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ABATEMENT OF CO₂ EMISSIONS BY MEANS OF MEMBRANES – CHARACTERIZATION OF INDUSTRIAL PEBAX™ FILMS

The present work aims at prospective use of industrially available Pebax™ resin breathable films (Arkema) as membranes for CO₂ separation from flue gas. The time-lag permeation and the microgravimetric techniques were used for the determination of the diffusion, sorption and permeation through Pebax™ 1074, 6100, 1657 and 3000 extruded films. The results indicate that the whole series of Pebax™ films is highly permeable to CO₂ with the best value for the 6100 member, with a permeability coefficient of 100 barrers. In comparison with other polymer materials, the higher Pebax™ permeability to CO₂ is due to higher values of both the sorption and the diffusion coefficients.

Keywords: *carbon dioxide, selective membrane, separation, Pebax™*

1. INTRODUCTION

Nowadays global warming and the greenhouse effect have become two of the most important problems. The principal greenhouse gas is CO₂ and the bulk of scientific research has been devoted to dealing with this source of pollution. Because most of the world's energy comes from the burning of fossil fuels, any measure directed to abating CO₂ emissions would be costly in the global economy. The fundamental question is how to do this without crucial structural changes in both human societies and natural ecosystems.

The technologies for an effective capture/sequestration of CO₂ from point sources (like power stations; about 35% of CO₂ emissions in the USA) are among various solutions proposed to control gas emissions. Classically, this can be done by scrubbing

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the flue gases with amine, in which CO₂ is absorbed. Due to the need of amine regeneration, the process requires significant energy and also chemical inputs to compensate the amine loss due to evaporation and/or formation of stable complexes with minor components in the feed. Membrane separation methods are particularly promising for CO₂ separation from flue gas due to high CO₂ selectivity, achievable fluxes and favourable process economics. Compared to absorption separation, the advantages of the membrane process are as follows:

1. It does not require a separating agent, thus no regeneration is required.
2. The systems are compact and lightweight, and can be positioned in any positions.
3. The modular design allows optimization of process arrangement by using multi-stage operation.

The commercial membranes for CO₂ separation are mainly prepared from cellulose acetate, polysulfones, and polyimides. However, these membranes primarily made for other gas processing are not optimized for flue gas separation. The selectivity of these membranes for CO₂/N₂ is generally in the range of 20 ~ 40, and the intrinsic permeability of these glassy membrane materials are lower than that of elastomers. Because of the specific features of the separation (i.e. great volumetric flow rate, low source pressure, high temperature, and a relatively low commodity value of CO₂), it would be interesting to obtain specific membranes for economical capturing of CO₂ from flue gas on a large scale.

The aim of the present work is to prospect the use of industrially available Pebax™ breathable films (Arkema) as membranes for CO₂ separation from flue gas. Pebax™ is the registered name of four series of thermoplastic elastomers made from polyamide-polyether block copolymers. Depending on the nature and the proportion of the blocks, films of different mechanical and permeation properties are obtained. They are not designed for membrane separation purposes, but high performance membranes for phenol extraction from aqueous solutions were made from members of one series, the series 33 [1]. In 1990, BLUME et al. in their patent [2] claimed that members of the other series can be used to design composite membranes of high selectivities and permeabilities to acid gases. Pebax™ block copolymers are easily processable materials of good transport and mechanical properties. Nevertheless, permeation data are scarcely available for the CO₂-selective Pebax™ materials. As far as we know, only the complete data on water transport through a Pebax™ 2533 membrane were reported by GUGLIUZZA and DRIOLI [3], and those on gases that pass through a Pebax™ 1657 membrane, by KIM and LEE [4]. In this work, we focused our attention on the Pebax™ 1074, 6100, 1657 and 3000 extruded films, the members of the Pebax™ series that would exhibit high performance in CO₂ separation from other gases.

2.2. EXPERIMENTAL

2.2.1. CHEMICALS

The breathable Pebax™ films made from polyamide-co-polyethyleneglycol series were kindly provided by Arkema Corp. Their general characteristics, as provided by the manufacturer, are given in table 1. All other chemicals were purchased from Aldrich and used without any further purification. In the Pebax™ chains, short polyamide blocks of defined length alternate with polyether blocks to make up a macromolecule of total molecular weight of ca. 50 000. The chemical structures of the polyether and polyamide blocks are presented in figure 1.

