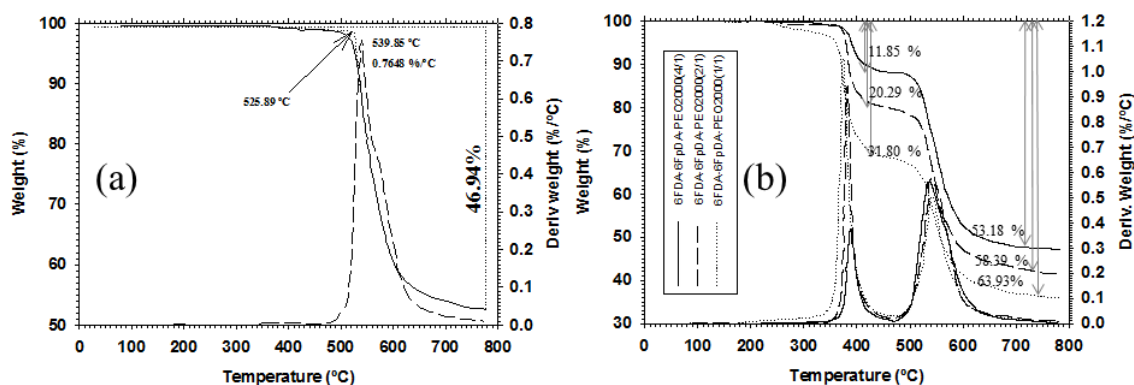

Fig. 3. (a) TGA results for the 6FDA-6FpDA polyimide and (b) TGA thermograms for the copolyetherimides: 6FDA-6FpDA-PEO2000 (4/1) (solid line), 6FDA-6FpDA-PEO2000(2/1) (dashed line) and 6FDA-6FpDA-PEO2000 (1/1) (dotted line). All of them prior to partial pyrolysis.

In the thermogravimetric analysis of these copolymers, two degradation steps were observed, one of them appeared at temperatures below 400 °C and was associated with the degradation of the PEO chains, and other near 540 ºC, which is similar to the degradation temperature of the homopolymer 6FDA-6FpDA. The weight percentages found by TGA for the losses assigned to the PEO moieties were a little higher than those expected for theoretical ones, as shown in Table IV. This lower weight loss could be explained by the existence of crosslinking processes what, as mentioned, was already detected in the solubility experiments.

Table IV. Weight loss percentages.

Copolymer	1st peak		% Tar residue at 800ºC
	% Theor. loss	% Exp. Loss	
6FDA-6FpDA-PEO2000(1/1)	29.1	31.8	36.1 (36.0)*
6FDA-6FpDA-PEO2000(2/1)	17.4	20.3	41.6 (42.4)*
6FDA-6FpDA-PEO2000(4/1)	9.6	11.9	46.8 (46.6)*

* Values corresponding to the residue assuming 53 % losses of 6FDA-6FpDA and the experimental losses for the copolymer.

Regarding the carbonaceous residues at 800 ° C, they can be compared with those evaluated by assuming 53 % losses for the 6FDA-6FpDA polyimide (see Figure 3-a). Note that there is a reasonable agreement, what means that the same degradation process for the 6FDA-6FpDA aromatic part is achieved with or without the presence of PEO in the polyimide. Therefore, it is possible to eliminate in a selective way the aliphatic PEO from the copolymer structure with no apparent effect in the aromatic structure but the presence of small amounts of crosslinking.

Once proved that it was possible to attain the whole and selective elimination of the PEO portion from the block copolymer, a thermogravimetric study under isothermal conditions for these polymers was carried out. From dynamic TGA, it was determined that the maximum degradation rate associated to the loss of PEO appeared at around 390 °C. Therefore, a temperature of 390 °C was chosen for the isothermal experiments. In Figure 4 the thermogram for 6FDA-6FpDA-PEO2000(2/1) is shown. Note that, in this case, the degradation weight loss was 19.35 % (20.3% was the theoretical one). After the isothermal treatment, the obtained material showed excellent mechanical properties. This fact is not frequent because pyrolysis commonly compromises mechanical properties giving brittle materials. With these data, a method consisting in heating the polymer under inert nitrogen atmosphere at 150 ºC/15min, 200 ºC/30min, 250 ºC/15min, 350 ºC/15min, 390 ºC/30min was chosen.

For blends, similar degradation paths were observed, although in this case the PEO removal temperature range was a little bit wider. After the PEO degradation treatment, it was observed (by ATR-FTIR and TGA) that the final structures of thermally treated 6FpDA-PEO2000 copolyetherimides and blends matched with that of 6FDA-6FpDA.

It should be noted that the PEO removal temperature is quite high, higher than the Tg of 6FDA-6FpDA, what could lead to a high physical aging. From an industrial point of view, the application of thermal processes under air conditions could be significantly beneficial. Thus, it was carried out a dynamic TGA under air for 6FDA-6FpDA-PEO2000(2/1). The results of TGA under N_2 and air are compared in Figure 4-b. The Figure showed that, under air, the PEO degradation temperature was lower. In this case, the process (after an induction time) started at temperatures lower than 300 ºC (60 ºC lower than the value observed under N_2). Thus, the almost complete removal of PEO

could be achieved at 290 ºC after residence times of 30 min, Consequently, a thermal protocol was applied to polymer blends using the following treatment in air: 150 ºC/15min, 200 ºC/30min, 250 ºC/15min, 290 ºC/30min. Afterwards, a quick heating rate (40 ºC/min) above the Tg (330º C) was performed in N_2 atmosphere to ensure the complete loss of PEO. The material extracted from the oven had lost practically all the PEO and it still showed excellent mechanical properties.
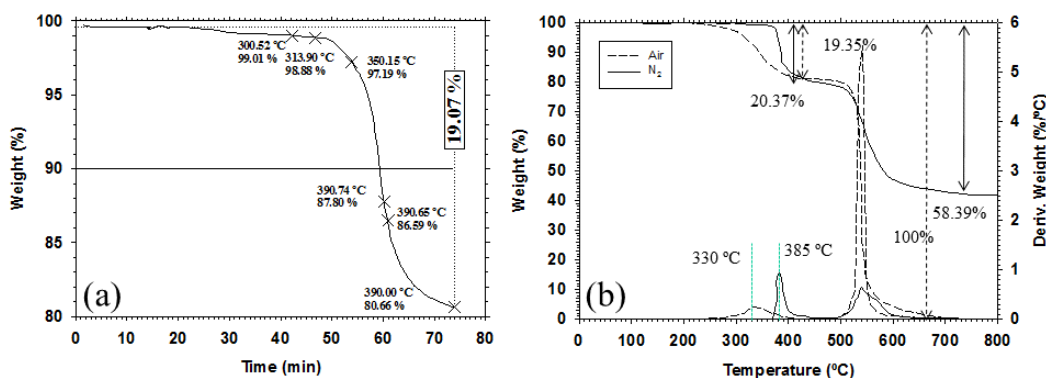

Fig. 4. (a) TGA with a heating ramp until 390 °C and isothermally during 15 min for the 6FDA-6FpDA-PEO2000(2/1) copolyetherimide and (b) TGA for the 6FDA-6FpDA-PEO2000(2/1) copolyetherimide pyrolized in both N_2 and air atmospheres.

The glass transition temperatures of the polymers were determined by differential scanning calorimetry (DSC). In all cases the homopolymer, the copolymers and the blends did not present any crystallinity peak, confirming their amorphous nature.

For the 6FDA-6FpDA homopolymer polyimide, a Tg of 308 ° C was measured. In the case of the PEO containing copolymers, it was not possible to observe the two Tg values corresponding to both the soft segments and the hard portions. The soft PEO segments should have a Tg between -55 and -25 ° C, whereas the aromatic portion of the copolyimides should show Tg values below that of 6FDA-6FpDA (308 ºC). The lack of detection of two different Tg confirms that no phase segregation was attained [33]. This observation was confirmed by SAXS, where no typical segregation peaks were observed [32]. Also, the partially pyrolized systems did not show any thermal transition due to densification and crosslinking processes.

Because the aromatic segments could be plasticized by the presence of CO_2, DSC experiments under a CO_2 atmosphere, of copolymers and blends, were planned and carried out. A single global Tg could be detected and the obtained results are presented in Figure 5. There it is showed that there is a clear decrease in Tg when the CO_2

pressure is increased with quite similar results for different PEO contents (see Table I to correlate PEO percentages for each material).
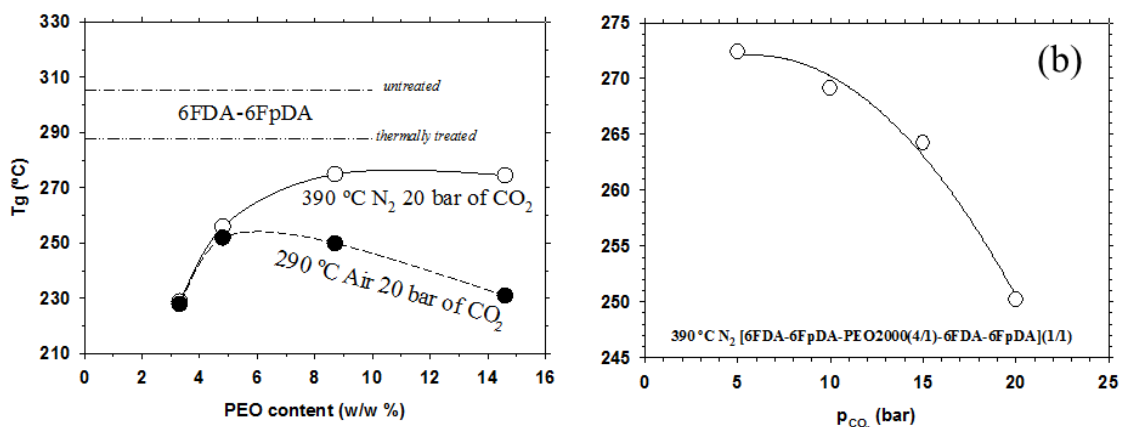

Fig. 5. Fig. 5.- DSC results for Tg (after thermal treatment) as a function of the initial PEO content for 20 bar CO₂ (a) and for the [6FDA-6FpDA-PEO2000(4/1)-6FDA-6FpDA](1/1) blend treated at 390˚C in N₂ as a function of CO₂ pressure (b).

