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Filler-polymer combination: a route to modify gas transport properties of a polymeric membrane

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Abstract

Polydimethylsiloxane (PDMS) has been used as host matrix to prepare hybrid membranes, by a dry phase inversion process, where fillers with different surface and molecular sieving properties have been dispersed. The hybrid membranes have been characterised morphologically by scanning electron microscopy (SEM) and their gas transport properties have been measured at different temperatures.

The influence of the temperature and different fillers on the gas separation performance of hybrid membranes has been analysed. These membranes showed higher selectivity values for some gas pairs combined to lower permeabilities with respect to pure PDMS films, as consequence of the contribution of the filler to the transport. A proper filler choice could be used to meet some specific requirements in industrial gas separations.

Keywords: Gas separation; Hybrid membranes; PDMS

1. Introduction

Membrane operations are an innovative gas separation technology successfully used on industrial scale. Operating simplicity, intrinsic modularity and absence of additives to perform the separation are some of their strong points with respect to the traditional separation methods. The performance of commercial membranes are limited by a trade-off between productivity and selectivity.

Three main approaches can be followed in principle to improve the performance of the current polymeric membranes: synthesis of new polymers or functionalisation of some present polymers; development as membranes of more selective materials (e.g. carbon, metals, perovskites); preparation of composite membranes, where inorganic fillers with specific characteristics are dispersed into polymeric materials. The first two routes present high manufacturing costs and stability problems can occur during operations for inorganic membranes.

Zeolites are alumino-silicates crystalline composed of AlO_4 and SiO_2 tetrahedra, which build up a network of channels and cavities. The interconnected micro crystalline voids and channels are responsible for the very specific properties of these adsorbents. The micropore aperture size is typically in the range of molecular dimensions, i.e. 3–10 Å. Consequently, they are capable to separate molecules on the basis of shape and size differences. Furthermore, varying the Si/Al ratio during synthesis, it is possible to change their adsorption properties because this ratio determines the number of cations and thus the hydrophilicity of the zeolites. Finally, these materials present high thermal and chemical stability. For these reasons, the zeolite membranes offer potential applications in different industrial processes. However, their application at industrial level as membranes is strongly limited by reproducibility problems in the preparation step [1], presence of intercrystalline defects in the zeolite layer and high manufacturing costs [2].

Silicalite-1 is a zeolite with MFI topology characterized by a hydrophobic character, due to the absence of Al in the structure, and two different types of channels: straight channels having an opening size of (5.4×5.6) Å that intersect with sinusoidal channels with opening size of (5.1×5.5) Å. Silicalite-1 membranes can be used in

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organic/water separation [3]. When they are used in gas separation only poor selectivity values are obtained, as reported in literature [4,5]. Different permeability and selectivity values for the same gas species are measured in similar operating conditions due to the presence of defects into the membrane structure. Common types of defects are pinholes and cracks. Pinholes depend by the composition of the synthesis mixture synthesis time and temperature. Instead, cracks may form during the calcination process for different thermal expansion between zeolite layer and support.

NaA zeolite, with LTA topology, presents a hydrophilic nature and pore dimension of 4 Å. This zeolite in virtue of a narrow pore opening, capable to discriminate between molecules as O_2 and N_2, is used in air separation. Most of the studies on NaA membranes are focussed on the dehydration of organic solutions [6] and only few gas permeation studies are reported [7].

NaX zeolite, with FAU topology, is used commercially as an adsorbent and catalyst. This zeolite is usually synthetised in the sodium form with a Si/Al ratio in the range 1.0–1.5, that confers a strong hydrophilic character. NaX has pores and supercages of 7.4 and 13 Å respectively. The problems already discussed for silicalite-1 and NaA zeolite membranes are also found for FAU topology membranes [8].

A way to overcome the problems of the zeolite membranes, keeping the interesting properties of the zeolites, is the crystal dispersion in a proper polymeric matrix.

Graphite is used to improve the performance of different materials in areas where low weight to strength ratio and mechanical resistance are required [9]. However, no evidence of its use in permeation units is present in literature.

Polydimethylsiloxane (PDMS) has been selected because it was historically and still largely used in composite membranes and its behaviour results representative of that of rubbery polymers.

The incorporation of zeolite crystals into rubbery polymers has been widely studied for application in pervaporation with encouraging results in terms of permeability and selectivity [10]. However, few studies on hybrid membranes applied in gas separations have been performed.

Paul and Kemp [11] proposed that immobilising 5A (LTA) zeolite crystals into PDMS materials causes a very large increase in the diffusion time lag but the effects are minor in the steady-state permeation. This phenomenon can be used to design effective protective coatings, packaging materials, where fillers are added to gain barrier properties, and timed release mechanisms. Jia et al. [12] found that the presence of silicalite-1 into PDMS membrane facilitates the permeation of smaller molecules (CO_2, N_2, O_2), but it hinders the passage of bigger molecules (CH_4). The permeability for oxygen, nitrogen and carbon dioxide increases up to a 64 wt% silicalite-1 content before decreasing at higher concentration. On the contrary, methane permeability continuously decreases with the increase of the zeolite concentration in the range 50–70 wt%. This behaviour determines, for example, a decrease of the CH_4/N_2 selectivity with the zeolite concentration. Duval et al. [13] examined the effect of different fillers (silicalite-1, 5A, NaX) into two rubbery polymers (PDMS and propylene–ethylene rubbery). They found that permeability and CO_2/CH_4 selectivity, at room temperature (24 °C), increase with filler concentration when silicalite-1 and FAU type zeolites are used. Also O_2/N_2 selectivity increases when silicalite-1 concentration increases. On the contrary, the 5A zeolite does not improve the membrane performance.

Gas permeability increases without a significant change for selectivity in silicalite-1-PDMS membranes at 28 °C when crystal size raises [14].

All these studies and relating permeation tests, carried out at room temperature, show an evident effect of the zeolite crystals on gas transport through PDMS membranes. In our study the influence of the temperature and different fillers (silicalite-1, NaX, NaA and graphite) on the gas separation performances of PDMS-based hybrid membranes has been explored.

2. Experimental part

2.1. Materials

The fillers (silicalite-1, NaX, NaA and graphite) used in this study were purchased by Aldrich. Zeolite crystals before using were activated at 500 °C and stored into a dryer to avoid water adsorption.

The PDMS employed to prepare the membranes (Sylgard (R) 184 silicone elastomer) was supplied by Dow Corning Co. The elastomer kit contains a base (specific gravity at 25 °C 1.05 g/cm^3, viscosity 5000 cSt) and a curing agent (specific gravity at 25 °C 1.03 g/cm^3, viscosity 110 cSt).