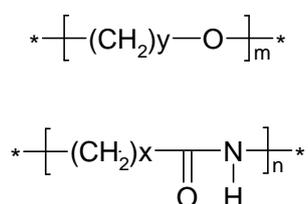


Fig. 1. Chemical structures of polyether and polyamide blocks

Table 1

General characteristics of the Pebax™ samples studied

Pebax™	Block	PA/PEG mass ratio	Shore D hardness	Density	Melting point (°C)
Pebax™ 1074	PA12/PEG	1/1	40	1.07	158
Pebax™ 6100	PA12/PEG	3/1	60	1.04	170
Pebax™ 1657	PA6/PEG	1/1	40	1.14	204
Pebax™ 3000	PA12/PEG	1/1	35	1.02	158

The polyether block is poly(ethylene oxide) ($y = 2$), while the polyamide is PA 12 ($x = 11$) for all samples, except for Pebax™ 1657 ($x = 5$). Pebax™ 3000 is made of a blend of Pebax™ 1074 with an undisclosed additive.

2.2.2. GAS PERMEATION MEASUREMENTS

Carbon dioxide and nitrogen permeation properties of Pebax™ films were determined by using the permeation apparatus shown in figure 2. Before measurement,

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the permeation cell (XX45047 Millipore filtration cell adapted for gas permeation) was completely evacuated by applying vacuum on both sides of the film for at least 1 h. Then, the upstream side was provided with the gas to be tested (CO_2 or N_2) at the pressure of p_1 (3 bar). The downstream-side pressure p_2 , that increases due to the buildup of the gas permeated through the membrane, was monitored as a function of time. p_2 in the calibrated downstream volume was thus measured using a sensitive pressure gauge (0–10 mbar, Effa AW-10-T4) linked to a data acquisition system.

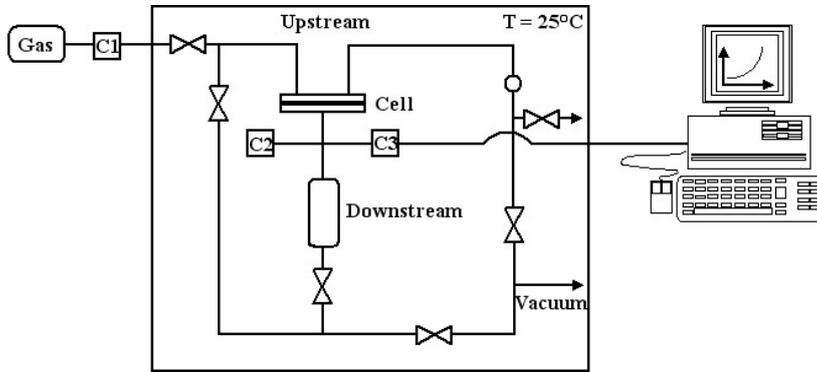


Fig. 2. Diagram of the permeation apparatus

Results allow us to plot the curve representing p_2 versus time, as illustrated in figure 3. The permeability coefficient P was calculated using the variable pressure method [5], assuming $p_1 \gg p_2$:

$$P = \frac{J_{st} \times d}{p_1}, \quad (1)$$

where d is the sample thickness and J_{st} is the steady-state gas flux obtained from the slope of the steady-state part of the curve (figure 3).

A time-lag diffusion coefficient D was calculated from the time-lag θ given by the intercept of the steady-state asymptote on the time axis (figure 3):

$$D = \frac{d^2}{6\theta}. \quad (2)$$

In this calculation, the diffusion coefficient is assumed to be time- and concentration-independent in the transient diffusion process. This is likely true for gases and elastomers.

The solubility coefficient S is given by the ratio of the permeability to the diffusion coefficient, while the selectivity coefficient α_B^A is defined by the ratio of the permeability coefficients determined for gases A and B, respectively:

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

$$\alpha_B^A = \frac{P_A}{P_B}. \quad (4)$$

In order to assess the reproducibility of data obtained for each gas, 5 measurements were carried out per Pebax™ sample.