It was observed an initial increase of Tg when the percentages of initial PEO was increased. This fact could agree with the general inverse correlation of Tg and plasticization [5, 34]. A minimum of plasticization seems to be observed for PEO contents in the range from 5 to 15 %. Moreover, plasticization effects seem to be more intense for the membrane thermally treated at 290 ºC in air than for that threated at 390 ºC in N_2. However, the plasticization range seems to be narrower for the thermally treated membrane under air. Note that although the Tg of the homopolymer was higher than that of the thermally treated blends, this does not allow a comparison of their plasticization ability as far as the Tg-plasticization correlation would only exist for analogous polymer series. Moreover, the macromolecular chains of the aromatic units of blends consist of mixtures of long units (derived from the homopolymer) and shorter ones (derived from the aromatic blocks of the copolymers). And thus, the final Tg (without taking into account the increase of Tg due to crosslinking) should be lower than that of the homopolymer.

3.1. Gas Permeability and Selectivity

In Figure 6-8, the N_2 and CO_2 permeabilities and the corresponding selectivity, measured at 3 bar, are shown versus the PEO percentage for the copolymers and blends, and also for the thermally treated membranes at 290ºC in air and 390 ºC in N_2. As commented above, it seems clear that permeability decreases with increasing precursor

PEO contents. It appears, thus, that the action of adding PEO hinders permeation probably because free volume is filled out with the flexible PEO chains. For similar PEO percentages, permeability was higher for the partially pyrolized membranes, which seems reasonable whether it is supposed that the increase of fractional free volume (due to the removal of the PEO moieties) is compensated by the reduction of FFV due to crosslinking and also to the shrinkage derived from the movement of the aromatic moieties at these temperatures. The process of blending increases permeability as far as it adds free volume within the added 6FDA-6FpDA as observed by Fu and co-workers [18].
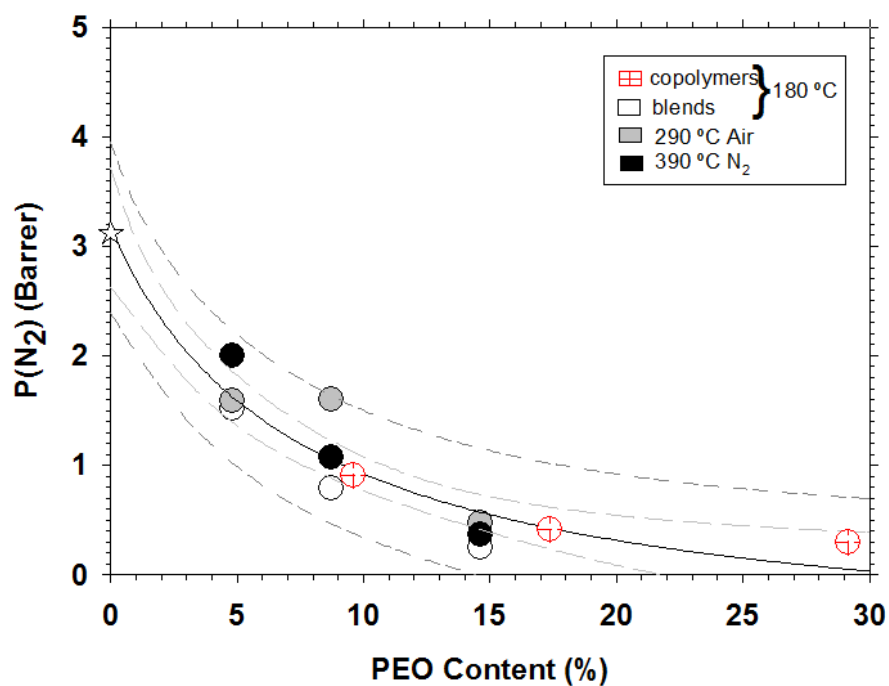
Fig. 6. N$_2$ permeability at 3 bar as a function of PEO percent. The star corresponds to pure 6FDA-6FpDA.
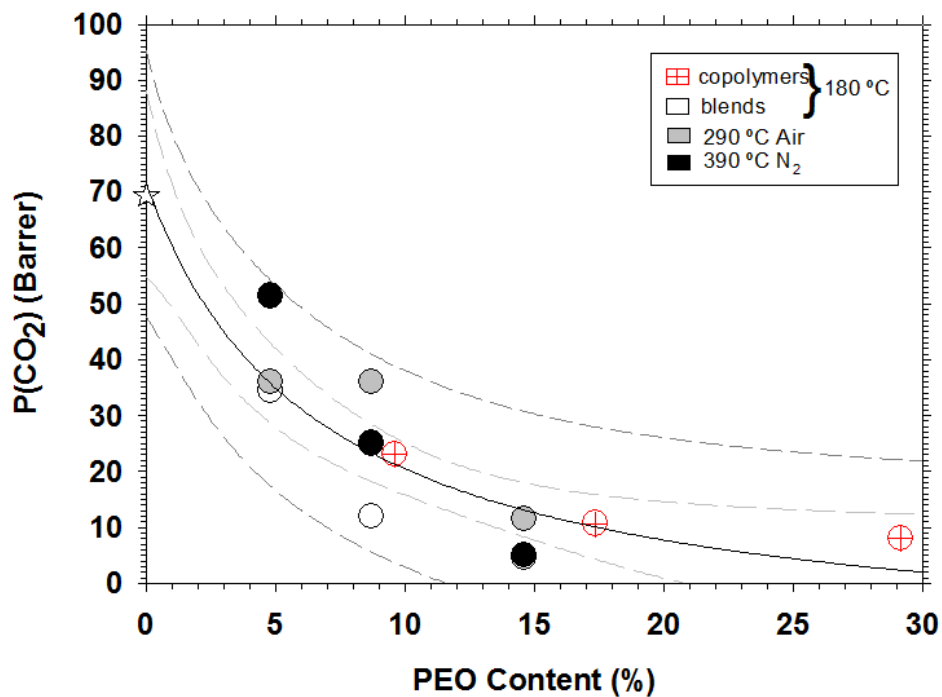
Fig. 7. CO$_2$ permeability at 3 bar as a function of PEO percent. The star corresponds to pure 6FDA-6FpDA.
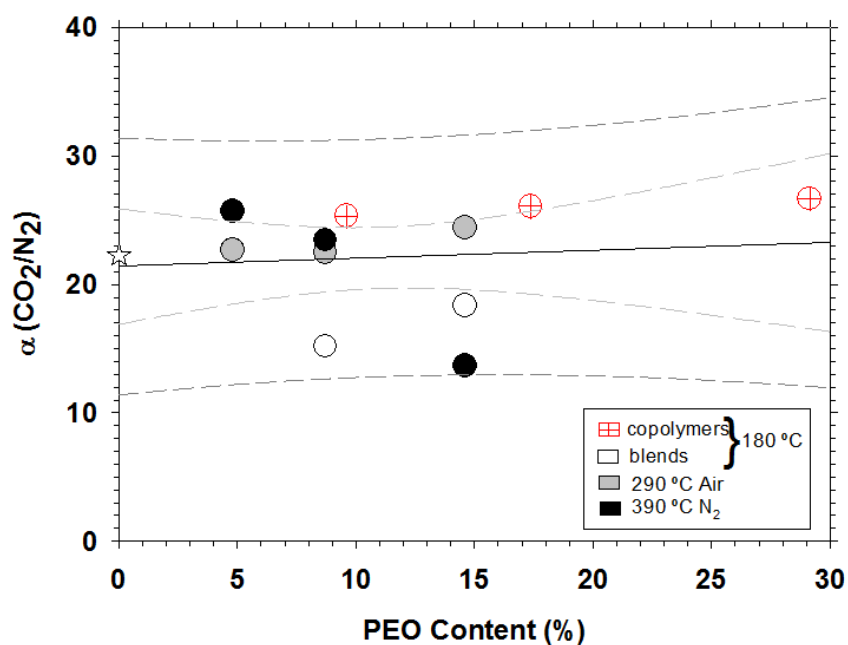
Fig. 8. CO$_2$/N$_2$ (c) selectivity at 3 bar as a function of PEO percent. The star corresponds to pure 6FDA-6FpDA.

