

ABS copolymer-activated carbon mixed matrix membranes for CO₂/CH₄ separation

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Abstract

The performance of various novel mixed matrix composite (MMC) membranes for separation of CO₂ from CH₄ was investigated as a function of carbon loading. Acrylonitrile–butadiene–styrene (ABS) copolymer was used as the polymer matrix and two micro-mesoporous activated carbons (AC) were chosen as inorganic fillers.

A thorough analysis of the effect of temperature and pressure on the permeation rates of CO₂ and CH₄ and selective properties of the ABS-AC composite membranes was done. Measurements were made for each system at four different temperatures in the range 20–50 °C, and in the feed pressure range from 2 to 8 × 10⁵ Pa. The ABS-AC membranes showed a simultaneous increase of CO₂ gas permeabilities (40–600%) and CO₂/CH₄ selectivities (40–100%) over the intrinsic ABS permselectivity by increasing the percentage of carbon loaded in the mixed matrix composite membrane.

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1. Introduction

The permanent challenge in membrane technology is to improve the existent membrane processes, as well as to extend the range of application of this technology. There is a high number of opportunities to extend membrane markets for gas separations, however, the existing membrane materials, membrane structures, and synthesis processes are inadequate to fully exploit these opportunities. Therefore, much of the research work is being devoted to the proposal of new membrane materials and the development of new membrane structures that exhibit both a higher selectivity and intrinsic permeability to specific gases.

In particular in the past two-decade, two types of materials have extensively been studied in terms of their high performance in presence of aggressive agents. These two classes are: cross-linked polymers and the mixed matrix materials

[1]. The mixed matrix composite membranes, constituted by two interpenetrating matrices of different materials, offer the potential of combining the polymers processability with superior gas separation properties of rigid molecular sieving materials. The successful implementation of this membrane development lies on both, the selection of polymeric matrix and inorganic filler, and the elimination of interfacial defects.

Pioneer works related with the improvement of these membrane materials have been carried out by some authors [2–5]. It has been generally observed that when using rubbery polymers as membrane matrix there exist an adequate contact between the disperse phase of the molecular sieve and the polymeric phase. However, the high gas fluxes of these polymeric rubber matrixes can lead to low improvement in the mixed matrix membrane selectivity. According to Paul and Kemp [2], the incorporation of zeolite 5 A into silicone rubber did not improve the separation properties of the polymer. In their patent, Kulprathipanja et al. [3], have reported O₂–N₂ gas permeation in composite membranes

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made from silicalite-1 as filler and cellulose acetate as polymer matrix. They found an increase on O₂/N₂ separation factor (from 2.99 to 4.06) by increasing the silicalite content. Jia et al. [6] also found that the silicalite filled silicone rubber (PDMS) membranes possess higher O₂ permeabilities (from 571 to 655 barrer) and O₂/N₂ selectivities (from 2.14 to 2.92) than unfilled membrane. Duval et al. [7] prepared carbon molecular sieves and zeolite filled membranes. Their results showed that zeolites such as silicalite-1, 13X and KY improve, to a large extent, the separation properties of otherwise poorly selective rubbery polymers towards a mixture of CO₂/CH₄ while the carbon molecular sieves did not improve the separation performance.

The adhesion between the polymer phase and the external surface of the particles appeared to be a major problem when glassy polymers are used in the preparation of such membranes. It seems that the weak polymer–filler interaction makes the filler tend to form voids in the interface between the polymer and the filler. Various techniques have been employed to improve the polymer–filler contact. For example Duval et al. [8] in their preparation of zeolite filled glassy polymer membranes, found a poor adhesion between the polymer phase and the external surface of the particles. To overcome this problem various methods were investigated to improve the internal membrane structure, such as, surface modification of the zeolite external surface, preparation above the glass transition temperature and heat treatment.

Interesting performance results in mixed matrix membranes of polyethersulfone and hydrophilic zeolites 13X and 4A have been obtained by Sürer et al. [9]. For both zeolitic additives, gas permeabilities (N₂, O₂, Ar, CO₂, H₂) and selectivities are enhanced by increasing zeolite loadings. High amount of zeolite induces formation of microporous cavities and channelling, demonstrating the weak interactions and incompatibility of these materials. Vankelecom et al. [10] investigated the incorporation of zeolites in polyimide (PI) membranes. The preparation method employed in their composite membranes induces an anisotropic structure in the membrane with a weak adhesion between the PI matrix and the zeolite filler. As a tool to improve zeolite incorporation in polyimide films, silylation of the zeolite outer surface has been made [11], with non-appreciable improvement of the polymer–filler contact. Zimmerman et al. [12] and Mahajan et al. [13,14] proposed some material selection criteria and preparation protocols in order to match the necessary transport characteristics of materials to form high performance mixed matrix materials for gas separation.

Among those works related with addition of carbon molecular sieves to polymeric matrices, it is worthy to note the recent work of Vu et al. [15]. They have prepared mixed matrix membranes by using carbon molecular sieve particles as the selective inorganic filler. The CMS was incorporated into two continuous commercial glassy polymer matrices: Ultem[®] 1000 (a polyetherimide) and Matrimid[®] 5218 (a polyimide). These CMS mixed matrix membranes

exhibited excellent polymer–filler contact and a remarkable higher performance compared with those of the intrinsic polymer matrix. For example, pure gas permeation test in Ultem[®]-CMS and Matrimid[®]-CMS mixed matrix membranes, showed enhancements by up to 40–45%, respectively in CO₂/CH₄ selectivity over the intrinsic selectivity of the pure Ultem[®] and Matrimid[®] polymer matrices.