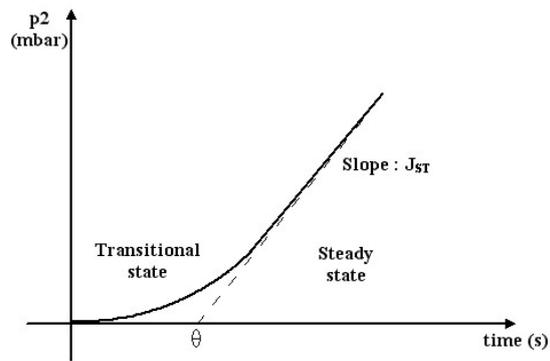


Fig. 3. Trend of the curve describing the downstream pressure versus time

The film thickness was determined by means of a Mitutoyo® micrometer. To obtain feasible values, the thickness was determined in 9 spots on each sample.

2.3.2.3. GAS SORPTION MEASUREMENTS

Sorption of carbon dioxide and nitrogen by Pebax™ films was determined and characterized by using the electronic microbalance, IGA-002, depicted in figure 4 and supplied by Hiden Analytical Ltd., Warrington (UK). After transferring the sample of the Pebax studied to the sample pan (G), the system was evacuated for about one week by a turbomolecular pump. The sample environment temperature was controlled by a sensor (H). Then the gas pressure was increased in different levels. At each step, the weight gained by the sample due to gas sorption was measured by electromagnetic compensation (E) between tare (F) and sample when the equilibrium was established.

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The cycle was completed due to step by step decrease in the gas pressure which allowed us to obtain the desorption isotherms.

The solubility coefficient was determined from the slope of the sorption isotherm. As far as the diffusion coefficient is concerned, we were not able to determine its value due to the fast sorption kinetics in these elastomers compared with the gas transport from the sorption chamber inlet to the sample.

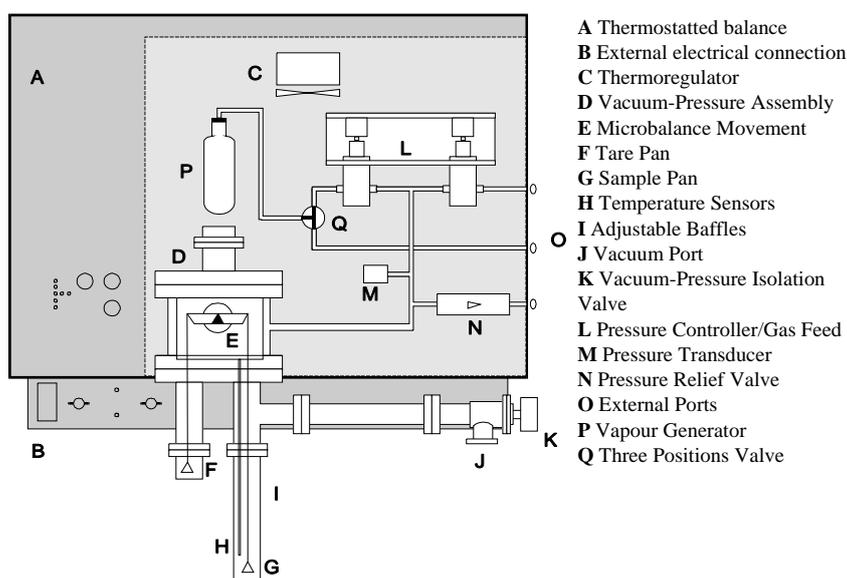


Fig. 4. Electronic microbalance set-up (IGA 002-Hiden Analytical)

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3.3. RESULTS AND DISCUSSION

3.3.1. GAS PERMEATION MEASUREMENTS

The permeation experiments were carried out with Pebax™ 1074, 6100, 1657 and 3000 extruded films at 3 bars and 25 °C. The results obtained for CO₂ and N₂ gases are summarized in tables 2 and 3.