The solvent used for all membrane samples is dichloromethane (CH_2Cl_2) by Carlo Erba reagenti (purity >99.5%).

2.2. Membrane preparation

PDMS membrane samples were prepared by pouring in a casting ring on a Teflon plate a dope solution (dissolving in CH_2Cl_2 curing agent and base with a ratio 1:10 on weight basis) stirred magnetically for 5 h. The films were evaporated before in air overnight and then in a oven for 6 h at 80 °C to allow the cross-linking of the material; finally, the final was peeled from the Teflon plate. Also hybrid films were prepared by casting on a Teflon plate from the polymer solution in which the fillers were dispersed. After a first evaporation step in air at room temperature, the

films were cured in a oven under vacuum for at least 6 h at 80 °C. The composition of all suspensions is expressed by considering a weight percentage (wt%) of the zeolite crystals with respect to the total solute mass.

2.3. Membrane characterization

The membrane thickness was measured by using a digital micrometer (Carl Mahr D7300 Esslingen a.N.) averaging 15 measurements; the standard deviation calculated on the sample was about 8%.

Filler size and its dispersion inside each hybrid membrane were analysed by using a Cambridge Zeiss LEO 400 scanning electron microscope (SEM). Membrane samples were broken in liquid nitrogen to keep unalterated the film structure and coated with gold to reduce the charging effects on the polymer surface.

Energy dispersive X-ray (EDX) technique was used to evaluate the Si/Al ratio of the zeolite crystals. This microanalysis was realised using an EDAX-Phoenix instrument (detector Super Ultra Thin Window, Si/Li crystal analyser).

The experimental equipment used to carry out the permeation rate experiments was manufactured by GKSS Forschungszentrum GmbH (Germany). It consists of a permeation cell that represents the heart of the system, connected, by means of a series of pneumatic controlled valves, to the feed and permeate sides, where two pressure transducers measure the pressure level. The whole system is placed in an air thermostated chamber and all feeding, evacuation and temperature setting operations of the system are controlled via software. The permeation cell, where a flat membrane sample is set on a sintered steel support, is composed by two parts pneumatically pressed each other on a Vyton o-ring that seals the membrane. The basic principle of the test unit is a pressure measurement, independent from gas type, that is easy related to a flux density measure.

Gas permeation tests were carried out in a temperature range of 15–65 °C, feeding the single gases (purity level 99.998%) at atmospheric pressure and keeping the permeate side under vacuum (10^{-2} mbar).

The same protocol has been followed for pure polymer and all hybrid samples. A PDMS membrane has been prepared as reference material to compare the performance of the different hybrid films. The gases have been tested in the following order: N_2, O_2, CH_4, He and CO_2. Before each measure the system has been evacuated on both feed and permeate sides for at least 6 h, and between two cycles of measure, at different temperatures, purging of the system by using nitrogen has been performed.

The permeation of a gaseous penetrant through a pure polymer matrix is controlled by two main parameters: the diffusion coefficient (D), a kinetic factor, strongly linked to the molecular size of the species and the solubility coefficient (S), a thermodynamic factor, that is a measure of the mutual affinity between penetrant and polymer matrix [15]. Therefore, the equation that describes the permeability is the following:

$$P = DS \tag{1}$$

Permeability, defined as volumetric flow rate which penetrates a defined membrane area under a fixed pressure difference and normalised on membrane thickness, measures the intrinsic value of the permeation rate of a species in a specific material. In the following this coefficient is expressed in barrer unit, where

$$1\ \text{barrer} = 10^{-10}\,\frac{\text{cm}^3(\text{STP})\text{cm}}{\text{cm}^2\ \text{s cmHg}}$$

Permeability values reported in this work are obtained as average of at least three measurements in steady state condition, with a standard deviation always less than 2%.

The dependence of the permeation rate from the temperature is typically described, for an activated process, by the following equation:

$$P = P_0 \exp\left(\frac{-E_{\text{att}}}{RT}\right) \tag{2}$$

where P_0 is a front factor, R is the gas constant, T is the absolute temperature, E_{att} the apparent activation energy for the permeation process.

Thus, in a semi log plot of the permeability versus the reciprocal of the temperature, the slope of the line represents the activation energy of the permeation process that is a measure of the temperature influence for the specific gas-polymer combination.

Time lag method has been used to estimate the diffusion coefficient trough PDMS pure film, according to the equation:

$$D = \frac{l^2}{6\theta} \tag{3}$$

where l is the membrane thickness and θ is the time lag obtained extrapolating to the time axis the linear part of the experimental curve in the permeate pressure vs. time plot [16]. In fact, for ideal systems, where diffusion coefficient is independent from the gas concentration, the amount of penetrant that permeates through the membrane as function of the time is represented by a curve in the transient state that becomes a line when steady-state conditions are attained.

The gas solubility through PDMS films has been calculated as ratio between steady state permeability and diffusivity values, the last one obtained using Eq. (3).

As reported in literature, in the hybrid membranes the presence of fillers increases the diffusion time lag as consequence of immobilising adsorption that requires an additional time to accumulate the excess penetrant before steady-state can be reached. This effect depends on filler type, concentration and operating conditions [11]. Therefore, because it is no possible to distinguish completely the sorption and diffusion steps in the permeation process when

particles able to adsorb gas species are dispersed in a continuous phase, simple time lag theory can not used to determine quantitatively the diffusion coefficient in composite materials.

The ideal selectivity (α_{ij}) between two different gases (i and j) is defined as the ratio of the single gas permeabilities:

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

and it provides a useful measure of the intrinsic permselectivity of a given membrane for the i and j components. D_i/D_j is the mobility selectivity term, while S_i/S_j represents the solubility selectivity.

Maxwell model has been used to interpret some experimental results measured through the hybrid samples. The equation for the theoretical calculation is the following [17]:

$$P_h = P_c\left[\frac{P_d + 2P_c - 2\Phi_d(P_c - P_d)}{P_d + 2P_c + \Phi_d(P_c - P_d)}\right] \quad (5)$$

where P_h is the permeability of the hybrid sample, Φ_d is the volume fraction of dispersed phase, P_c and P_d represent the gas penetrant permeabilites in the continuous and dispersed phases, respectively. In particular, PDMS permeability and filler volume fraction values are those measured in this study. The transport properties of the filler were calculated on the basis of diffusion and adsorption data available in literature, assuming that the permeability is the product of diffusive and adsorption terms. However, the literature values relative to the filler transport properties show a wide difference between theoretical and experimental data [18,19].