The present work proposes an alternative preparation of mixed membranes for CO₂/CH₄ separation by using inorganic filler materials that differ substantially from those molecular sieves normally used. The employed materials were two micro-mesoporous activated carbons, having different adsorptive capacity for polar and unsaturated compounds (i.e. CO₂, olefins) with respect to non-polar and saturated ones (i.e. CH₄, paraffin) [16–18]. As polymeric material, ABS copolymer that combines adequate selectivity properties of a glassy polymer with rubber high permeabilities [19], was selected. CO₂–CH₄ system was chosen for separation due to the importance of their commercial use and purification. To have proper comparison of CO₂–CH₄ permselectivities with previous results on pure ABS [19], our permeation and separation experiences with mixed matrix ABS-carbon membranes were performed in the temperature range 293–323 K and upstream pressures from 2×10^5 to 8×10^5 Pa. It had been demonstrated that under these experimental conditions the effect of plasticization appears to be negligible for CO₂/ABS system [19].

2. Experimental

2.1. Materials

2.1.1. Polymer characteristics

ABS copolymer Lustran[®] 246 provided by Bayer (Argentina) was used as continuous phase of the mixed matrix membranes. Its glass transition temperature of 110 °C and its approximate chemical composition (60% styrene, 27% acrylonitrile and 13% butadiene) was determined elsewhere [19]. It was found that pure CO₂ and CH₄ permeabilities (P_i) and selectivities ($\alpha_{\text{CO}_2/\text{CH}_4}$) at different temperatures could be predicted from:

$$P_{\text{CO}_2} \text{ (barrer)} = 6.1 \times 10^2 \exp(-1570/T) \quad (1)$$

$$P_{\text{CH}_4} \text{ (barrer)} = 9.96 \times 10^3 \exp(-3320/T) \quad (2)$$

$$\alpha_{\text{CO}_2/\text{CH}_4} = 6.12 \times 10^{-2} \exp(1750/T) \quad (3)$$

Eqs. (1)–(3) are valid within the pressure range of $2\text{--}10 \times 10^5$ Pa and temperature range of 293–323 K. The ABS density was $\rho_c = 1.05 \text{ g/cm}^3$.

2.1.2. Inorganic filler analysis

Two different activated carbons (AC) were used as inorganic dispersed phase. The Maxsorb carbon (AC1), a powder with high surface area, was purchased from The Kansai

Coke & Chemical Co. Ltd. (Japan). The other filler, a commercial active carbon (AC2), was provided by Merk (Germany).

Physical properties: The structural characteristics of the activated carbons were determined by the sorption technique. Nitrogen adsorption isotherms at 77 K were obtained by using a Micromeritics ASAP 2010 instrument. The mean particle size of both carbons was visualized by optical microscope (NanoScope[®] model OMV-PAL) and the image analysis was made with a Jandel[®] ScanPro software.

Gas adsorption: The adsorptive capacity of activated carbons to pure CO₂ and CH₄ gases were determined. Equilibrium sorption of pure gas by AC was measured by the pressure decay method [19]. The equipment consists basically of two chambers A and B, with well-known volumes, separated by a valve. The powder carbon sample was placed in the adsorption cell B and the gas under study was laid up to the chamber A at the desired pressure. After this, the valve was opened for a short time to allow gas to flow into the sample chamber. Sorption isotherms were measured by using interval experiments, with increasing gas pressures. After equilibrium conditions were reached, the amount of gas adsorbed (n_i) was calculated from the difference between the initial (p_i) and final pressure (p_e) in the sample chamber using the ideal gas law, as:

$$n_i = \frac{(p_i - p_e)V_1}{R_g T} \quad (4)$$

where V_1 is the free volume of adsorption cell, and R_g the gas constant.

Pure CO₂ and CH₄ gases were obtained from Air Liquid (Argentina) and had a specified purity of 99.99%.

2.2. Preparation of mixed matrix membranes

The ABS-AC mixed matrix membranes were prepared by the following method:

- First an ABS polymer solution was prepared by dissolving 12% (w/v) of ABS in Cl₂CH₂ solvent, stirring continuously with a magnetic bar during 4 h at 298 K.
- The Erlenmeyer glass containing the ABS solution was introduced in an ultrasonic bath. Then, the corresponding amount of activated carbon was gently added to the ABS solution under mechanical stirring and sonication at ambient temperature (298 K) during 1 h. Sonication and stirring enhance the homogeneous distribution of the carbon particles in the polymer solution decreasing the formation of carbon agglomerates.
- The amount of carbon charged to the polymeric solution was between 2 and 10% (w/w) (carbon/polymer) for AC1 and 20–40% (w/w) for AC2. Composite mixed matrix membranes presenting fissures and poor mechanical properties were obtained when higher amounts of carbon were used.

- The mixed ABS-carbon solution obtained was filtered with a sieve filter (mesh #400), which allows to retain carbon agglomerates bigger than 20 μm. To determine the total amount of carbon remaining in the filtered mixed solution, the carbon deposited in the sieve was washed with Cl₂CH₂, dried under vacuum at 373 K and weighed.
- Finally, composite mixed matrix membranes were prepared from the ABS-carbon mixed solution by the casting–evaporation process. Casting was performed at 298 K in air (relative humidity of 45%) using a film extensor at a designated thickness (400 μm) onto a glass plate. Evaporation was carried out at 353 K under vacuum during 48 h to remove any residual solvent. The thicknesses of the resulting membranes were measured with a Köfer micrometer (precision ± 1 μm). Membrane thicknesses were obtained from the average of at least 30 measurements on a membrane surface of 12 cm².

The physical characteristics of the prepared mixed matrix membranes are given in Table 1, in which the filler volume fraction (ϕ_f) has been calculated from:

$$\phi_f = \frac{V_f}{V_f + V_p} = \frac{m_f}{m_f + m_p(\rho_f/\rho_p)} \quad (5)$$

where V_f , ρ_f , V_p and ρ_p are the volume and density of the carbon and polymer (ABS), respectively.

