Role of the Diffusion in the Transport of Gas Species through Polymer Membranes
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Introduction
Membrane-based gas separation is becoming a significant unit operation in chemical and process industry; the productivity is determined by the permeation rate of the species through the permselective film, while the purity level is mainly established by the separation factor. Specifically, the separation of gaseous mixtures by means of non-porous polymeric membranes is based on differences of gas diffusivity and solubility in the membrane material and the evaluation of the role of these two factors is an important aspect. Thus, the development of membranes based on more permselective materials is a fundamental challenge for enhancing the competitiveness of this environmental friendly technology.

The determination of the temperature influence on the main transport parameters in the material is an important task for an useful application of the membranes in gas separation at industrial level.

Materials and methods
Among the materials belonging to the glassy polymers category, the polysulfone (PSf) Udel supplied by Amoco Performance Products, Inc., USA, was compared to the PEEK-WC, a polyetheretherketone modified supplied by the Chanchung Institute of Applied Chemistry, Academia Sinica. The former polymer, with a glass transition temperature (Tg) close to 190 °C, is widely used in commercial gas separation membranes, the latter has good mechanical and thermal properties (Tg ~ 230 °C), is soluble in several organic solvents, has already been successfully investigated, at laboratory scale, for flue gas separation [Clarizia, 1996], packaging applications [Torchia \textit{et al.}, 2004], and to prepare thin flat-membranes, also with asymmetric morphology [Jansen \textit{et al.}, 2005]. Styrene-butadiene-styrene triblock copolymer (SBS), used as component of commercial adhesives and sealants but also as polymer modifier, was studied as an example of rubber material. Two different (21 wt.% and 30 wt.%) styrene contents has been considered and indicated in the following as SBS\textsubscript{21} and SBS\textsubscript{30}, respectively.

Polymers were dissolved, at room temperature, in the respective solvent at a concentration of 12 wt\%. The purity of all solvents (Carlo Erba reagents) is higher than 99.5%. The solutions were magnetically stirred for at least 24 h in order to allow a complete dissolution of the polymer before their casting by means of an adjustable hand-casting knife (dry phase inversion method). A glass and a Teflon plate were used as a casting surface for the glassy and rubbery polymers, respectively. The films were left to evaporate over night at room temperature, then set in an oven under vacuum to complete the removal of the solvent. According to the boiling point of the solvent and the nature of the polymer, the treatment under vacuum (temperature and time) was defined to avoid the presence of residual solvent in the specimens.

In table 1 some additional information about the materials used in this work are summarized.
Table 1. Chemical structure of the polymers, solvents and their boiling points.

<table>
<thead>
<tr>
<th>Chemical structure</th>
<th>Solvent</th>
<th>Boiling point, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEK-WC, powder</td>
<td>CH₂Cl₂</td>
<td>39.8</td>
</tr>
<tr>
<td></td>
<td>CHCl₃</td>
<td>61.2</td>
</tr>
<tr>
<td>PSf, pellets</td>
<td>CH₂Cl₂</td>
<td>39.8</td>
</tr>
<tr>
<td></td>
<td>CHCl₃</td>
<td>61.2</td>
</tr>
<tr>
<td>SBS, pellets</td>
<td>Toluene</td>
<td>110.6</td>
</tr>
</tbody>
</table>

The gas permeability through the isotropic non-porous polymeric membranes was measured on an air thermostated apparatus, equipped with a pressure detector. The principle of the measurement is to evacuate the downstream side of the membrane to about 5·10⁻² mbar, provide the upstream side with the selected gas at a constant pressure for the test, and monitor the permeate pressure increase in a calibrated downstream receiving container. Permeation coefficient ($P$) is then calculated from the slope of the straight line that depicts the steady-state time-pressure relationship, according to time-lag ($θ$) method, while the diffusion coefficient ($D$) can be correlated to $θ$, as certain assumptions are valid, by the simplified equation $D = \frac{l^2}{6·θ}$ [Crank, 1975].

In the following for all gas species $P$ will be expressed in barrer (1 barrer = 10⁻¹⁰ $\frac{cm^3(STP)·cm}{cm^2·cmHg·s}$), while $D$ in $\frac{cm^2}{s}$.

Results and discussion

Scanning Electron Microscope micrographs, reported in figure 1, confirmed the isotropic morphology of the defect-free specimens and their homogeneous thickness, measured by means of a digital micrometer. The surfaces of all membrane samples appear totally defect-free at a magnification of 24000 times.
Figure 1. a) Cross section and b) top view surface of PEEK-WC and PSf film samples, prepared under controlled solvent evaporation in air.