3. Results and discussions

3.1. SEM and EDX analyses

In Table 1 are reported the mean value of the filler size and Si/Al ratio of the different zeolite crystals used for hybrid membrane preparation. The Si/Al value indicates the hybrophobic character of silicalite-1 as consequence of aluminium absence; at the same time, this ratio shows as the NaA zeolite is more hydrophilic with respect to NaX zeolite. The average value of the graphite particles is 1.5 μm.

For each filler concentration have been prepared hybrid membranes with three different thickness values (100, 150 and 500 μm) on which the permeation flux values were normalised. Good agreement has been found between micrometer measurements and SEM observation.

Table 1
SEM and EDX analyses of inorganic fillers

Sample	Crystal size (μm)	Si/Al (−)
Silicalite-1	1.7	∞
NaA zeolite	4.0	1.20
NaX zeolite	2.3	1.50

The cross-section images of silicalite-1-PDMS membranes are shown in Fig. 1. At low (15 wt%) and medium (30 wt%) zeolite concentration (Fig. 1(a) and (b)), they show a not homogeneous distribution of the crystals due to their sedimentation towards the membrane side in contact with the Teflon plate (upper side in Fig. 1(a) and (b)). A better crystal distribution is observed at high zeolite concentration (50 wt%, micrograph 1c). This result depends on viscosity of the suspension, difference of density between particles and polymer and also presence of interactions among filler particles. However, for thinner membranes it is possible to observe an improvement of filler distribution at the same zeolite content (Fig. 1(d)). Furthermore, all micrographs show how the crystals are embedded in the rubbery matrix, while cluster formation is observed only at high zeolite concentration. Similar results have been also found for the membrane samples loaded with the other inorganic particles investigated in this study.

3.2. Permeation tests

3.2.1. PDMS membranes

To investigate the gas transport properties of the membranes prepared in this work, a set of permeation tests has been carried out using the apparatus described in Section 2.

In the pure PDMS the permeability, measured in the temperature range (15–65 °C), increases with the temperature for all species considered and the permeation rate order is the following: $CO_2 > CH_4 > O_2 > He > N_2$.

In an Arrhenius' type plot it is possible to observe how the most permeable gas, carbon dioxide, is less affected by temperature, whereas for the remainder gases a stronger influence has been calculated (Fig. 2(a)). To explain this result can be useful to analyse the two contributions (D and S) to the permeability coefficient that are differently influenced by the working temperature.

In rubbery polymers the permeation rate is controlled by the solubility that is mainly determined by the ease of condensation of gas molecules. Thus CO_2 and CH_4, that are more condensable with respect to the other ones, are also the more permeable species in PDMS. The differences in terms of solubility are less important for permanent gas and so their diffusion coefficients influence their permeation rate. In pure polymer when the temperature rises, the diffusivity for CO_2, CH_4 and O_2 increases, while the solubility decreases, as shown in Fig. 2(b) and (c) respectively. Thus both gas diffusivity and solubility obey to the Arrhenius' law as function of the temperature; the activation energy for the diffusion ($E_{att,D}$) and the enthalpy of sorption (ΔH_S) values of the three gases in PDMS are summarised in Table 2.

The selectivity for the gas pairs (CO_2/CH_4, CH_4/He,

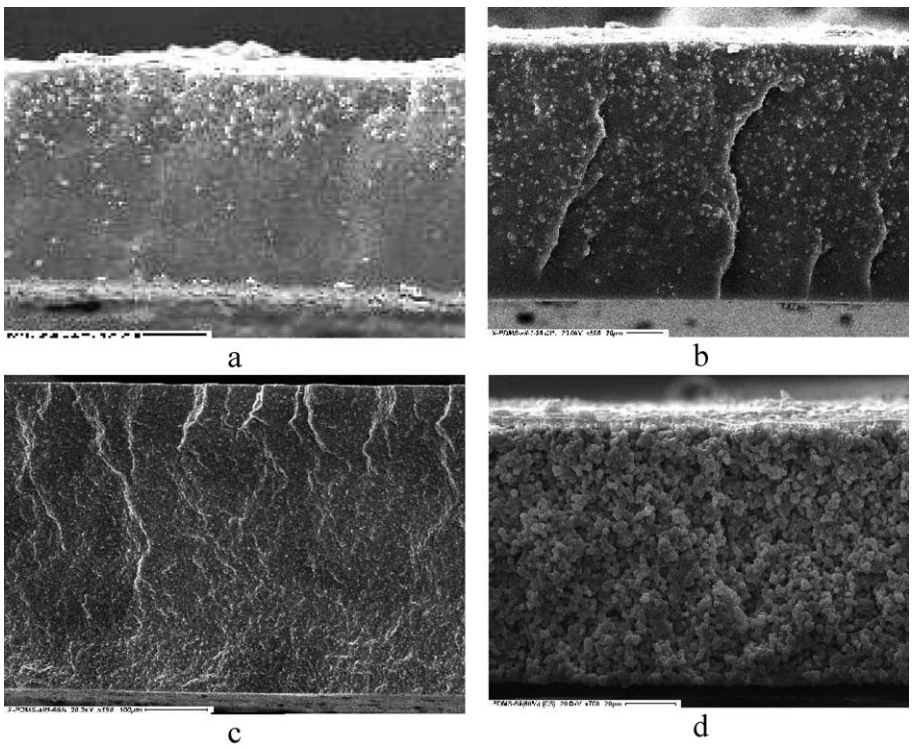

Fig. 1. Cross section of different hybrid samples (a) silicalite-1-PDMS, 15 wt%, (b) silicalite-1-PDMS, 30 wt%, (c) silicalite-1-PDMS, 50 wt% thick sample, (d) silicalite-1-PDMS, 50 wt% thin sample.

O_2/N_2) tends to decrease when the temperature rises (see Table 3), as direct consequence of the different behaviour of the investigated gases in pure PDMS membranes. In fact, the solubility decay for CO_2 and, in part, for CH_4 is more significant than that measured for O_2, He and N_2, whereas, the increase in the diffusivity coefficient is more important for these permanent gases.