2.3. Characterization of mixed matrix membranes

2.3.1. Morphological characterization

To investigate the morphology of composite ABS-AC membranes with different carbon percentages, electron micrographs were obtained by an environmental scanning electron microscope Philips XL30 ESEM. The ABS-AC films were fractured in liquid nitrogen and mounted on sample holder. SEM images were examined using an accelerating voltage of 15 kV.

2.3.2. Gas permeability measurements

The permeability of pure CO₂ and CH₄ gases was measured by using a classical time lag apparatus. The effective membrane area was 11.34 cm² and permeate constant volume was 36.4 cm³. The amount of gas transmitted at time

Table 1
Some physical characteristics of the ABS-AC membranes

Activated carbon	ABS-AC membrane	% AC (w/v)	Filler volume fraction (ϕ_f)	Thickness (μm)
AC1	M02	2	0.074	76.5
	M05	5	0.166	103
	M07	7	0.240	97.2
	M10	10	0.290	122
AC2	M20	20	0.388	84.63
	M25	25	0.456	88.45
	M33	33	0.552	80.09
	M40	40	0.624	85.04

t through the ABS membrane was calculated from the permeate pressure (p_2) readings in the low-pressure side. The inherent leak rate in the downstream side determined after evacuating the system was measured for each experimental run. Permeability constants (P) were obtained directly from the flow rate into the downstream volume upon reaching the steady state as:

$$P = \frac{B\ell}{T_c p_1} \frac{dp_2}{dt} \quad (6)$$

where the cell constant $B = 11.53 \text{ (cm}^3 \text{ (STP) K) / (cm}^2 \text{ cmHg)}$; dp_2/dt in cmHg/s; high-pressure side p_1 in cmHg; membrane thickness ℓ in cm.

3. Results and discussions

3.1. Active carbon properties

3.1.1. Structural characteristics

Two different methods were used to obtain the relevant carbon characteristics from the N_2 adsorption experimental results, i.e. the BET equation and density functional theory (DFT). Even though the BET equation is not applicable to micropores and overestimates the surface area, it is measured because it is generally used. The DFT method is being used increasingly for the description of adsorption in micropores and is considered to be the best available approximation. We have used the DFT method (a standard method included in the software package of the volumetric ASAP 2010 equipment), assuming slit pore geometry, to obtain the pore width (d_p) distributions for both samples. These are shown in Fig. 1 where the distributions have been determined from the pore volume. It is observed that AC1 mainly has a micropore structure ($7 < d_p < 30 \text{ \AA}$), whereas AC2 shows a micro-mesoporous structure ($7 < d_p < 400 \text{ \AA}$). The relevant characteristic data for the two carbons are listed in Table 2.

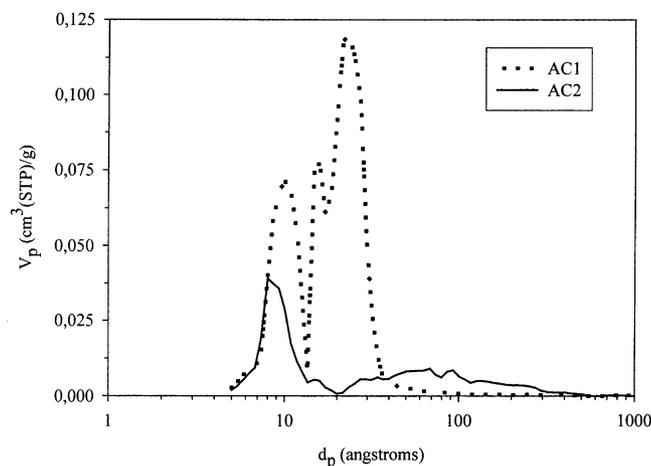


Fig. 1. Pore size distributions for AC1 and AC2 obtained by the DFT method.

Table 2

Activated carbon characteristics

Property	AC1	AC2
Surface area (BET), S_w (m^2/g)	3272	818
Monolayer capacity (BET), V_m ($\text{cm}^3(\text{STP})/\text{g}$)	752	188
Surface area (DFT), S'_w (m^2/g)	1850	635
Apparent density, ρ_f (g/cm^3)	0.28	0.42
Mean pore width size, d_p (\AA)	21.7	28.2
Mean particle size, σ (μm)	0.90	4.47

As it can be seen the AC1 surface area and monolayer capacity are practically four times higher than that of AC2.

Fig. 2 shows the normalized particle size distributions of activated carbons. This distribution was obtained after sweeping a thicker layer of powder scattered on the sample holder. Image analysis of the particle size (σ) indicates that AC1 carbon has a narrower particle size distribution (σ between 0.2 and 20 μm) with a distribution centred at lower values than the AC2 sample (σ between 0.2 and 100 μm). The minimum observable particle size (0.2 μm) was delimited by the microscope resolution. The presence of high particle sizes ($>0.2\text{--}0.3 \mu\text{m}$) may possibly be caused by some kind of interaction between the original carbon particles, which in turns produces carbon agglomeration. This assumption is reinforced by the fact that, when a thicker layer of powder is observed through the microscope, much bigger particle sizes are found. Table 2 summarizes the particle mean size for the AC powders.