Table 2

Gas permeability, diffusion and solubility coefficients
at 3 bars and 25 °C for various Pebax™ films

Sample	CO ₂	N ₂
Permeability coefficient (1×10^{-10} cm ³ (STP) cm/cm ² s cm Hg)		
Pebax™ 1074	25.5	0.58
Pebax™ 6100	100	2.44
Pebax™ 1657	97.9	2.04
Pebax™ 3000	45.8	2.86
Diffusion coefficient (1×10^{-7} cm ² /s)		
Pebax™ 1074	1.7	0.39
Pebax™ 6100	6.1	9.1
Pebax™ 1657	5.0	4.2
Pebax™ 3000	4.4	4.8
Solubility coefficient (1×10^{-4} cm ³ (STP)/cm ³ cm Hg)		
Pebax™ 1074	147	16
Pebax™ 6100	164	3
Pebax™ 1657	197	8
Pebax™ 3000	106	6

Table 3

Ideal selectivity coefficients at 3 bars and 25 °C
for various Pebax™ films

Sample	$\alpha_{N_2}^{CO_2}$
Pebax™ 1074	43.8
Pebax™ 6100	41.0
Pebax™ 1657	48.0
Pebax™ 3000	16.0

The Pebax™ films studied in this work seem to exhibit the properties requested. Indeed, the permeability of our membranes is in the range of 50–100 barrers which is clearly superior to those of commercial membrane materials (about 10 barrers). Moreover, the values obtained for the CO₂/N₂ selectivity, which amounts to 50, are also better than those of commercial membranes (20–40). Note that Pebax™ 3000 exhibits the lowest performances in terms of permeability and selectivity. The best Pebax™ is that consisting of the same mass fraction of PA6 and PEG (table 1). Apparently, PA6 blocks impart high CO₂/N₂ selectivity to the Pebax™ films. The well-known higher crystallinity of PA6 domains, compared with PA12 ones (due to the higher content of amide groups that promote hydrogen bonding), would lead to a peculiar phase morphology that unfavours nitrogen permeation. As supposed, high Pebax™ permeability

to CO₂ is induced by high values of solubility coefficients compared with those of N₂. Indeed, the solubility coefficients for CO₂ are superior to $100 \cdot 10^{-4} \text{ cm}^3 \text{ (STP)} \cdot \text{cm}^{-3} \cdot \text{cmHg}^{-1}$, whereas the latter for N₂ are inferior to $20 \cdot 10^{-4} \text{ cm}^3 \text{ (STP)} \cdot \text{cm}^{-3} \cdot \text{cmHg}^{-1}$. Moreover, as far as diffusion coefficients are concerned, we observe only a small difference between CO₂ and N₂, thus permeability coefficients of CO₂ are largely superior to those of N₂.

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3.2.3.2. GAS SORPTION MEASUREMENTS

The sorption experiments were carried out with Pebax™ 1074, 6100 and 1657 extruded films at 25 °C. Different gas pressures were applied, namely 200, 400, 600, 800 and 1000 mbars. The results obtained for CO₂ and N₂ gases are gathered for the three Pebax™ films in figure 5. The linear isotherms are consistent with the Henry-type mechanism of sorption which involves a simple dissolution of gas in the liquid-like elastomers.

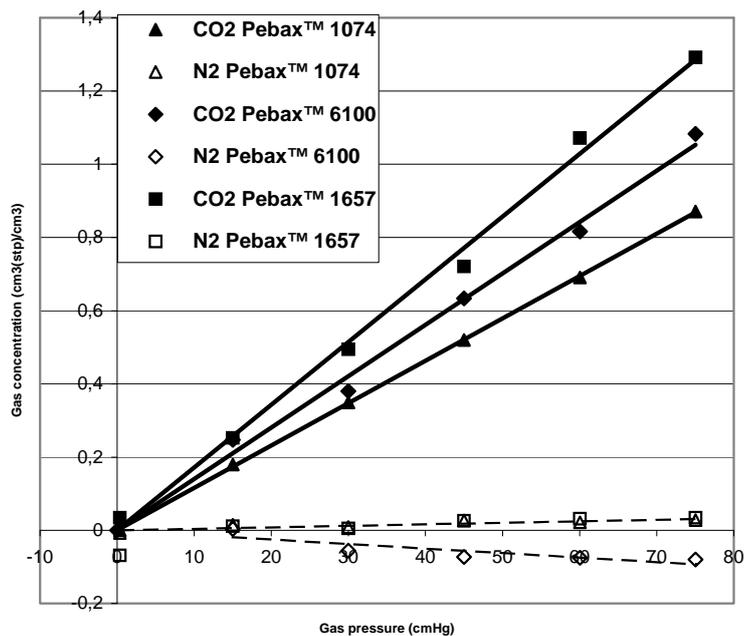


Fig. 5. Sorption isotherms

The values of the sorption isotherm slopes gave us directly the solubility coefficient values (table 4), which are pressure-independent.