3.2.2. Hybrid samples

Silicalite-1 into the PDMS matrix modifies the permeation rate for all gases studied, in particular when crystal concentration rises. This effect is significant for CH_4 and He, less important for O_2 and N_2 and it is practically negligible for CO_2. In silicalite-1 crystals the most adsorbed species is CO_2 followed by CH_4, N_2, O_2 and He. Furthermore, if the surface sorption mechanism controls the transport through the membrane the same permeation order will be measured. However, the permeation rate trend measured through the silicalite-1 loaded PDMS samples differs from those of the silicalite-1 and pure PDMS. Although all investigated gas species present kinetic diameter smaller than silicalite-1 pores, the molecular sieving mechanism through the filler strongly influences the gas transport. It is possible to explain this result assuming that the polymer partially occludes the zeolite pores. Thus, the presence of zeolitic crystals determines a substantial increase of the permeation rate for He, particularly passing from 30 to 50 wt%; on the contrary methane, characterised by highest kinetic diameter, presents an evident lowering of the permeation rate. A less marked decay of O_2 and N_2 permeation rate is also measured. Consequently, at medium crystal concentration (30 wt%) CH_4, O_2, and He permeances are comparable, while at high concentration (50 wt%) the permeation rate order becomes $He > O_2 > CH_4$ (Fig. 3).

This behaviour is still more evident at high temperature, when the gas diffusivity contribute becomes more important. The major affinity of CO_2 for the filler balances the molecular-sieving effect that silicalite-1 partially exerts on it. Furthermore, the CO_2 permeability measured through

Table 2
Apparent activation energy for permeation ($E_{att,P}$), diffusion ($E_{att,D}$) and sorption processes calculated for pure PDMS films

	$E_{att,P}$ (kJ/mol)	$E_{att,D}$ (kJ/mol)	ΔH_S (kJ/mol)
CO_2	2.70	12.20	−9.50
CH_4	9.70	14.90	−5.20
O_2	10.50	14.70	−4.20

Table 3
Ideal selectivity values measured through pure PDMS membranes

T, °C	α_{ij}		
	CO_2/CH_4	CH_4/He	O_2/N_2
15	3.20	2.20	2.20
35	3.30	1.90	2.00
60	2.60	1.60	1.80

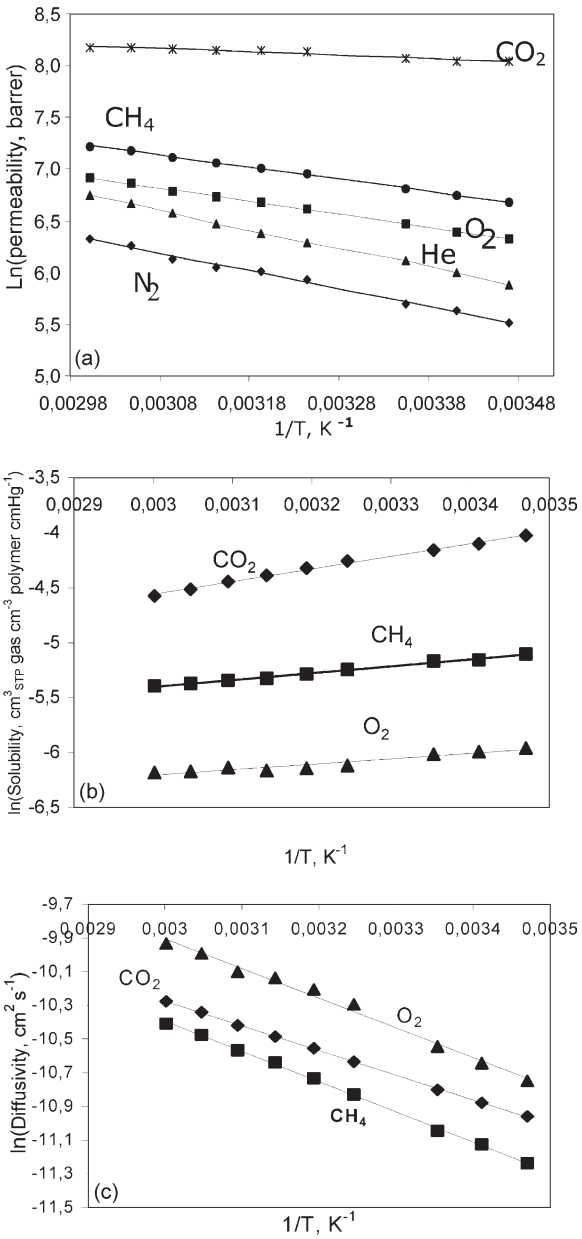

Fig. 2. Temperature dependence of the PDMS permeability coefficient (a); Temperature dependence of the PDMS solubility coefficient for CO_2, CH_4 and O_2 (b); Temperature dependence of the PDMS diffusion coefficient for CO_2, CH_4 and O_2 (c).

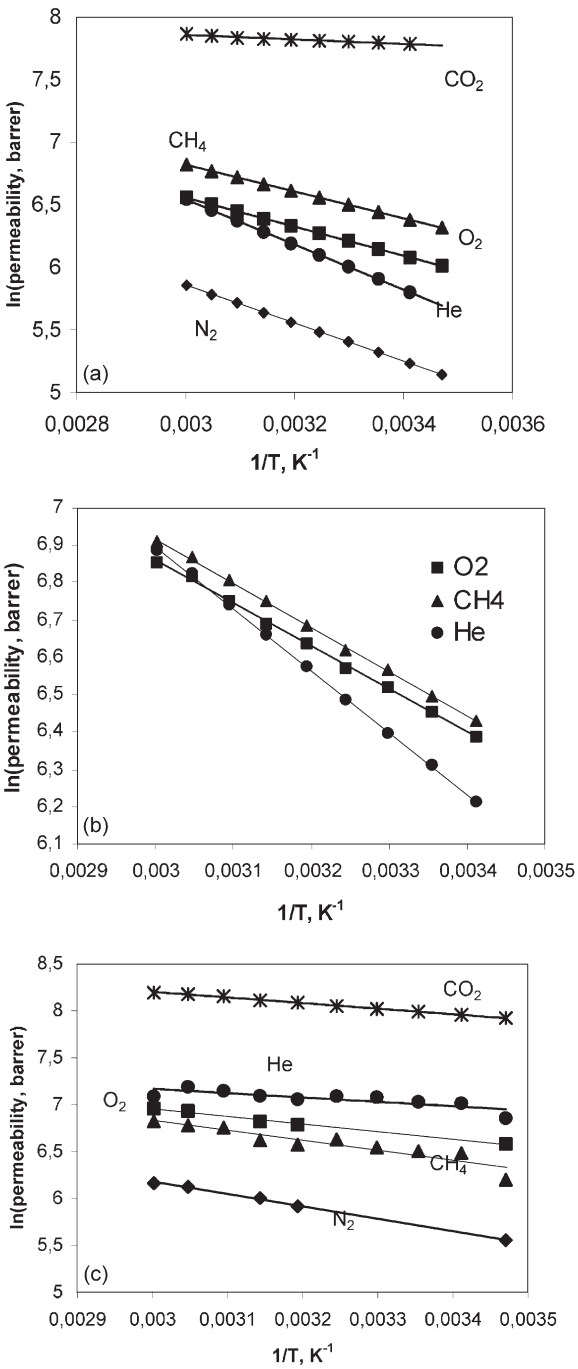

Fig. 3. Permeability (barrer) for different gases vs. reciprocal of temperature (K^{-1}), (a) silicalite-1-PDMS, 15 wt%, (b) silicalite-1-PDMS, 30 wt%; (c) silicalite-1-PDMS, 50 wt% membrane samples.