3.1.2. Gas adsorption properties

Sorption measurements on activated carbons were made for each gas in the temperature range of 293–323 K and equilibrium pressures between 2 and $8 \times 10^5 \text{ Pa}$. Figs. 3 and 4 show the representative adsorption isotherms for CO_2 and CH_4 , respectively, where the normalized molar concentration of adsorbed molecules or surface adsorbed concen-

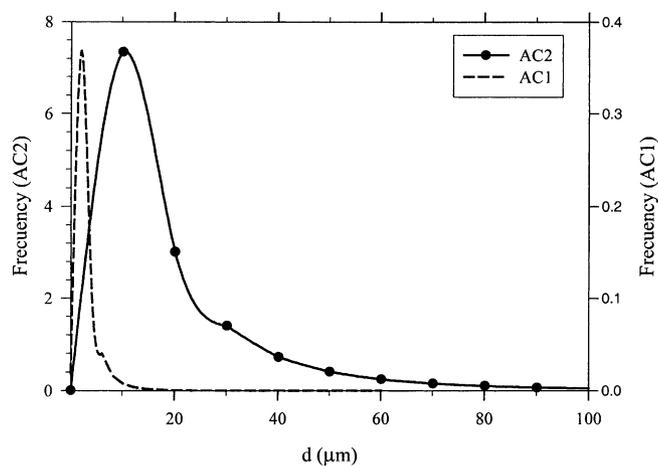
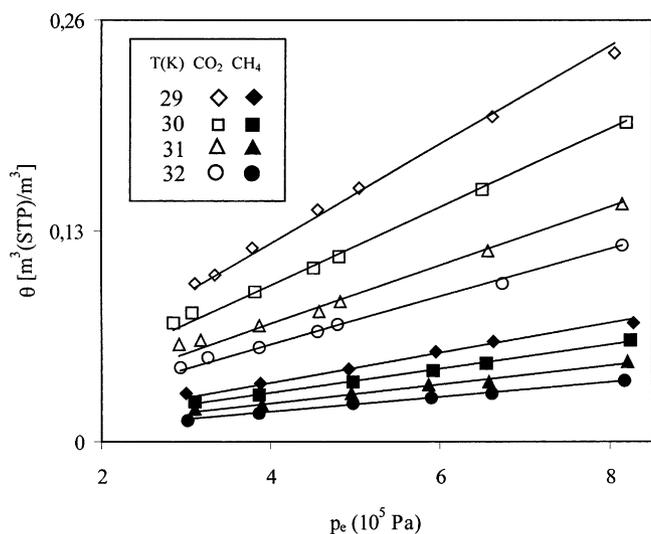


Fig. 2. Particle size distribution for AC1 and AC2 from optical microscopy imaging.

Fig. 3. CO₂ and CH₄ adsorption isotherms for AC1 carbon.

tration (θ) in STP conditions has been calculated from:

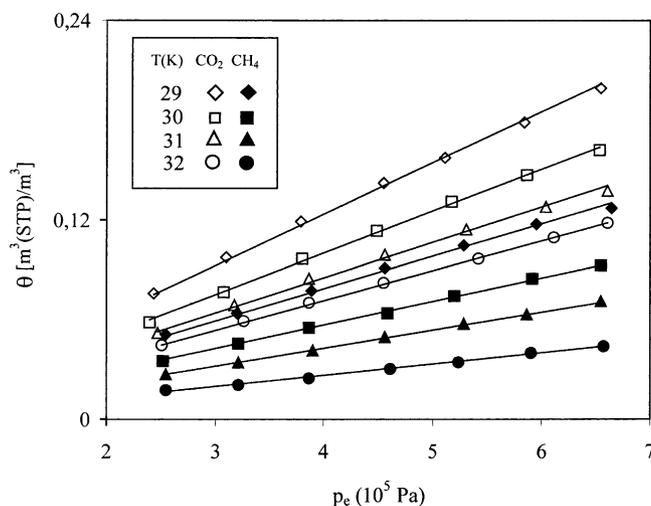
$$\theta = 22.4 \frac{n_i}{m_s V_m} \times 10^3 \quad (7)$$

m_s being the amount of carbon (g) charged to the cell. These isotherms are practically linear in the whole range of pressure and temperature studied. Thus the total concentration of adsorbed gas (θ) can be describe by the Henry's law:

$$\theta = Kp \quad (8)$$

where K is the gas–solid partition coefficient. K parameters as calculated by fitting the straight lines of θ versus p are summarized in Table 3.

From these results it can be observed the typical adsorption behavior of gas on the solid surface, that is, the amount of adsorbed gas increases with gas pressure and decreases for increasing temperatures. The selective gas capacity of carbon adsorption for two different gases can be related to

Fig. 4. CO₂ and CH₄ adsorption isotherms for AC2 carbon.Table 3
Gas–solid partition and selectivity coefficients for adsorption

T (K)	K ($\times 10^7$ m ³ (STP)/m ³ Pa)				α^a ($K_{\text{CO}_2}/K_{\text{CH}_4}$)	
	CA1		CA2		CA1	CA2
	CO ₂	CH ₄	CO ₂	CH ₄		
293	3.057	0.914	3.077	1.960	3.35	1.57
303	2.417	0.752	2.505	1.420	3.21	1.76
313	1.821	0.593	2.125	1.078	3.07	1.97
323	1.490	0.462	1.792	0.662	3.22	2.71

the selective adsorption coefficient (α^a) by:

$$\alpha^a_{(\text{CO}_2-\text{CH}_4)} = \frac{K_{\text{CO}_2}}{K_{\text{CH}_4}} \quad (9)$$

The selective adsorption coefficients calculated (Table 3) show clearly that activated carbons have a higher adsorption selectivity for CO₂ (polar gas) than for CH₄ (non-polar compound). In effect, AC1 is 3–3.5 times more selective for CO₂ adsorption than CH₄, whereas AC2 is 1.6–2.7 times more selective.