In Figure 9, the CO_2 permeability is shown for the [6FDA-6FpDA-PEO2000 (4/1)-6FDA-6FpDA](1/1) membrane (initial 4.8 % PEO content before partial pyrolysis) treated at 290 ºC in air versus feed pressure, compared with that of pure 6FDA-6FpDA. The observed results corresponded to membranes pressurized at 40 bar in a CO_2 atmosphere during 3 days prior to the shown up-and-down cycle of applied pressure drops. It is clearly seen that the CO_2 permeability of pure 6FDA-6FpDA increased largely, showing a significant hysteresis. For the blend, the change of permeability was negligible and no hysteresis could be seen (compare these results with those results shown in Figure 7 for a sample treated at 3 bar).
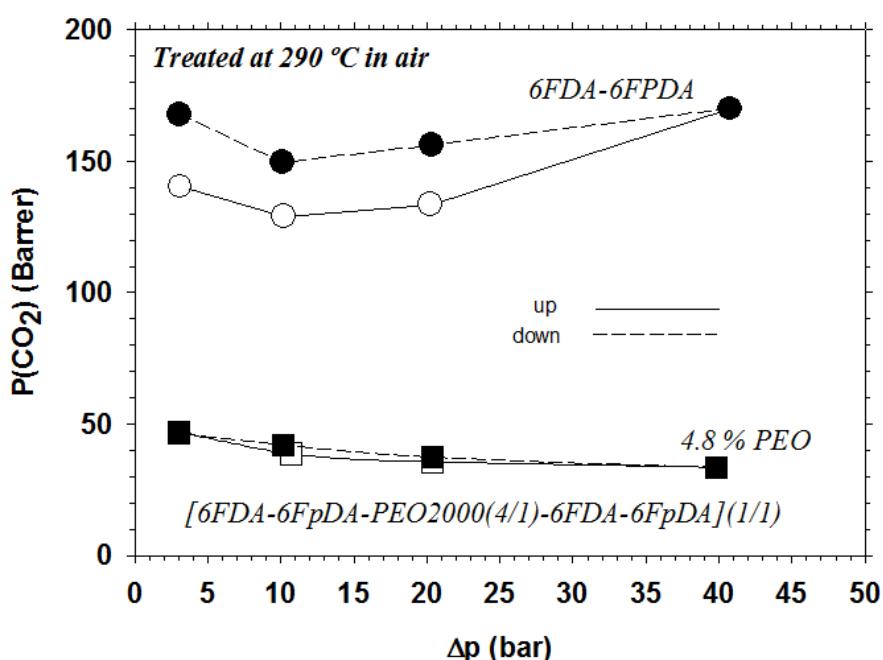
Fig. 9. CO_2 permeability, after 3 days in a 40 bar CO2 atmosphere, as a function of pressure for the [6FDA-6FpDA-PEO2000 (4/1)-6FDA-6FpDA](1/1) (4.8 % PEO content) blend treated at 290 °C in air as compared to that of the pure 6FDA-6FpDA (a) and as a function of PEO content at 3 bar before any CO_2 pressurization.

In Figure 10, CO_2/N_2 selectivity values are depicted for the [6FDA-6FpDA-PEO2000 (1/1)-6FDA-6FpDA](1/1) (14.6 % PEO content) blend treated at 290 ºC under air (8-b). The corresponding selectivity of the pure 6FDA-6FpDA polyimide is shown for the sake of comparison. It seems evident that selectivity of the blend rather increased as compared to that of the pure polyimide showing a small hysteresis. Attending to those results, it seems clear that, in spite of the low Tg revealed in Figure 5-b, the blends thermally treated in air at 290 ºC showed very small plasticization.
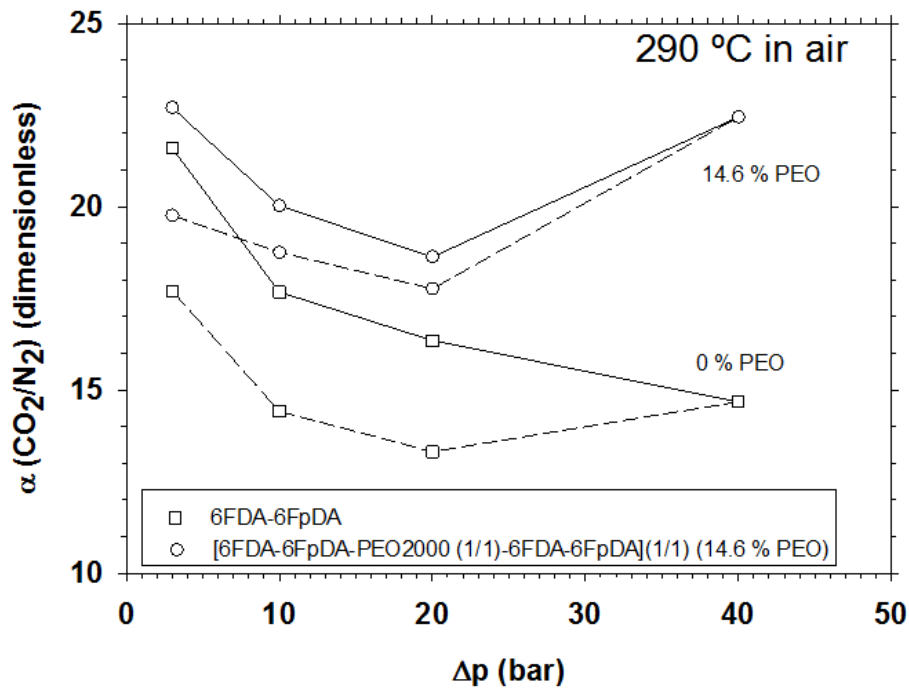
Fig. 10. CO_2/N_2 selectivity as a function of pressure for the blend [6FDA-6FpDA-PEO2000 (1/1)-6FDA-6FpDA](1/1) (14.6 % PEO content) treated at 290 °C in air.

Robeson's plots, for the blends [6FDA-6FpDA-PEO2000(4/1)-6FDA-6FpDA](1/1) with or without thermal treatments at 390ºC in N_2 and at 290 ºC in air and untreated, are shown in Figure 11 (CO_2/CH_4 in Figure 9-a and O_2/N_2 in Figure 9-b). In both cases, data corresponded to measurements performed at 3 bar and 30 ºC. The pure 6FDA-6FpDA and the corresponding copolymer, 6FDA-6FpDA-PEO2000(4/1), are included for comparison. Permeability decreased for CO_2 and remained almost constant for O_2 but selectivity increased, especially for the O_2/N_2 pair. Therefore, the treatment was improving the selectivity whereas the separation mechanism was mainly controlled by diffusivity, as in the case of the separation O_2/N_2.
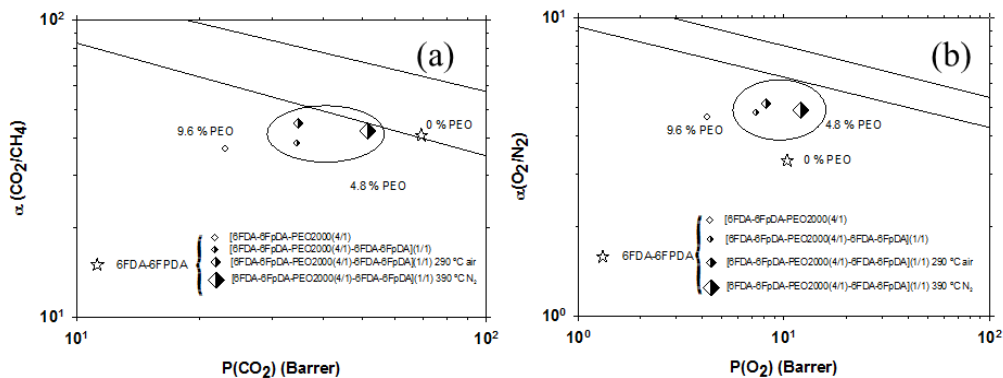
Fig. 11. Robeson plot for the pairs CO$_2$/CH$_4$ (a) and O$_2$/N$_2$, for the [6FDA-6FpDA-PEO2000(4/1)-6FDA-6FpDA](1/1) blend, the pure aromatic polyimide and the corresponding copolymer.

4. CONCLUSIONS

It has been confirmed that the partial pyrolysis of polyetherimides (having different PEO amounts) blended with pure aromatic polyimides is a valid method for the design of a new generation of materials for gas separation with better plasticization resistance.

In this context, 6FDA-6FpDA-PEO2000+6FDA-6FpDA blends, with different proportions of PEO were obtained. The homopolyimide (6FDA-6FpDA) and the (6FDA-6FpDA-PEO2000 x/1) copolyimides were synthesized using the two-step method (cyclodehydration from the polyamic acid) with high yields and excellent inherent viscosities. It was confirmed, by TGA and ATR-FTIR, the existence of a wide enough window of temperature to selectively remove the PEO from the copolyimides and blends materials without producing the degradation of the aromatic polyimide.

The partial pyrolysis of PEO moieties could be achieved under inert or oxidizing atmosphere, under air. The PEO degradation temperature was lower than the Tg of the aromatic polyimide. Also, it was observed that after the thermal process, a certain level of crosslinking was present by TGA and ATR-FTIR, it was demonstrated that this partial pyrolysis produces a similar material to that of the aromatic portion of the block copolymer, 6FDA-6FpDA. All the polymers and blends (neat and partially pyrolyzed ones) showed good mechanical properties able to resist high pressures as gas separation membranes.