hybrid samples does not suffer an appreciable variation with respect to the PDMS film. These considerations are confirmed by a selectivity analysis for different gas pairs.

The CO_2/CH_4 selectivity increases with crystal concentration due to the molecular sieving mechanism exerted by the zeolitic pores partially plugged by the polymer. The effect is more significant moving from 15 to 30 wt%. On the contrary, the selectivity decreases with the temperature as already observed for PDMS, whereas CO_2 permeability increases with the temperature independently on silicalite-1 content. However, at low and medium temperature values in the investigated range, it decreases with the filler content, while at 60 °C it increases with zeolite concentration (see Table 4).

The CH_4/He selectivity measured trough hybrid membranes is always lower than pure PDMS. At low (15 wt%) and medium (30 wt%) crystal concentration the same trend of the PDMS, as function of the temperature, is confirmed. At high concentration (50 wt%) the trend is opposite because selectivity value lightly increases with temperature. This fact depends on increase of helium permeability with

Table 4
CO_2 permeability and CO_2/CH_4 selectivity values for different silicalite-1-PDMS samples

T (°C)	Silicalite-1-PDMS, 15 wt%		Silicalite-1-PDMS, 30 wt%		Silicalite-1-PDMS, 50 wt%	
	P_{CO2} (barrer)	α_{CO_2/CH_4} (−)	P_{CO_2}, (barrer)	$\alpha_{CO2/CH4}$, (−)	P_{CO2}, (barrer)	$\alpha_{CO2/CH4}$, (−)
15	3150	4.30	3120	5.20	2760	5.50
40	3320	3.30	3310	4.10	3250	4.50
60	3460	2.80	3500	3.50	3610	3.90

respect to the methane one because at high zeolite content the molecular sieving contribute becomes still more important.

Selectivity trend versus temperature for O_2 and N_2 is similar to that measured in PDMS films, but the absolute values are higher than those measured trough PDMS in the whole temperature range. This improvement is still explainable by considering the molecular sieving effect.

The introduction of NaX zeolite into polymeric matrix produces a generalised permeability lowering. This result is especially evident at high crystal concentration. The permeation order of the species is the same of pure PDMS in the 15–65 °C temperature range. These experimental results, combined to the opening of the NaX pores significantly wider than silicalite-1 pores and kinetic diameter of the gases considered, suggest that the polymer completely fills the zeolitic pores. Thus, the filler can exhibit only the sorption properties on the external surface because both molecular sieving and surface diffusion within the pore network are prevented. In Table 5 are summarised the CO_2 permeability and selectivity values at different temperatures.

Carbon dioxide at low temperature presents high solubility into the polymer and for this reason the contribute of the crystals to the transport is limited. Besides, the methane presents lower affinity for the crystal surface and so the CO_2/CH_4 selectivity is close to that intrinsic of the polymer. At high temperature the CO_2 solubility into the PDMS decreases and the crystal contribute to the transport becomes more important. However, the CO_2 moves more easily than CH_4 on crystal surface and so the selectivity value becomes higher than pure polymer, at high NaX zeolite content (50 wt%). The CO_2/CH_4 selectivity calculated for the sample containing NaX 50 wt% remains higher than of the sample at lower zeolite concentration when temperature is higher than 35 °C (see Table 5).

The most significant changes in the CO_2 permeation rate are observed moving from medium (30 wt%) to high (50 wt%) zeolite concentration, rather than operating at concentration lower than 30 wt%.

At low temperature the helium permeates preferentially into the polymer because it presents no affinity for the crystals, on the contrary the methane can move also on the crystal surface. This behaviour determines an increase of the CH_4/He selectivity with respect to the pure polymer.

At high temperature, the crystal contribute to the transport decreases, then the transport of the methane is completely controlled by the polymer and the same occurs for helium. Therefore, the CH_4/He selectivity values in the hybrid matrix are close to those ones measured in pure polymer. The concentration of the NaX crystals does not affect further the selectivity values for this gas pair (see Table 5).

The O_2/N_2 selectivity is similar to the pure polymer in the whole temperature range. These gases permeate exclusively into the polymer matrix since both dissolve little on the crystal surface. Thus the crystals presence affects in the same way the permeation rate of the two gases.

On the basis of pore size (4 Å), the polymer can not penetrate into the zeolitic channels but it simply envelops the particle. Thus, NaA zeolite keeps its properties as individual crystal. Carbon dioxide tends to be adsorbed strongly into zeolite pores; consequently its transport is delayed. On the contrary, the other species (He, O_2, N_2, CH_4) having low affinity for the crystals prefer to move into the polymer rather than to adsorb on crystal surface before reaching the channel network of the zeolite particles. However, for all species the filler acts as an obstacle determining a more tortuous path during the permeation process. When temperature rises, the permeation rate of all gases increases as already observed for PDMS based films except for CO_2 that presents an almost constant value of permeability. The CO_2 trend as function of the temperature is confirmed at different crystal concentrations. As

Table 5
CO_2 permeability and different gas selectivity values for NaX-PDMS samples

T (°C)	NaX-PDMS, 15 wt%				NaX-PDMS, 30 wt%				NaX-PDMS, 50 wt%			
	P_{CO_2} (barrer)	α_{CO_2/CH_4} (−)	$\alpha_{CH_4/He}$ (−)	α_{O_2/N_2} (−)	P_{CO2} (barrer)	α_{CO_2/CH_4} (−)	$\alpha_{CH_4/He}$ (−)	α_{O_2/N_2} (−)	P_{CO_2} (barrer)	α_{CO_2/CH_4} (−)	$\alpha_{CH_4/He}$ (−)	α_{O_2/N_2} (−)
15	2070	3.90	2.40	2.30	1860	3.90	2.40	2.30	890	3.80	2.40	2.10
35	2160	3.20	2.00	2.10	2020	3.30	2.00	2.10	1060	3.60	2.00	2.00
65	2420	2.55	1.60	1.90	2390	2.60	1.60	1.90	1330	3.00	1.60	1.90

consequence of this result, the selectivity values of CO_2 with respect to the other species decrease if compared to the pure polymer values especially when the NaA zeolite concentration increases (Fig. 4(a) and (b)).