3.2. Mixed matrix membrane properties

3.2.1. Morphological and structural characteristics

Fig. 5 shows representative SEM images of ABS-AC1 cross-section films. These micrographs reveal clusters of AC1 carbon of different sizes randomly distributed into the polymeric matrix, where there exists a tight interfacial contact between the polymeric and filler phases. The sizes of the observable clusters, referred as their sphere diameter, are between 3 and 30 μm . Although there exist smaller particles, due to the low polymer-carbon phase contrast they cannot be clearly detected by this technique.

SEM images of ABS-AC2 membranes are shown in Fig. 6. When the AC2 concentration was 25% p/p or less (Fig. 6a) the mixed matrix membrane had similar morphology than ABS-AC1 membranes, with AC2 observable clusters between 3 and 20 μm . As the filler content increases, a more homogeneous distribution of AC2 clusters in the matrix is observed (Fig. 6b). Figures show that when AC2 concentration is 33% p/p or higher, the carbon clusters create holes like porous structures in the polymeric matrix in which they fit. On the other hand, Fig. 6b indicates that the increase in the volume fraction occupied by the filler may produce both a contact between the carbon clusters and void spaces around the carbon agglomerates. The possible channel formation will produce an increase in the gas permeability with a decrease in the membrane selectivity. This will be discussed in the next section dealing with the permeability data of pure gases in the composite films.

Fig. 7 shows pictures of the top surface (exposed to air during casting process) for the M10 and M33 membranes. In all cases these pictures show high roughness increasing as more carbon is added to the polymeric matrix. The bottom surface (contacting glass during casting process) is always

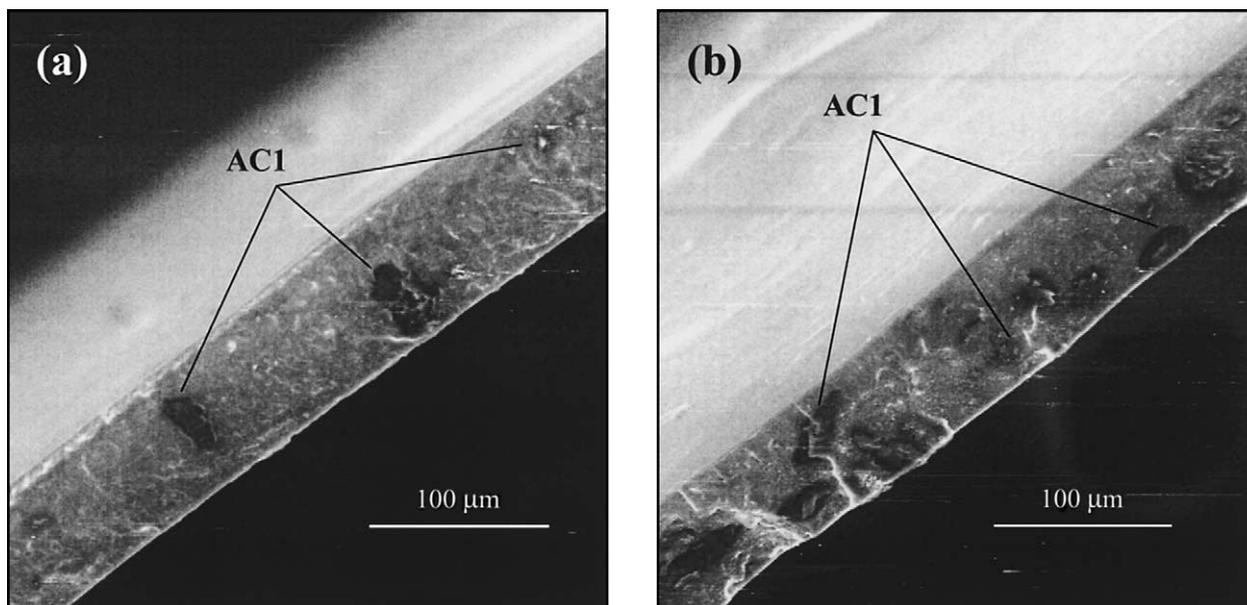


Fig. 5. SEM micrographs of the cross-section of mixed matrix membranes. (a) M02, (b) M07.

smoother than the top face. For both faces of the membranes, the polymeric phase appear as continuous and nonporous.

It seems clear that addition of activated carbon particles lead to a random agglomeration. The polymeric matrix nevertheless, always covers these agglomerates. The underlying activated carbon should explain the differences found in big scale roughness.

3.2.2. Gas permeability and selectivity properties

As mentioned, transport parameters for single gases were calculated from permeation experiments by the time lag method. Measurements were made for each system at four

different temperatures in the range 293–323 K, and in the feed pressure range from 2 to 8×10^5 Pa. The representative calculated permeability values for CO₂ and CH₄ at 293 and 323 K are presented in Figs. 8 and 9 in which the permeability data of ABS copolymer has been calculated from Eqs. (1) and (2). The same gas permeability–pressure behavior was observed for all gas–MMC systems and temperature analyzed. From these results it is evident that the upstream gas pressure or gas concentration in the range proposed has no significant effect on the gas permeability.