Permeability of the non-treated membranes decreased when the initial PEO content increased; or, alternatively, when the aromatic chain proportion decreased. Membranes made by thermal treatment under N$_2$ atmosphere at 390 ºC showed higher permeability values than those obtained by thermal treatment under air atmosphere at 290 º C. On the other hand, the permselectivity for several gas pairs was slightly higher for the samples thermally treated under air conditions. These effects were related to the presence of crosslinking reactions, which obviously are stronger, more extended, or more easily reached, in the case of a more oxidizing atmosphere. The plasticization

resistance resulted to be maximal for membranes that had initial PEO percentages in the range from 5 to 8 %.

The lower permeability values of the thermally treated membranes (under air and N_2) when compared with the neat 6FDA-6FpDA homopolymer could be explained by the high temperature employed. This temperature is enough to produce crosslinking and also favor the macromolecular chain mobility what is translated to a shrinkage of the material, bringing about a decrease of the fractional free volume.

This plasticization resistance was more efficient for polyimide blends thermally treated at 290 ºC in air, probably due to the existence of higher degrees of crosslinking due to the oxidizing atmosphere.

5. ACKNOWLEDGEMENTS

6. REFERENCES

[1] L.M. Robeson, Correlation of separation factor versus permeability for polymeric membranes, Journal of Membrane Science 62(2) (1991) 165-185.
[2] L.M. Robeson, The upper bound revisited, Journal of Membrane Science 320(1) (2008) 390-400.
[3] R.E. Kesting, A.K. Fritzsche, Polymeric gas separation membranes, Wiley1993.
[4] A. Bos, I.G.M. Pünt, M. Wessling, H. Strathmann, CO2-induced plasticization phenomena in glassy polymers, Journal of Membrane Science 155(1) (1999) 67-78.
[5] A.F. Ismail, W. Lorna, Penetrant-induced plasticization phenomenon in glassy polymers for gas separation membrane, Separation and Purification Technology 27(3) (2002) 173-194.
[6] A. Bos, I.G.M. Pünt, M. Wessling, H. Strathmann, Plasticization-resistant glassy polyimide membranes for CO2/CO4 separations, Separation and Purification Technology 14(1) (1998) 27-39.
[7] Y.J. Cho, H.B. Park, High Performance Polyimide with High Internal Free Volume Elements, Macromolecular Rapid Communications 32(7) (2011) 579-586.
[8] H. Ohya, V.V. Kudryavsev, S.I. Semenova, Polyimide Membranes: Applications, Fabrications and Properties, Taylor & Francis1997.
[9] Y. Xiao, B.T. Low, S.S. Hosseini, T.S. Chung, D.R. Paul, The strategies of molecular architecture and modification of polyimide-based membranes for CO2 removal from natural gas—A review, Progress in Polymer Science 34(6) (2009) 561-580.
[10] A. Bos, I. Pünt, H. Strathmann, M. Wessling, Suppression of gas separation membrane plasticization by homogeneous polymer blending, AIChE Journal 47(5) (2001) 1088-1093.
[11] K. Halder, M.M. Khan, J. Grünauer, S. Shishatskiy, C. Abetz, V. Filiz, V. Abetz, Blend membranes of ionic liquid and polymers of intrinsic microporosity with improved gas separation characteristics, Journal of Membrane Science 539(Supplement C) (2017) 368-382.

[12] S. Mosleh, M.R. Mozdianfard, M. Hemmati, G. Khanbabaei, Synthesis and characterization of rubbery/glassy blend membranes for CO2/CH4 gas separation, Journal of Polymer Research 23(6) (2016) 120.

[13] M.E. Rezac, E. Todd Sorensen, H.W. Beckham, Transport properties of crosslinkable polyimide blends, Journal of Membrane Science 136(1) (1997) 249-259.

[14] W.F. Yong, Z.K. Lee, T.-S. Chung, M. Weber, C. Staudt, C. Maletzko, Blends of a Polymer of Intrinsic Microporosity and Partially Sulfonated Polyphenylenesulfone for Gas Separation, ChemSusChem 9(15) (2016) 1953-1962.

[15] W.F. Yong, F.Y. Li, T.S. Chung, Y.W. Tong, Molecular interaction, gas transport properties and plasticization behavior of cPIM-1/Torlon blend membranes, Journal of Membrane Science 462(Supplement C) (2014) 119-130.

[16] K.-S. Liao, Y.-J. Fu, C.-C. Hu, J.-T. Chen, Y.-H. Huang, M. De Guzman, S.-H. Huang, K.-R. Lee, Y.C. Jean, J.-Y. Lai, Development of the Asymmetric Microstructure of Carbon Molecular Sieve Membranes as Probed by Positron Annihilation Spectroscopy, The Journal of Physical Chemistry C 117(7) (2013) 3556-3562.

[17] P.S. Tin, T.-S. Chung, A.J. Hill, Advanced Fabrication of Carbon Molecular Sieve Membranes by Nonsolvent Pretreatment of Precursor Polymers, Industrial & Engineering Chemistry Research 43(20) (2004) 6476-6483.

[18] Y.-J. Fu, C.-C. Hu, D.-W. Lin, H.-A. Tsai, S.-H. Huang, W.-S. Hung, K.-R. Lee, J.-Y. Lai, Adjustable microstructure carbon molecular sieve membranes derived from thermally stable polyetherimide/polyimide blends for gas separation, Carbon 113(Supplement C) (2017) 10-17.

[19] H. Hatori, T. Kobayashi, Y. Hanzawa, Y. Yamada, Y. Iimura, T. Kimura, M. Shiraishi, Mesoporous carbon membranes from polyimide blended with poly(ethylene glycol), Journal of Applied Polymer Science 79(5) (2001) 836-841.

[20] X. Zhang, H. Hu, Y. Zhu, S. Zhu, Carbon molecular sieve membranes derived from phenol formaldehyde novolac resin blended with poly(ethylene glycol), Journal of Membrane Science 289(1) (2007) 86-91.

[21] L. Cui, W. Qiu, D.R. Paul, W.J. Koros, Physical aging of 6FDA-based polyimide membranes monitored by gas permeability, Polymer 52(15) (2011) 3374-3380.

[22] H. Chen, Y. Xiao, T.-S. Chung, Synthesis and characterization of poly (ethylene oxide) containing copolyimides for hydrogen purification, Polymer 51(18) (2010) 4077-4086.

[23] Y. Hirayama, T. Yoshinaga, Y. Kusuki, K. Ninomiya, T. Sakakibara, T. Tamari, Relation of gas permeability with structure of aromatic polyimides II, Journal of Membrane Science 111(2) (1996) 183-192.

[24] O. Ken-ichi, U. Nobuhiro, O. Shuusaku, T. Kazuhiro, K. Hidetoshi, Selective Permeation of Carbon Dioxide over Nitrogen through Polyethyleneoxide-Containing Polyimide Membranes, Chemistry Letters 22(2) (1993) 225-228.

[25] K.-i. Okamoto, M. Fuji, S. Okamyo, H. Suzuki, K. Tanaka, H. Kita, Gas permeation properties of poly(ether imide) segmented copolymers, Macromolecules 28(20) (1995) 6950-6956.

[26] H. Suzuki, K. Tanaka, H. Kita, K. Okamoto, H. Hoshino, T. Yoshinaga, Y. Kusuki, Preparation of composite hollow fiber membranes of poly(ethylene oxide)-containing polyimide and their CO2/N2 separation properties, Journal of Membrane Science 146(1) (1998) 31-37.

[27] M. Yoshino, K. Ito, H. Kita, K.-I. Okamoto, Effects of hard-segment polymers on CO2/N2 gas-separation properties of poly(ethylene oxide)-segmented copolymers, Journal of Polymer Science Part B: Polymer Physics 38(13) (2000) 1707-1715.

[28] E.M. Maya, D.M. Muñoz, A.E. Lozano, J. de Abajo, J.G. de la Campa, Fluorenyl cardo copolyimides containing poly(ethylene oxide) segments: Synthesis, characterization, and evaluation of properties, Journal of Polymer Science Part A: Polymer Chemistry 46(24) (2008) 8170-8178.

[29] D.M. Muñoz, E.M. Maya, J. de Abajo, J.G. de la Campa, A.E. Lozano, Thermal treatment of poly(ethylene oxide)-segmented copolyimide based membranes: An effective way to improve the gas separation properties, Journal of Membrane Science 323(1) (2008) 53-59.

[30] A. Marcos-Fernández, A. Tena, A.E. Lozano, J.G. de la Campa, J. de Abajo, L. Palacio, P. Prádanos, A. Hernández, Physical properties of films made of copoly(ether-imide)s with long poly(ethylene oxide) segments, European Polymer Journal 46(12) (2010) 2352-2364.

[31] R. Recio, L. Palacio, P. Prádanos, A. Hernández, Á.E. Lozano, Á. Marcos, J.G. de la Campa, J. de Abajo, Gas separation of 6FDA–6FpDA membranes: Effect of the solvent on polymer surfaces and permselectivity, Journal of Membrane Science 293(1) (2007) 22-28.

[32] A. Tena, A. Marcos-Fernández, L. Palacio, P. Cuadrado, P. Prádanos, J. de Abajo, A.E. Lozano, A. Hernández, Phase Segregation and Gas Separation Properties of Thermally Treated Copoly(ether-imide) from an Aromatic Dianhydride, an Aromatic Diamine, and Various Aliphatic Diamines, Industrial & Engineering Chemistry Research 51(9) (2012) 3766-3775.