PDMS samples loaded with graphite have been prepared at three different filler concentration (15, 30 and 50 wt%). High graphite-content membranes (50 wt%) have been resulted too fragile for permeation rate tests. The graphite particles act as an obstacle to the gas transport causing a permeation rate decay with respect to the PDMS membranes. Furthermore, the graphite acts as not permeable material, embedded into the polymeric matrix, and does not change the performance of the PDMS. This barrier effect becomes more significant at 30 wt% filler concentration (Fig. 4(c) and (d)). The separation factors do not change significantly and the permeation rate order through these hybrid films is the same of that one measured through the pure polymer.

3.3. Activation energy evaluation

The permeation tests carried out at different temperature values allowed to evaluate the influence of this parameter on the transport properties of the membranes according to Eq. (2) (see Table 3). The higher the temperature effect on the permeation rate is, the higher is its energy activation value.

In the PDMS the apparent activation energy ($E_{att,P}$) values for the single gas permeation rate show how the smaller and low permeable species (He, N_2, O_2) are more strongly influenced by an increase of temperature. Carbon dioxide is the species of which the permeation rate is less affected by a temperature change.

Silicalite-1 dispersed within the PDMS matrix determines a quite generalised lowering of the apparent activation energy values referring to PDMS. The most evident decrease with the filler concentration occurs for helium whereas for oxygen this decay is less marked. For nitrogen and methane the concentration affects lightly the values with a minimum registered at 30 wt% zeolite content. Carbon dioxide exhibits an anomalous behaviour because it is characterised by an increase of its temperature dependence with the silicalite-1 concentration: at low and medium silicalite-1 content this dependency remains lower

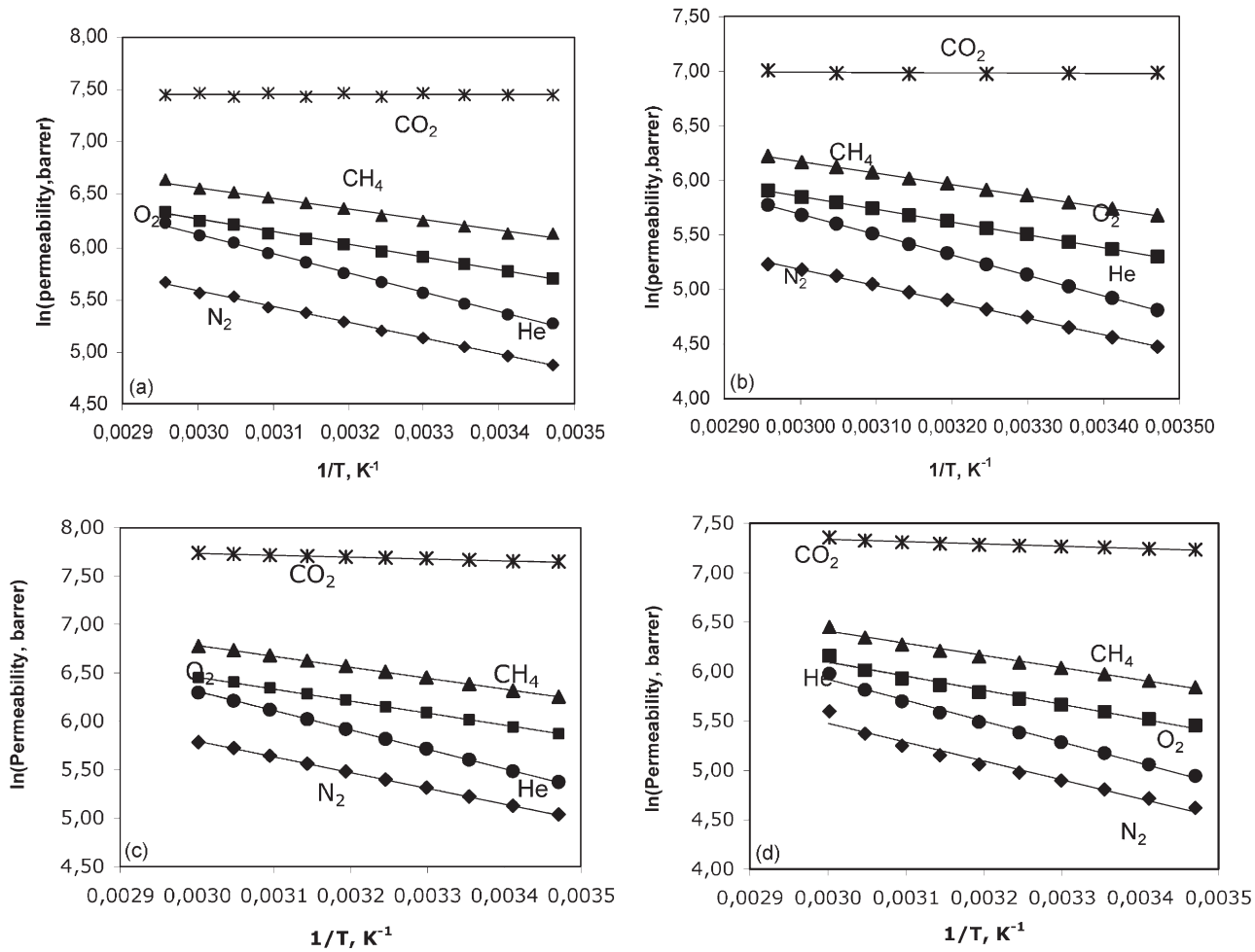

Fig. 4. Permeability (barrer) of carbon dioxide, methane, oxygen, helium and nitrogen vs. reciprocal of temperature (K^{-1}) (a) NaA-PDMS membrane, 15 wt%, (b) NaA-PDMS membrane 50 wt%, (c) graphite-PDMS membrane, 15 wt%, (d) graphite-PDMS membrane, 30 wt%.

than PDMS, while its $E_{att,P}$ around doubles, with respect to pure PDMS, for high zeolite content (50 wt%) samples.