Table 4 summarizes the average values of pure gas permeability P over the experimental gas pressure range studied

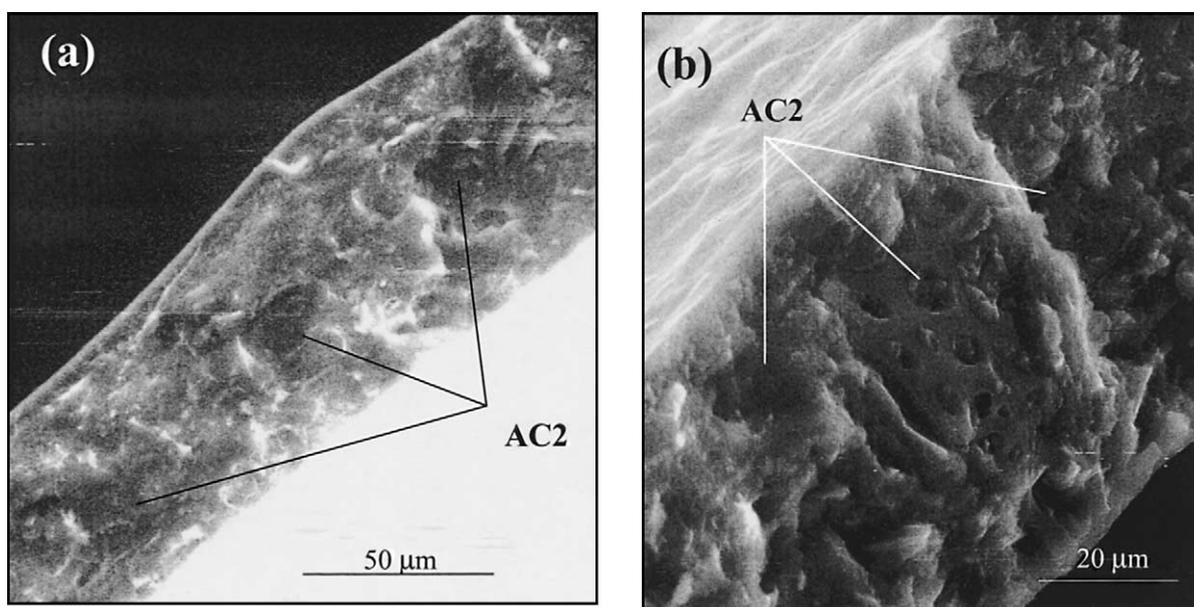


Fig. 6. SEM micrographs of the cross-section of mixed matrix membranes. (a) M25, (b) M33.

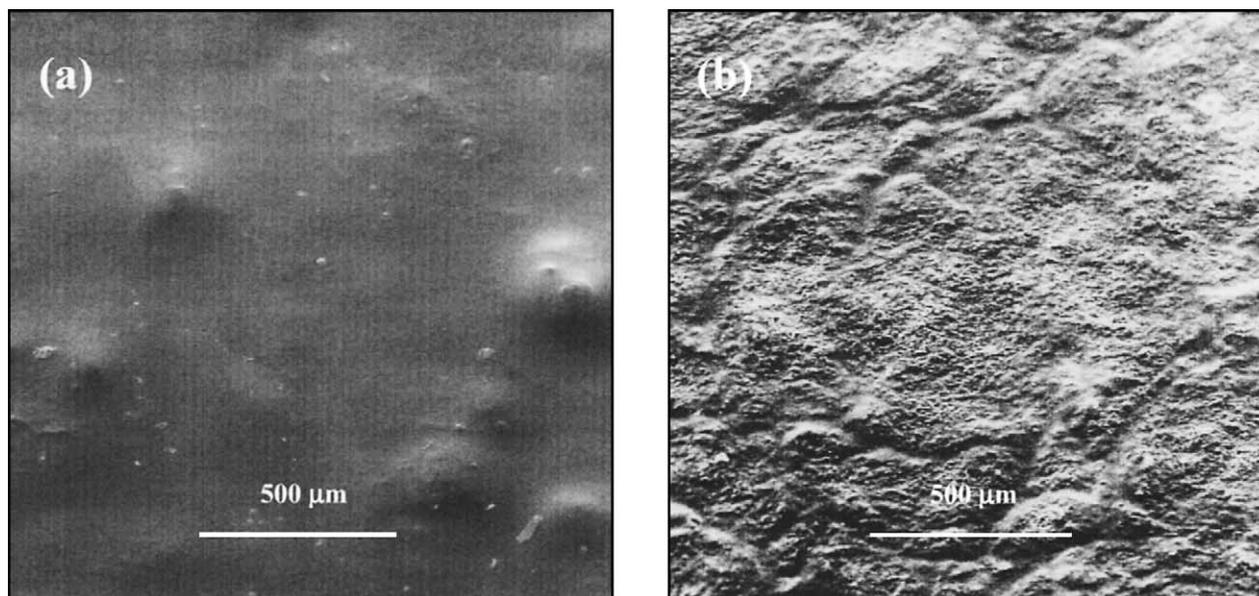


Fig. 7. SEM micrographs of the top surfaces of mixed matrix membranes. (a) M10, (b) M33.

at different temperatures and AC loaded in the composite membranes. The results reveal an increment on the gas permeability with the amount of carbon charged to the MMC membrane and the general trend in which gas permeation rate is enhanced with increasing temperature. The high increment on the gas permeabilities of the mixed matrix membranes over the pure ABS matrix (1.4–7.1 times higher) with increasing carbon loading can be in part attributed to the gas flux through the pores of the carbon particles.

The ideal separation factors (α) for CO_2/CH_4 through the ABS-AC mixed matrix membranes were evaluated from the average permeability data of Table 4 as:

$$\alpha_{(\text{CO}_2-\text{CH}_4)} = \frac{P_{\text{CO}_2}}{P_{\text{CH}_4}} \quad (10)$$

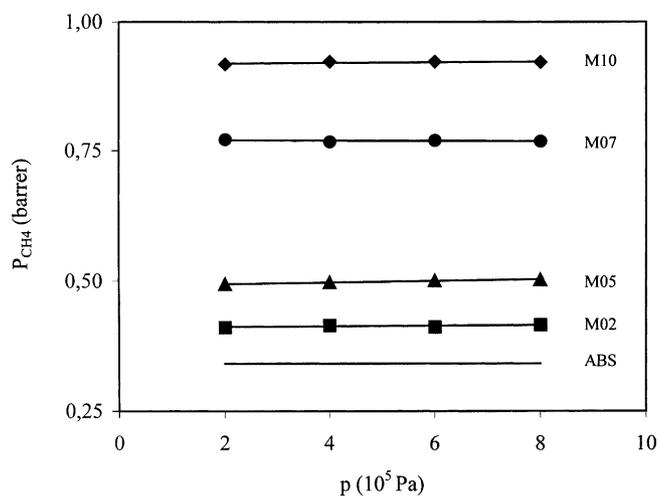


Fig. 8. Effect of the upstream pressure on CH_4 permeabilities for the ABS-AC1 membranes at 323 K.