Table 4

Gas solubility coefficients at a pressure in the range of 0–1 bar and 25 °C for various Pebax™ films

Sample	CO ₂	N ₂
Solubility coefficient ($1 \times 10^{-4} \text{ cm}^3 \text{ (STP)/cm}^3 \text{ cmHg}$)		
Pebax™ 1074	116	4
Pebax™ 6100	151	–
Pebax™ 1657	177	5

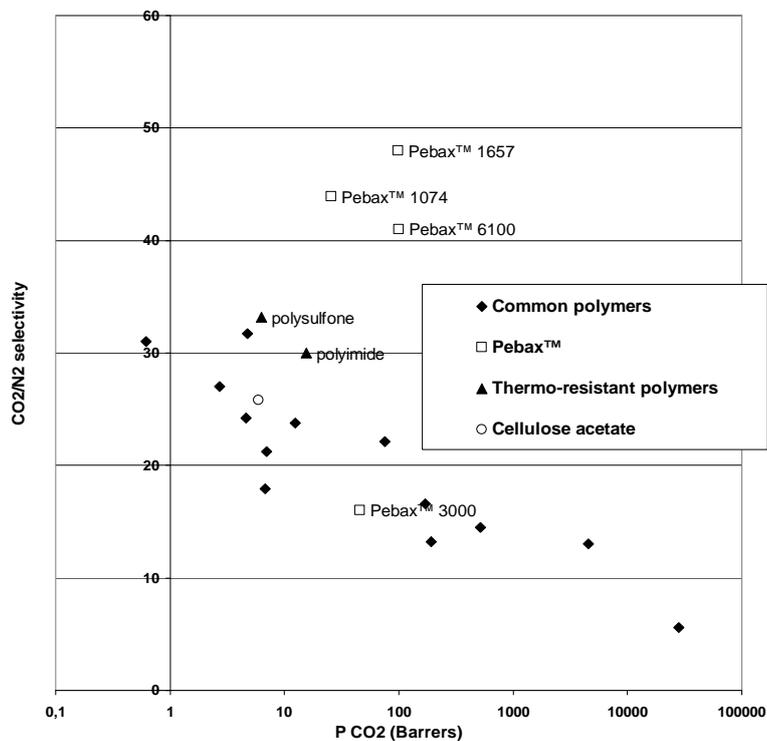
Fig. 6. CO₂/N₂ selectivity versus CO₂ permeability coefficient

Figure 5 shows clearly that all Pebax™ films sorb much more CO₂ than N₂. In fact, the amount of N₂ sorbed was close to the microbalance detection limit. This was probably the reason why we obtained a negative slope for Pebax™ 6100 in figure 5. Nevertheless, for the two other membranes, the calculated sorption coefficients are consistent with those obtained in the permeation measurements. The experimental conditions, in particular the pressure applied, are responsible for the differences in the values measured. We do not have a clear explanation for the high CO₂ sorption level in Pebax™ 1657, which has the same content of the polyether phase as Pebax™ 1074, and greater polyether content than Pebax™ 6100. Apparently, the PA phase plays also a role in the sorption mechanism. As the crystalline phase does not sorb gases, the additional sorption would occur in the interphase zones.

The CO₂ mitigation technologies currently investigated require CO₂ in a concentrated form. However, the concentration of CO₂ from large sources, such as flue gas from coal-fired power plants, approaches 15%. Therefore, the membranes should be optimized for the CO₂ capture from low-purity sources. The membranes would be even more attractive if they could resist high-temperature operations (from 100 to 400 °C) for their integration in power-generation plants and other industrial systems. Anyway, the Robeson selectivity versus permeability diagram (figure 6) that compares the performances of different polymer materials clearly shows the much higher performances of three Pebax™ membranes compared with the other common materials, including those frequently used for gas permeation membranes.

4. CONCLUSION

The Pebax™ series studied exhibit high intrinsic permeabilities due to their elastomer nature. The slightly higher CO₂ /N₂ selectivity can be attributed to a larger relative sorption of CO₂ compared with that of N₂. They are thus attractive materials for the fabrication of composite membranes with a dense Pebax™ layer of this type.

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