[33] A. Tena, A. Marcos-Fernández, A.E. Lozano, J.G. de la Campa, J. de Abajo, L. Palacio, P. Prádanos, A. Hernández, Thermally treated copoly(ether-imide)s made from bpda and alifatic plus aromatic diamines. GAS separation properties with different aromatic diamimes, Journal of Membrane Science 387-388(Supplement C) (2012) 54-65.

[34] K.K. Chee, Prediction of glass transition temperatures of plasticized polymers, European Polymer Journal 21(1) (1985) 29-31.

FIGURE CAPTIONS

Fig. 1. Scheme of the synthesis of the copolyetherimide 6FDA-6FpDA-PEO2000.

Fig. 2. Fig. 2.- FTIR of some films: (black) coplyetherimide 6FDA-6FpDA-PEO2000(1/1); (blue) 6FDA-6FpDA .

Fig. 3. (a) TGA results for the 6FDA-6FpDA polyimide and (b) TGA thermograms for the copolyetherimides: 6FDA-6FpDA-PEO2000(4/1) (solid line), 6FDA-6FpDA-PEO2000(2/1) (dashed line) and 6FDA-6FpDA-PEO2000 (1/1) (dotted line). All them prior to partial pyrolysis.

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Fig. 6. N_2 permeability at 3 bar as a function of PEO percent. The star corresponds to pure 6FDA-6FpDA.

Fig. 7. CO_2 permeability at 3 bar as a function of PEO percent. The star corresponds to pure 6FDA-6FpDA.

Fig. 8. CO_2/N_2 (c) selectivity at 3 bar as a function of PEO percent. The star corresponds to pure 6FDA-6FpDA.

Fig. 9. CO_2/N_2 selectivity as a function of pressure for the blends: [6FDA-6FpDA-PEO2000 (4/1)-6FDA-6FpDA](1/2) (3.3 % PEO content) (a) and [6FDA-6FpDA-PEO2000 (1/1)-6FDA-6FpDA](1/1) (14.6 % PEO content) (b).

Fig. 10. CO_2/N_2 selectivity as a function of pressure for the blend [6FDA-6FpDA-PEO2000 (1/1)-6FDA-6FpDA](1/1) (14.6 % PEO content) treated at 290 °C in air.

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TABLE CAPTIONS

Table I. PEO percentages in the blends prepared.

Table II. Results of viscosity.

Table III. Solubility of polymers in different solvents.