Figs. 10 and 11 show the relative effects of both the temperature and the amount of AC loaded on ideal separation factor. It is seen in these figures, the ABS-AC membranes show interesting CO_2-CH_4 permselectivities, 1.45–2.1 times higher than the pure ABS membrane. There is a simultaneous increase of gas permeabilities and selectivities by increasing the percentage of carbon loaded in the MMC membranes. The increasing selectivities with increasing AC content can not be due to a molecular sieving mechanism since the mean pore size of both dispersed phases (21.7 and 28.2 Å) are bigger than the molecular diameters of the permeate gases ($d_{(\text{CO}_2)} \cong 4.5 \text{ \AA}$; $d_{(\text{CH}_4)} \cong 3.9 \text{ \AA}$). Also, these high selectivities can not be attributed to a Knudsen mechanism as far as the CO_2 molecular weight is higher

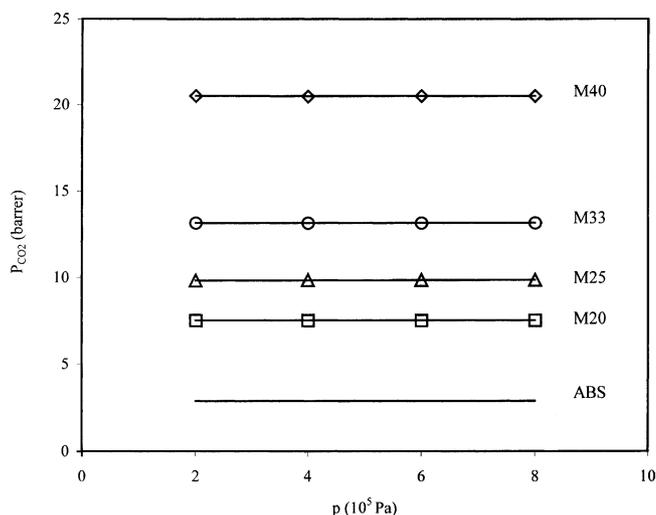


Fig. 9. Effect of the upstream pressure on CO_2 permeabilities for the ABS-AC2 membranes at 293 K.

Table 4
Average permeabilities of CO₂ and CH₄ on ABS-AC membranes

Gas	T (K)	P (barrer)								
		ABS-AC1				ABS-AC2				ABS
		M02	M05	M07	M10	M20	M25	M33	M40	
CO ₂	293	4.31	5.434	7.96	10.81	7.49	9.82	13.16	20.50	2.87
	303	5.04	6.847	9.70	13.41	8.43	11.44	14.43	22.64	3.43
	313	5.80	7.885	11.91	15.00	9.47	12.68	15.79	27.69	4.05
	323	6.67	9.077	15.46	18.40	10.13	14.09	17.92	31.67	4.72
CH ₄	293	0.162	0.183	0.250	0.315	0.264	0.302	0.321	0.406	0.119
	303	0.233	0.289	0.360	0.464	0.384	0.454	0.473	0.590	0.174
	313	0.308	0.382	0.533	0.614	0.496	0.617	0.692	1.052	0.246
	323	0.414	0.499	0.769	0.922	0.657	0.827	0.974	1.419	0.342

1 barrer = 10⁻¹⁰(cm³(STP)/cm² cmHg s).

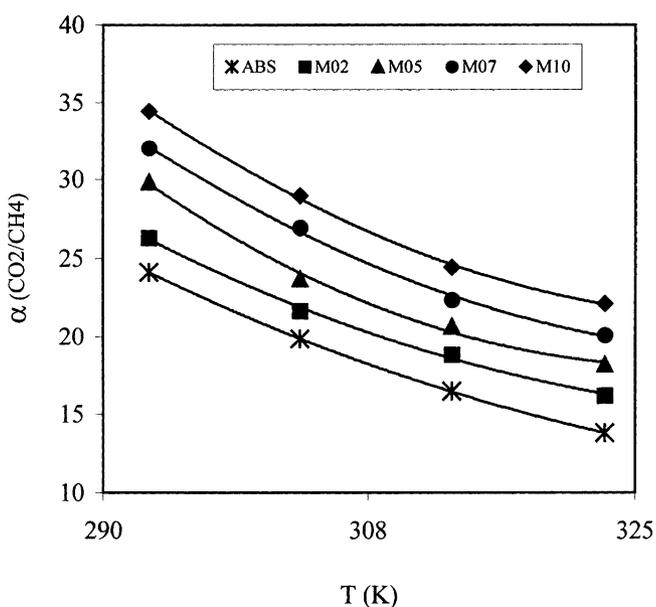


Fig. 10. CO₂/CH₄ selectivities of ABS-AC1 membranes as a function of temperature.