Apparent activation energy for the permeation process decreases with NaX concentration for all species, except for CO_2. However, only for nitrogen the temperature dependence is lower than that calculated for PDMS.

In the NaA-PDMS samples, temperature dependence is practically constant with the crystal concentration and it results for nitrogen, oxygen and methane lightly lower than pure polymer. On the contrary, for helium the $E_{att,P}$ is lightly higher with respect to the PDMS. For carbon dioxide a negligible effect of the temperature on its permeation rate has been measured. For this reason the addition of this zeolite type is the proper choice when a constant CO_2 permeability value, in a wide temperature range, combined to a low selectivity loss with respect to pure material is required.

The presence of graphite affects only marginally the temperature dependence of the hybrid samples. Apparent activation energy for the permeation process increases with filler concentration for all species. This value remains lower and higher than PDMS for CO_2 and helium, respectively. For the remainder gases no significant variation with respect to pure material has been calculated.

3.4. Preliminary comparison of theoretical and experimental data

Maxwell model was chosen to predict the performance of NaA-PDMS samples loaded with different zeolite contents as function of filler volume fraction value. Three different values representative of low, medium and high temperature were considered. The experimental permeation rate of N_2, O_2, CH_4 and CO_2 was compared with theoretical data for the same species. In all cases the model overestimates the experimental values but the difference is more significant at high temperature and when the volume fraction occupied by the filler is low (Fig. 5). The experimental CO_2 permeation rate values practically constant with the temperature at fixed filler volume fraction, as widely described in the discussion section, are confirmed by the model. However, the difference between theoretical and experimental values is still remarkable (Fig. 5(c)).

A possible explanation of this result is the not homogenous filler dispersion in the polymeric matrix at low concentration as observed in SEM images. Another cause that influences the results can be attributed to the discrepancy between literature zeolite diffusion and adsorption values available, obtained experimentally or theoretically, that were used in the Maxwell equation.

In literature the discrepancy between experimental and theoretical permeability values was justified by considering that the model does not incorporate the local specific driving force on the zeolite particle [20]. Furthermore, it is demonstrated that the properties of interphase between filler and polymer should be taken into account to predict the experimental data [21].

The experimental data confirm that intrinsic gas permeability of the filler assumed as single crystal is not

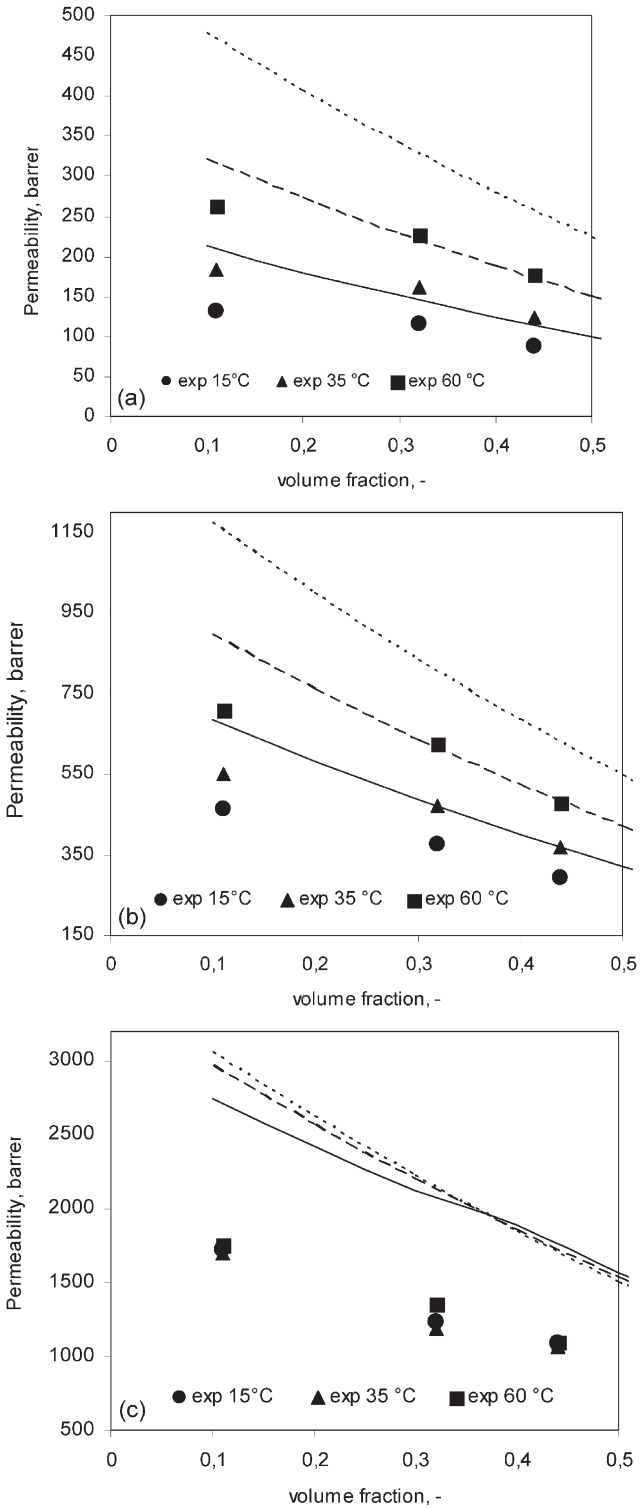

Fig. 5. Permeability for different gases of NaA-PDMS membranes vs. filler volume fraction: (a) N_2; (b)CH_4 and (c) CO_2. Solid line is for theoretical data at 15 °C, dashed line is for theoretical data at 35 °C, dotted line is for theoretical data at 60 °C. Symbols are used for experimental values.

realistic when it is part of a composite system where inorganic and organic phases are mutually influenced.

The experimental O_2/N_2 selectivities are always higher than theoretical values in the whole temperature range. This discrepancy is more marked at high temperature values (Fig. 6).

These results show how higher barrier properties (low permeability and high selectivity values) for the NaA-PDMS membranes were experimentally measured with respect to the Maxwell model prediction.

3.5. Final discussion and potentiality of these composite materials

On the basis of the results described in the previous section it is possible to summarise the main aspects emerged from this study Three different zeolite types have been investigated as filler for PDMS-based films; they present differences in terms of pore dimension and Si/Al ratio. Depending on their pore size and surface properties, zeolite crystals are able to discriminate gas species in terms of molecular size and affinity properties. When zeolite fillers are dispersed inside PDMS matrix they influence differently the transport of gas molecules as function of their micropore dimension, adsorption properties and interaction with host matrix.