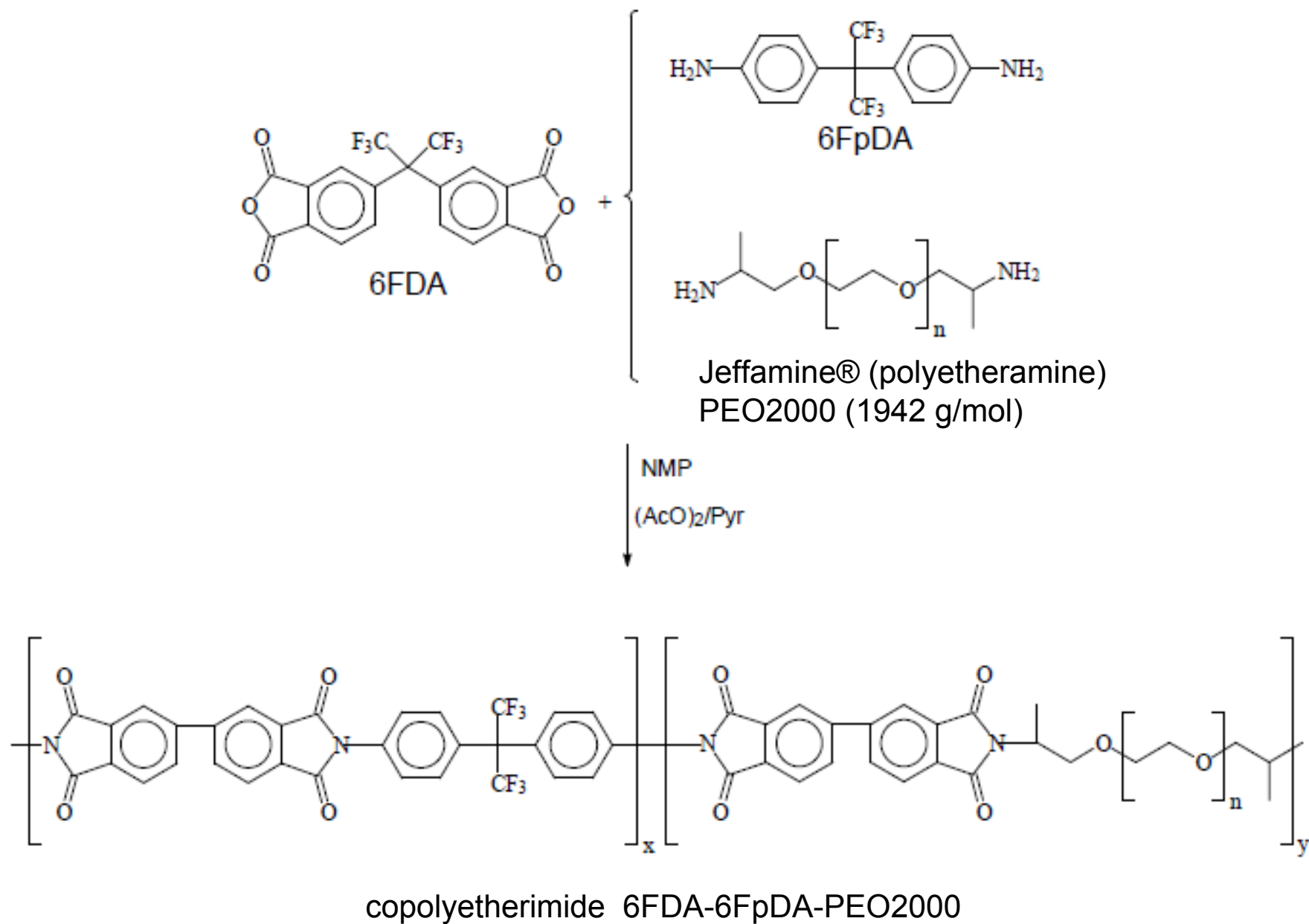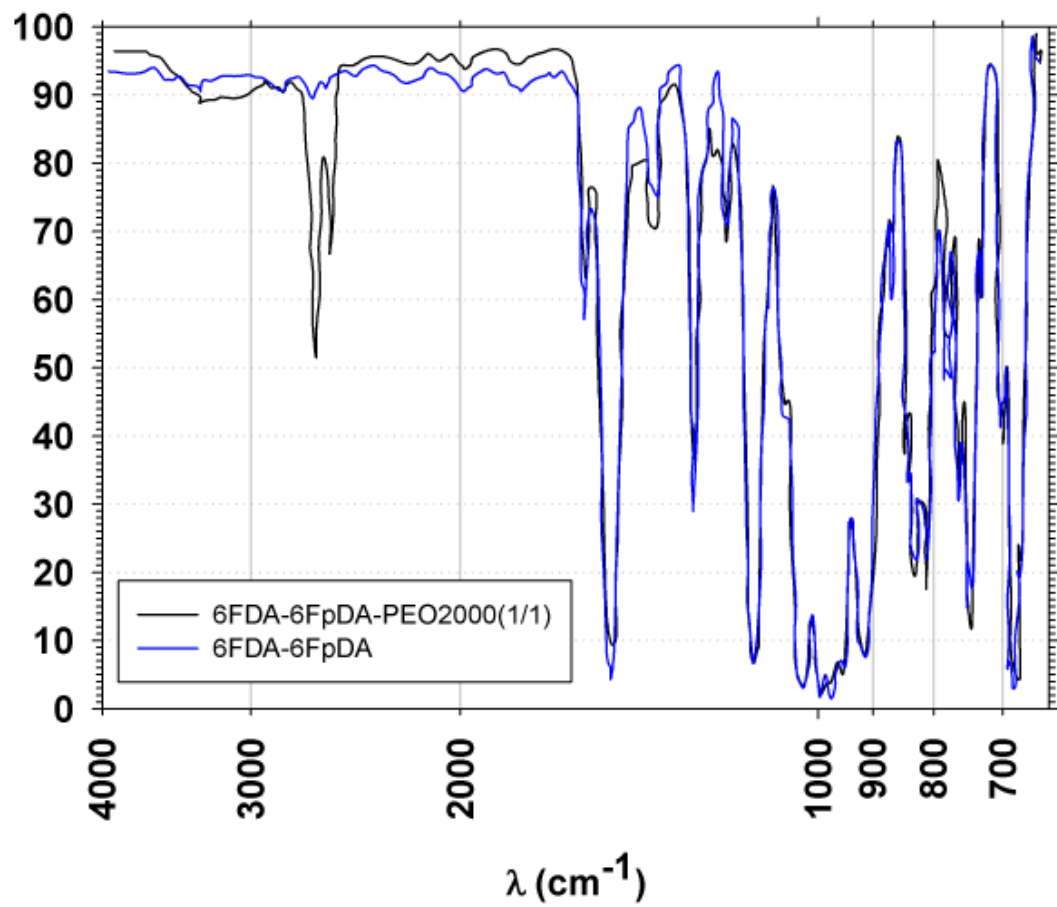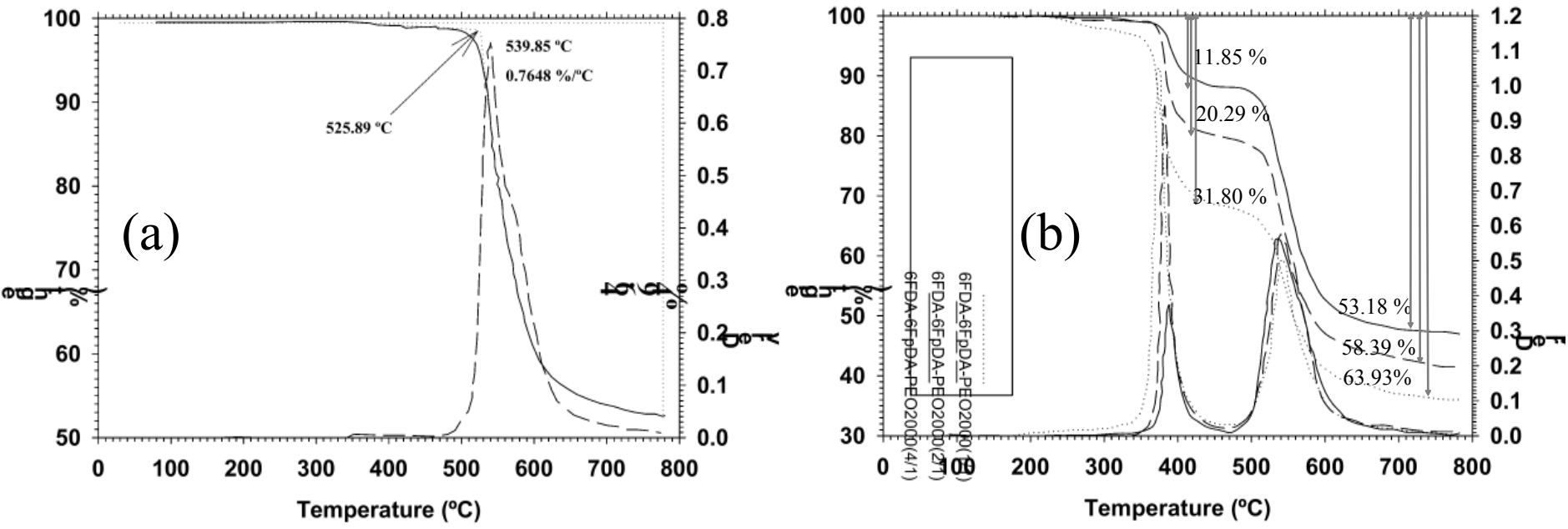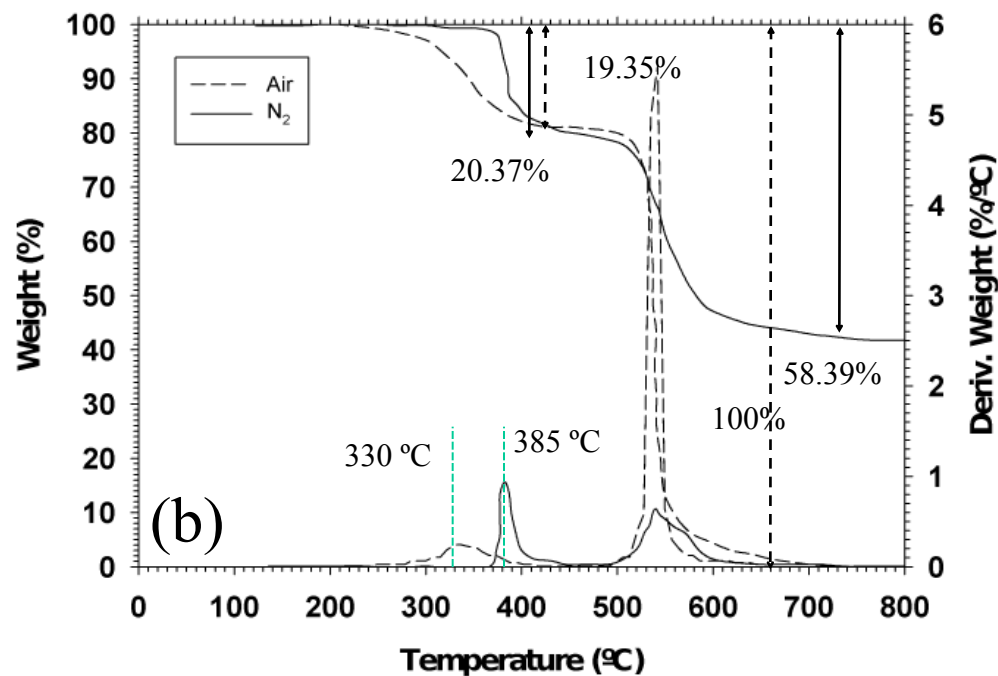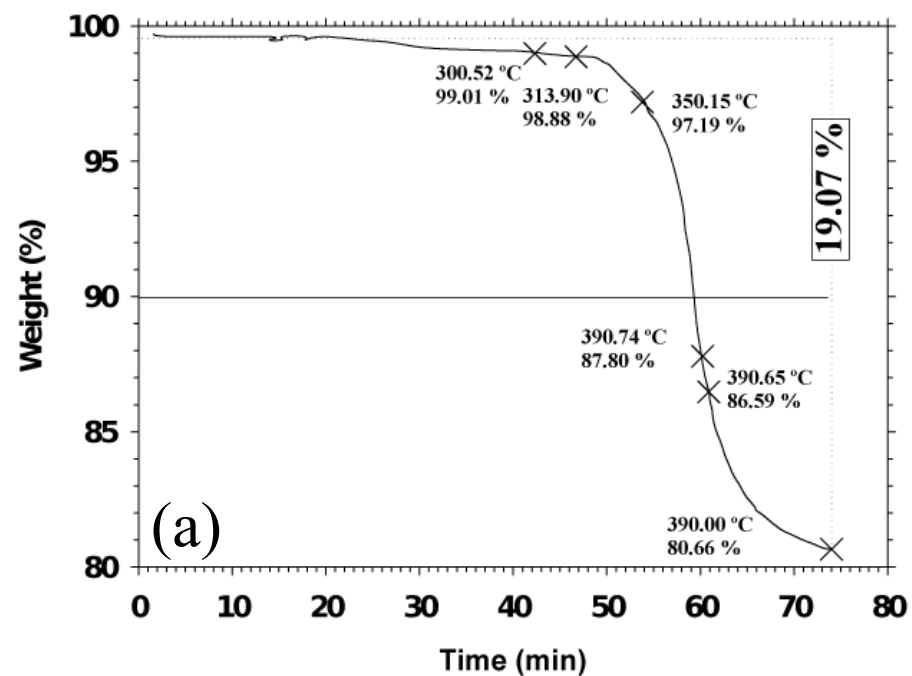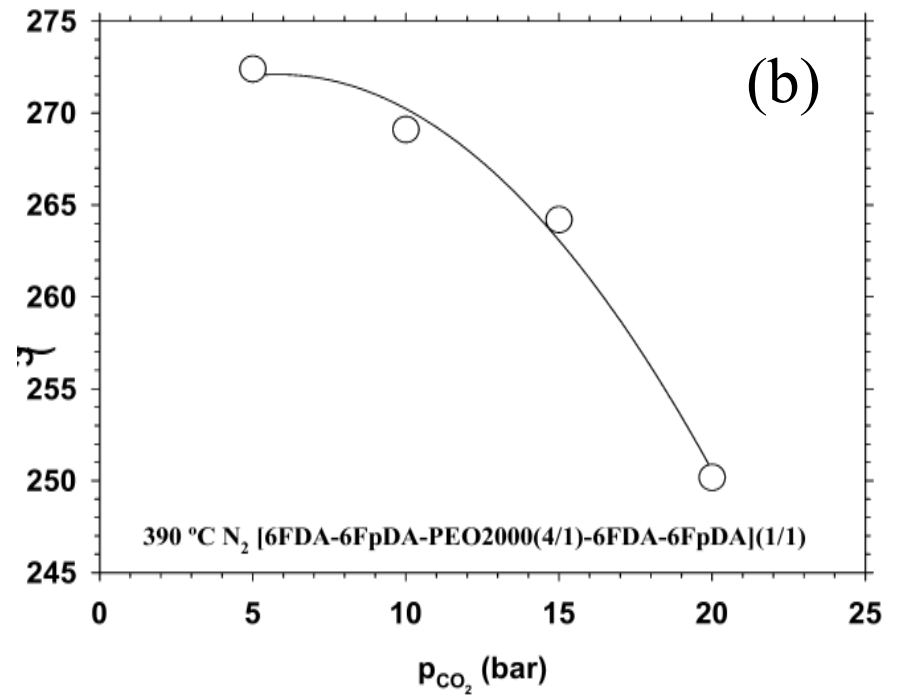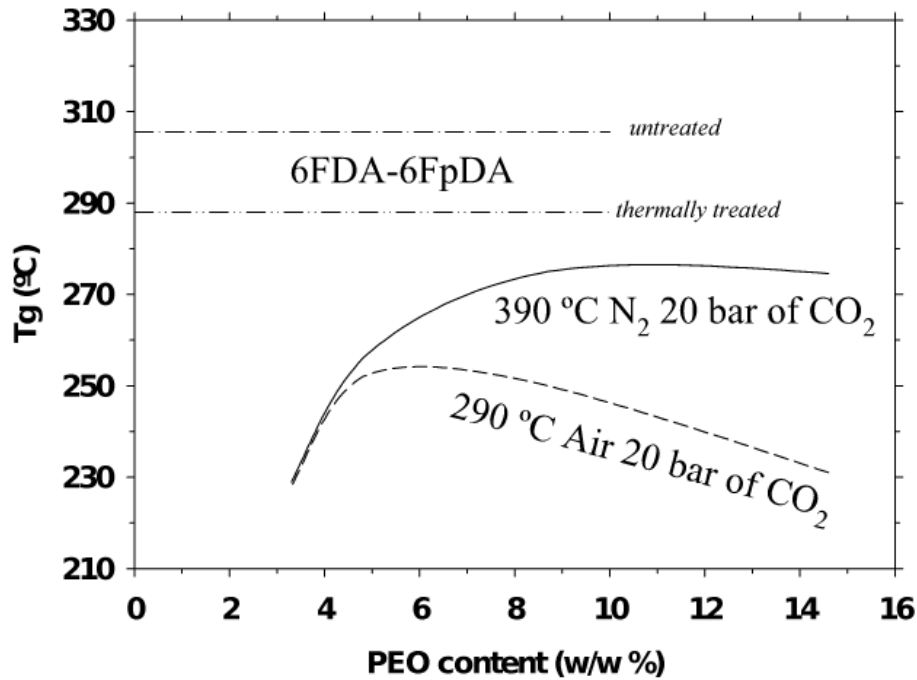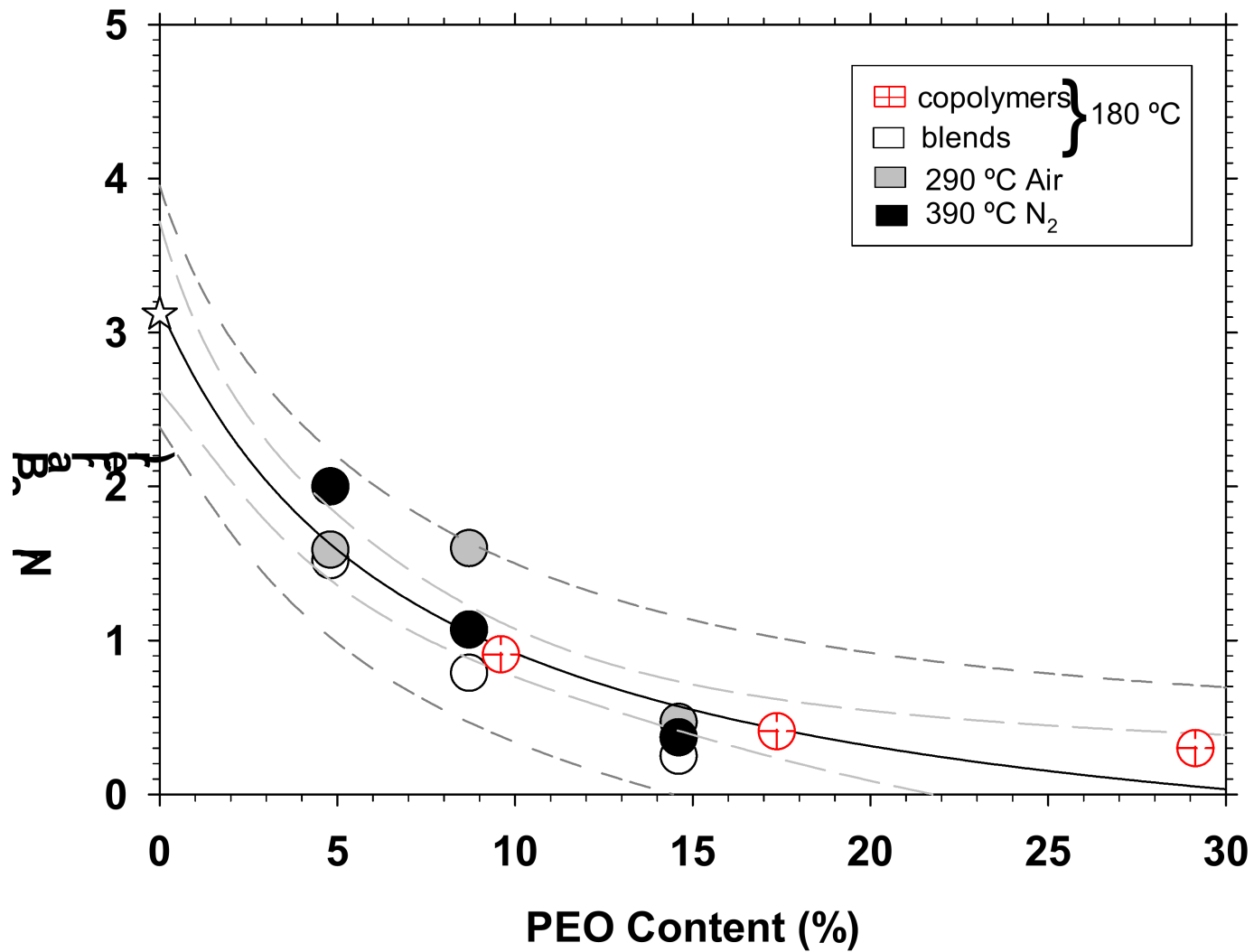*Table IV. Weight loss percentages.*