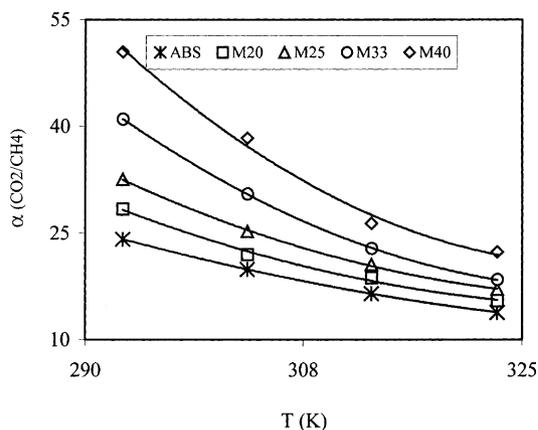


Fig. 11. CO₂/CH₄ selectivities of ABS-AC2 membranes as a function of temperature.

than the CH₄ one ($\alpha_{(\text{CO}_2/\text{CH}_4)}^K \cong 0.6$). These results could be partially explained considering the existence of a surface flux through the micro-mesoporous carbon media, with a mechanism of preferential surface diffusion of CO₂ (more adsorbable gas) over the CH₄ gas (less adsorbable). A better understanding of the transport mechanism through the ABS-AC membranes (solution-diffusion through polymeric matrix, gas diffusion in the carbon pores, gas surface diffusion on pore surface, etc.) could be achieved by carrying out several well-controlled gas flux experiments through pure activated carbons.

The two factors, permeability-pressure independence and ABS-AC permeability higher than those of pure ABS, indicates that the obtained composite membranes are defect free and/or without fissures. This tighter morphology between inorganic and organic phases are believed to arise from the partial compatibility of styrene-butadiene chains of ABS copolymer and the active carbon, implying that the polymer interacts strongly with the carbon framework. From this results it could be assume that the cavities or channels observed in the ESEM micrographs (Fig. 6b) were produced during the sample fracture process with liquid nitrogen.

4. Conclusions

Composite membranes were prepared using acrylonitrile-butadiene-styrene copolymer (ABS) and two different active carbons. The adsorptive capacity of active carbon to the pure CO₂ and CH₄ gases were determined. From these results it can be observed that AC1 is 3–3.5 more selective for CO₂ adsorption than CH₄, whereas AC2 is 1.6–2.7 times more selective. The SEM images of the mixed matrix cross-section films reveal AC clusters of relative high sizes (3–30 μm) randomly distributed into the polymeric matrix, where there exists a tight interfacial contact between the polymeric and filler phases. This tighter morphology between inorganic and organic phases are believed to arise from the partial compatibility of styrene-butadiene rubbery chains of ABS copolymer and the activated carbon structure.

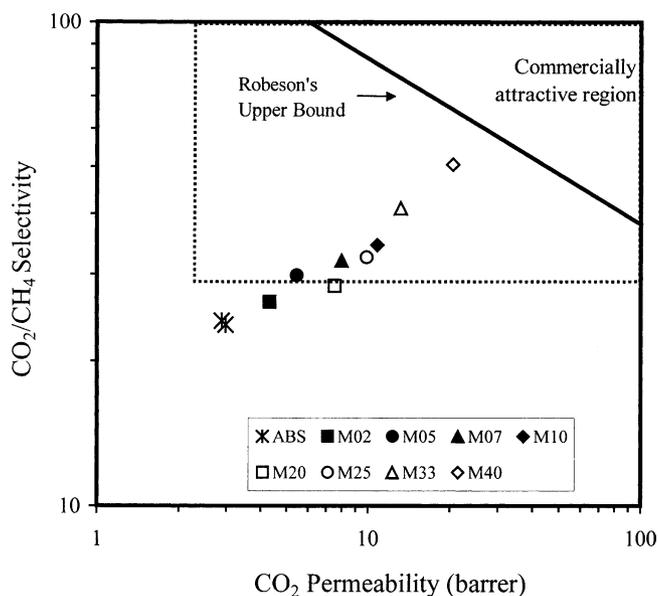


Fig. 12. Boundary diagrams of pure ABS membrane and ABS-AC composite membranes at 293 K.

For both AC filler, the measured pure gas permeabilities and calculated CO_2/CH_4 selectivities are substantially enhanced with the increasing AC loadings in the matrix ABS polymer. Fig. 12 shows the trade-off relations of CO_2 and CH_4 for the ABS-AC composite membranes and the pure ABS membrane at 20 °C. The inside the dashed rectangle region identifies commercially attractive gas transport properties for CO_2/CH_4 gas separation, obtained from data on cross-linked flat films [1]. Although the MMC membranes did not exceed the upper bound they displayed improved performances within the attractive region when activated carbon is incorporated in the ABS polymeric matrix. In particular ABS-AC membranes prepared with a concentration of AC1 = 10% or AC2 = 40% (w/w) showed the best gas separation performance at 20 °C ($P_{\text{CO}_2} = 11\text{--}21$ barrer; $\alpha_{(\text{CO}_2\text{--CH}_4)} = 35\text{--}51$) without compromising their mechanical stability. The MMC membranes containing AC2 filler showed the higher productivity and permselectivity. However, if the gas permeability and selectivity dependence on AC filler volume fraction (ϕ_f in Table 1) is analyzed, it can be seen that membranes prepared from AC1 carbon present the best performance. This can be attributed to the higher both specific surface and CO_2 adsorption selectivity of AC1 on AC2 carbon (see Tables 1 and 3).

The high CO_2 productivity and selectivity of ABS-AC membranes obtained in this research can be attributed in part to (i) the intrinsic permselectivities properties of ABS copolymer; (ii) the selective gas capacity of AC adsorption for CO_2 gas; and (iii) the tight interfacial contact between the polymeric phase and filler phase.

Future perspectives of this work should be devoted to improve ABS-carbon membranes performance. To achieve this goal, special effort will be necessary on the preparation

technique, to have a more homogeneous distribution of filler discrete entities ($<3 \mu\text{m}$) inside of the polymeric matrix.

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