First of all, permeation rates measured through the hybrid samples are of the same order of magnitude with respect to those of the pure PDMS; this result confirms in absolute way the absence of structural defects by virtue of a good adhesion between particles and polymer.

Small opening pore zeolite (NaA) are completely wrapped by the polymer and they act essentially as an active obstacle to the permeation of all gases. CO_2 is adsorbed inside the zeolite crystals with a further delay in its permeation rate. According to the strong affinity of CO_2 for NaA particles, the permeation rate of this gas is little influenced by temperature as confirmed by lower apparent activation energy value with respect to pure PDMS. The other gas species keep similar temperature dependence in NaA-PDMS samples with respect to the reference polymer.

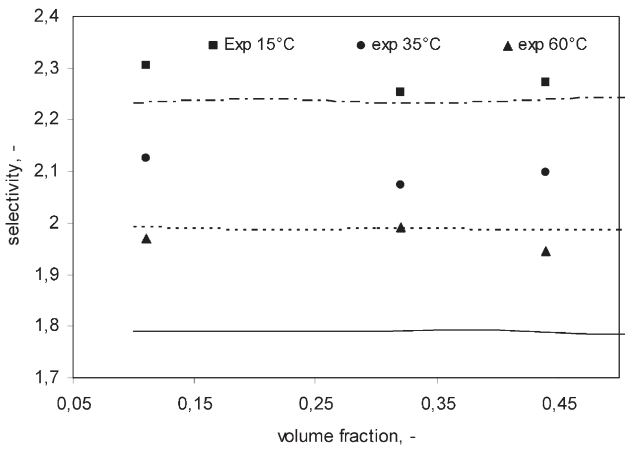

Fig. 6. O_2/N_2 selectivity for NaA-PDMS membranes at three different temperature values vs. zeolite volume fraction. Solid line is for theoretical data at 60 °C, dashed line is for theoretical data at 35 °C, dot-dashed line is theoretical at 15 °C. Symbols are used for experimental values.

Similar results occur when large pore zeolite (NaX) are dispersed in PDMS, as consequence in this case, of a complete pore plugging.

Differently from the NaA crystals, NaX zeolite determines, however, an increase of the temperature sensitivity of the gas permeability that is significant for CO_2 (its $E_{att,P}$ at high NaX content is almost 2.5 times higher than PDMS), see Table 6. Thus, by varying properly the working temperature, it is possible to modify in a significant way the permselectivity properties for a specific gas pair. The increase of the barrier transport properties with NaX and NaA concentration suggests a potential application in packaging field, meeting the requirements of specific fresh foods [22].

Silicalite-1 pore size is able to modify the permeation order of the host matrix ($CO_2 > CH_4 > O_2 > He > N_2$ for PDMS, $CO_2 > He > O_2 > CH_4 > N_2$ at high silicalite-1 content), reducing only partially the steady-state permeation rate of the gases. Apparent activation energy values for silicalite-1-PDMS samples show as the combined action of the silicalite-1 concentration and working temperature changes the gas permeation rate order with respect to the pure polymer opening new perspectives for some gas separations by using a proper combination of rubbery and glassy polymers (e.g. He recovery from natural gas).

The graphite resulted a completely not permeable material for the gas transport through the composite structure. In particular, the graphite particles lower the permeability of all components keeping the same permeation rate order and selectivity values measured through PDMS membranes. This barrier aspect of the graphite can be considered in the applications where PDMS permeation properties have to be controlled at fixed film thickness.

The permeation tests were repeated on the samples, stored at room temperature in air, also after 6 months and the transport properties (permeability and ideal selectivity) remained constant. This result is very important because the

Table 6
Apparent activation energy of permeation process for different gases, kJ/mol

Membrane	N_2	O_2	CH_4	He	CO_2
PDMS	14.30	10.50	9.70	15.20	2.70
silicalite-1-PDMS, 15 wt%	12.60	9.70	8.90	15.00	1.50
silicalite-1-PDMS, 30 wt%	9.70	9.50	9.90	13.80	2.00
silicalite-1-PDMS, 50 wt%	11.00	6.70	8.80	3.90	5.00
NaX-PDMS, 30 wt%	14.30	11.50	10.40	17.20	4.00
NaX-PDMS, 50 wt%	12.10	10.80	9.80	16.70	6.40
NaA-PDMS, 15 wt%	12.60	10.00	8.50	15.40	0.20
NaA-PDMS, 50 wt%	12.70	9.70	8.70	15.40	0.20
graphite-PDMS 15 wt%	13.40	10.40	9.40	16.50	1.60
graphite-PDMS, 30 wt%	15.80	11.70	10.30	17.60	1.90

zeolite crystals, extremely sensible to humidity when considered as individual units, become more stable when entrapped in a proper polymer matrix.

4. Conclusions

Stable and free defects hybrid PDMS-based membranes have been successfully prepared by controlled solvent evaporation method. The presence of the filler determines a change in the permeation rate of gaseous species in PDMS matrix with a consequent modification of the selectivity values but also a different response as function of the operating temperature.

Silicalite-1 plays the role of a molecular sieve in the hybrid membranes by faciliting the permeation of smaller molecules and hindering that of larger molecules. Thus the permeability of the helium, having smallest kinetic diameter, increases, whereas that of the methane, biggest molecule, decreases. Carbon dioxide permeability remains around constant due to the combined effect of sorption on the crystal surface and permeation through the host matrix.

NaX zeolite in the polymeric matrix lowers the permeability of all species investigated. In this case the filler does not exhibit molecular sieving effect because the polymeric chains completely fill the zeolitic pore. Thus, this zeolite type can exerts exclusively the sorption properties on the external surface of the crystal. The temperature strongly influences the gas permeation rate especially at high crystal concentration.

In the hybrid samples the NaA performs the properties as individual crystal. Carbon dioxide is adsorbed in the zeolite crystals because it presents high affinity for the zeolite walls: this behaviour implies a further decay of the permeability with respect to the pure PDMS. At fixed zeolite content the CO_2 permeability remains around constant with the temperature.

Graphite particle, differently from zeolite materials, behaves as not permeable obstacle to the transport for all gases investigated and for this reason lowers the permeability without any influences on their ideal selectivity.

The experimental permeation rate of N_2, O_2, CH_4 and CO_2 for NaA-PDMS samples was compared with theoretical data for the same species. Maxwell model does not fit adequately these data due to the literature filler permeabilities are not representative of the crystal behaviour in hybrid sample.

Acknowledgements

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