copolyetherimide 6FDA-6FpDA-PEO2000

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Fig. 5.- DSC results for Tg (after thermal treatment) as a function of the initial PEO content for 20 bar CO_2 (a) and for the [6FDA-6FpDA-PEO2000(4/1)-6FDA-6FpDA](1/1) blend treated at 390˚C in N_2 as a function of CO_2 pressure (b).

Fig. 6. N_2 permeability at 3 bar as a function of PEO percent. The star corresponds to pure 6FDA-6FpDA.

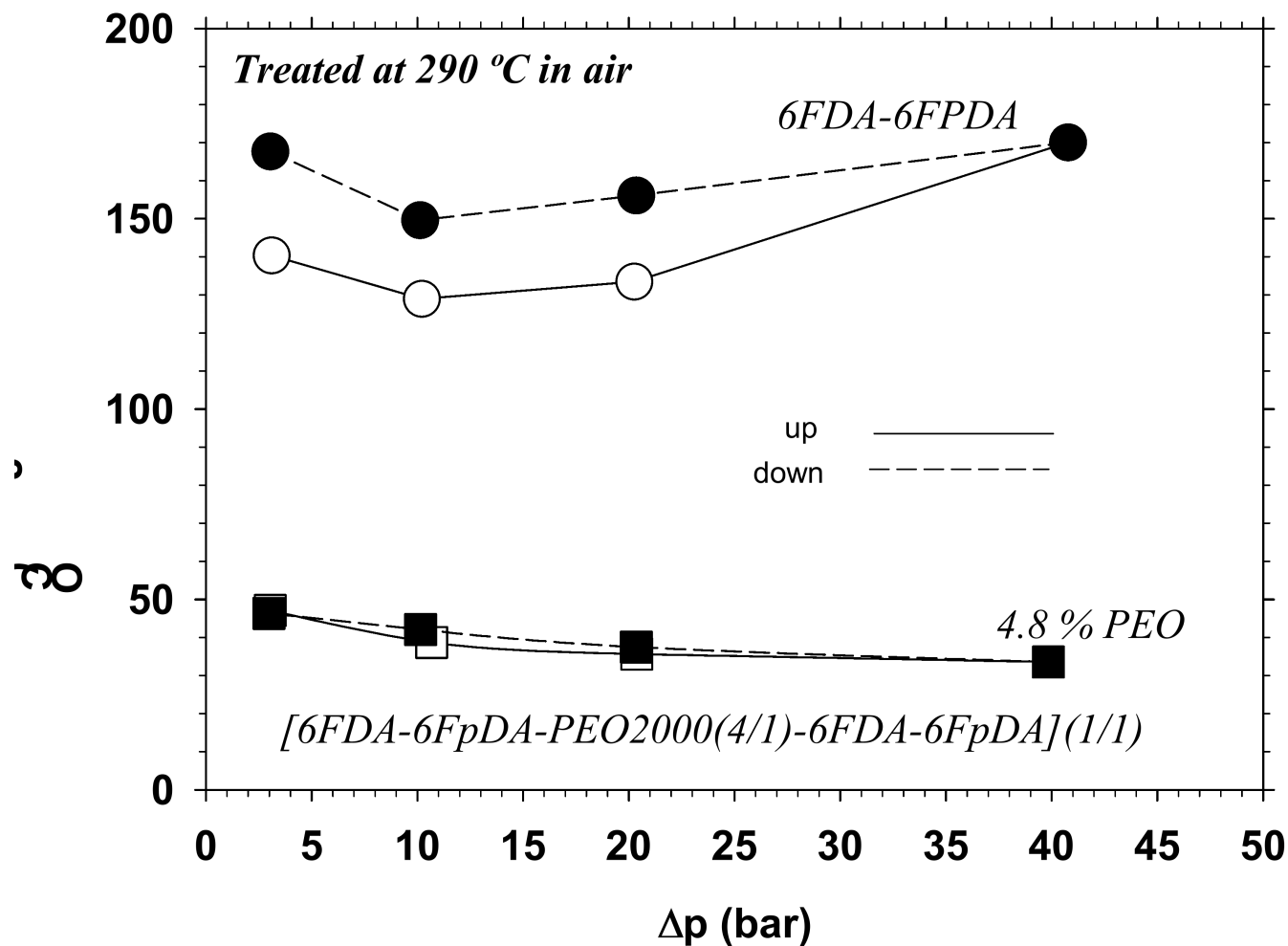Fig. 7. CO_2 permeability at 3 bar as a function of PEO percent. The star corresponds to pure 6FDA-6FpDA.

Fig. 8. CO_2/N_2 (c) selectivity at 3 bar as a function of PEO percent. The star corresponds to pure 6FDA-6FpDA..

Fig. 9. CO_2 permeability, after 3 days in a 40 bar CO2 atmosphere, as a function of pressure for the [6FDA-6FpDA-PEO2000 (4/1)-6FDA-6FpDA](1/1) (4.8 % PEO content) blend treated at 290 ºC in air as compared to that of the pure 6FDA-6FpDA (a) and as a function of PEO content at 3 bar before any CO_2 pressurization.
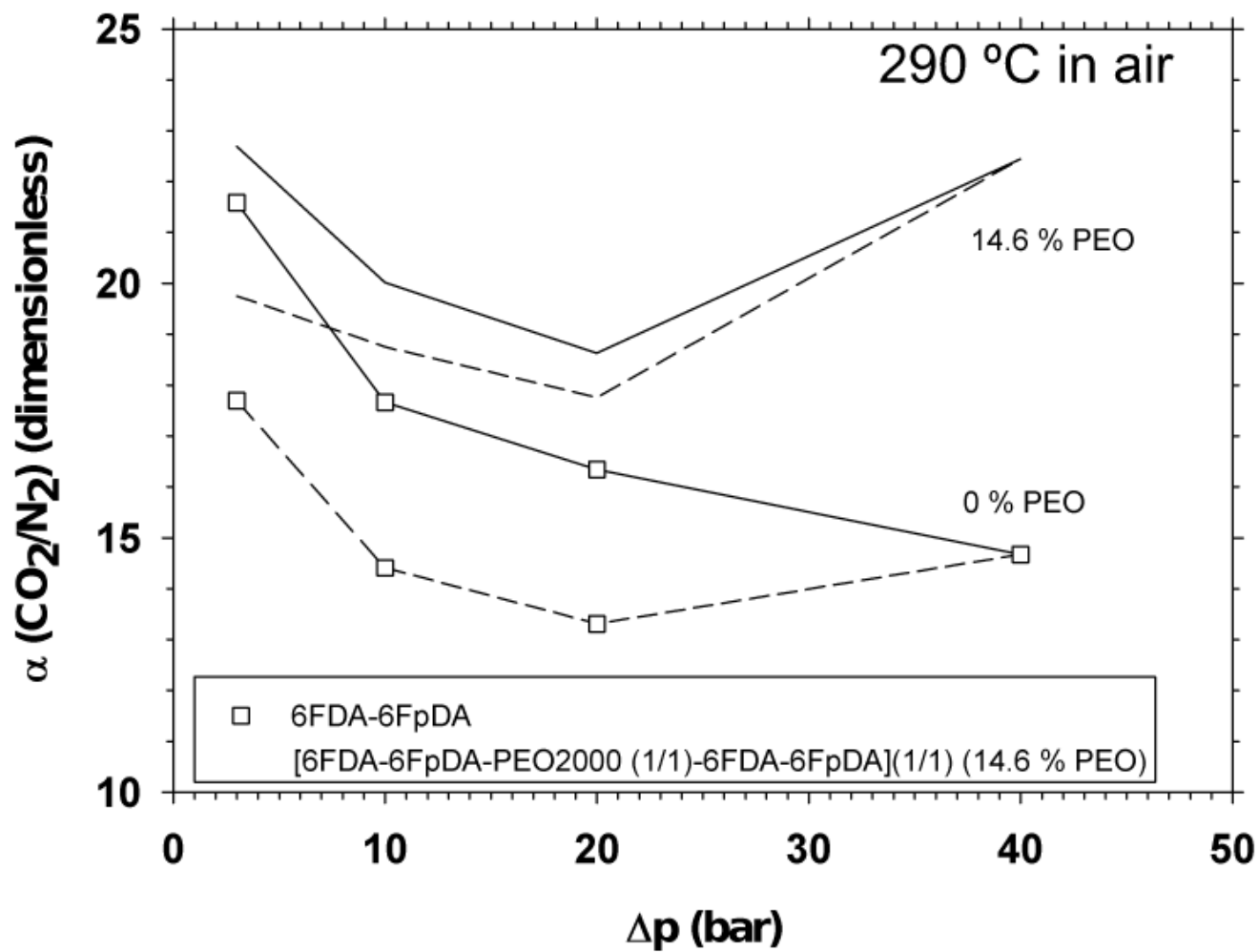
Fig. 10. CO_2/N_2 selectivity as a function of pressure for the blend [6FDA-6FpDA-PEO2000 (1/1)-6FDA-6FpDA](1/1) (14.6 % PEO content) treated at 290 ºC in air.
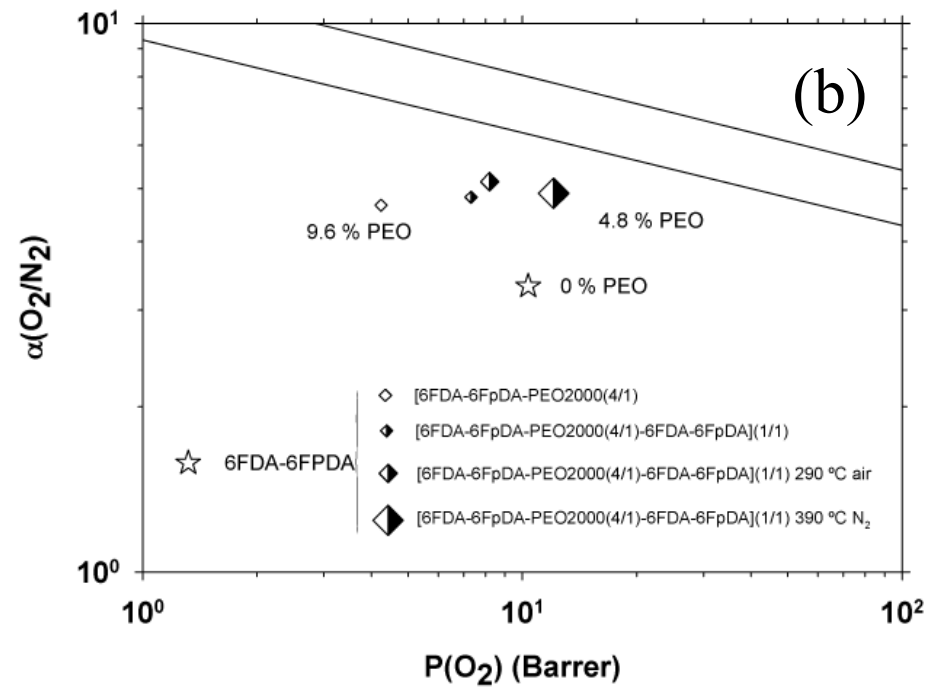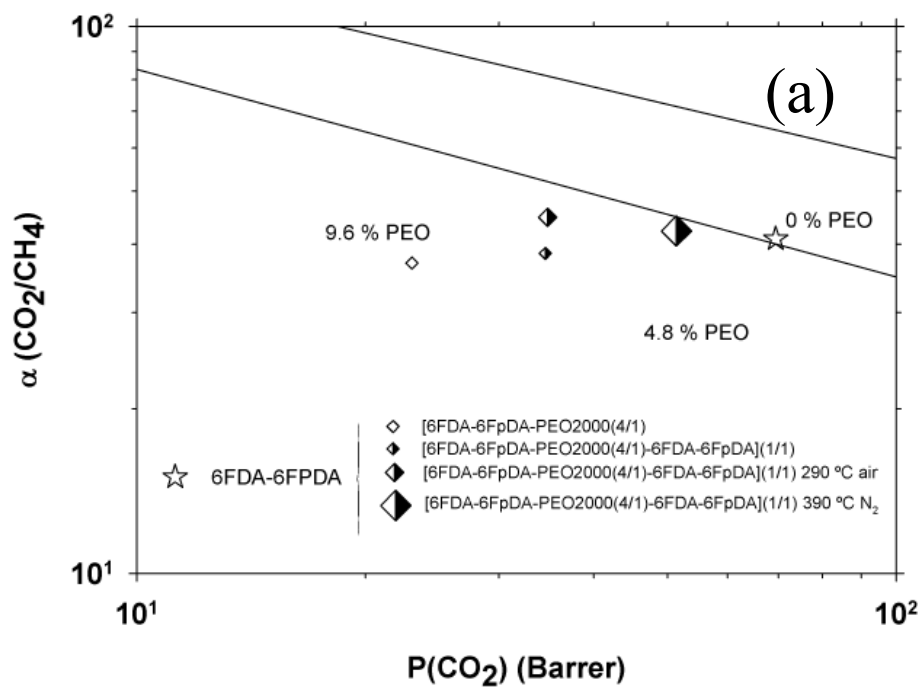
Fig. 10. Robeson plot for the pairs CO_2/CH_4 (a) and O_2/N_2 (b), for the materials and treatments shown on the figure.