The permeation rate tests were carried out by using different pure gases at atmospheric pressure on feed side in a temperature range of 15-70 °C. As discussed in the previous section, diffusion coefficient was calculated in the same temperature range. The selectivity was calculated as ratio between the permeability values of the species.

The behavior of both transport parameters as a function of the operation temperature is illustrated in figures 2-5.

![Figure 2. Gas permeability vs. the reciprocal of temperature in a PEEK-WC membrane.](image)

By considering that both permeation and diffusion are endothermic processes, a temperature rise produces an increase of P and D for all gases, but in different way. Less permeable species are affected mainly on their permeation rate, whereas gases with a big
kinetic diameter on the diffusion term. As a consequence the selectivity decreases with the temperature. This behavior is observed by both glassy and rubbery polymers.

Since in a semi-log plot of $P$ versus the reciprocal of absolute temperature (K) a linear trend is obtained, it suggests that permeability obeys to the Arrhenius’ law as temperature changes. Similarly also for diffusion coefficient a dependence on temperature of the same time occurs.
In SBS, at both styrene contents, the same permeation rate order, in the whole temperature range, is observed: \( \text{CO}_2 \gg \text{H}_2 \gg \text{CH}_4 \gg \text{O}_2 \gg \text{He} \gg \text{N}_2 \).

On the contrary, the diffusion order is: \( \text{He} > \text{H}_2 > \text{O}_2 > \text{N}_2 > \text{CO}_2 > \text{CH}_4 \), according to the crescent sequence of kinetic diameters except for \( \text{CO}_2 \).

As shown in figure 4, carbon dioxide, the most condensable species with a high affinity for SBS, results the most permeable according to the preponderant role of S for gas separation in elastomers. Therefore, the permeation rate of \( \text{CO}_2 \) is less affected by temperature changes.

In more detail, in SBS\(_{30}\), as operating temperature moves from 20 °C to 60 °C, nitrogen permeability increases of four times, whereas the diffusion coefficient goes up of 3.5 times (see, figure 5). In the same temperature range a similar effect on \( D \) is observed for oxygen, but the absolute increment for \( P \) is lower than for nitrogen (about 3.7 times). On the contrary, carbon dioxide is characterized by a doubling of its permeation rate whereas its \( D \) becomes almost four times higher. Also for methane, solubility coefficient moderates the behavior of \( P \) with the temperature; thus an increase of three times for \( P \) is coupled to an increment of four times for \( D \). As to hydrogen, the same enhancement for \( P \) and \( D \) is observed with the temperature.

![Figure 5. Gas diffusion coefficient vs. the reciprocal of temperature in a SBS\(_{30}\) membrane.](image)

A similar trend has been noticed for the SBS at lower styrene content (21 wt.% SBS\(_{21}\)). By comparing the transport properties of the two SBS polymers, significant differences are determined by the styrene amount. Thus, although both gas permeation and diffusion rates order through the two SBS polymers is the same, at 20 °C SBS\(_{30}\) results less permeable of about 30% with reference to \( \text{N}_2 \), \( \text{CH}_4 \), \( \text{He} \) and \( \text{H}_2 \), while for \( \text{O}_2 \) and \( \text{CO}_2 \) the decrease is close to 40%. As temperature rises, the difference in the permeation rate decreases for all species but in a different way. Thus, SBS\(_{30}\) results less permeable and more sensitive to temperature changes than SBS\(_{21}\).

For what concerns the glassy polymers (PEEK-WC and PSf), the same order of permeation rate is observed: \( \text{H}_2 > \text{He} > \text{CO}_2 > \text{O}_2 > \text{CH}_4 \sim \text{N}_2 \), while the diffusion order is the following: \( \text{He} > \text{H}_2 >> \text{O}_2 > \text{CO}_2 > \text{N}_2 > \text{CH}_4 \). Thus, in these polymers the gases having a small kinetic diameter are more permeable proving that the diffusion coefficient affects the gas
permeation rate more in glasses than in rubbers. Only CO₂, in virtue of a significant contribution of solubility term to the permeability, stands apart this trend resulting faster than oxygen and nitrogen that have a smaller kinetic diameter. Also for these materials carbon dioxide is the gas whose permeation rate is less affected by a temperature change.

Similar permeation values have been measured for PSf and PEEK-WC membranes (figure 2), while the diffusion coefficient in PSf (figure 3) resulted for some species two times higher than in PEEK-WC. As a consequence of the predominant role of the diffusion for gas little soluble (e.g. H₂, He, N₂), the selectivity of these pairs shows an analogous trend to the mobility selectivity as temperature rises. Vice versa when the selectivity of CO₂ to other gases is considered, the contribution of diffusivity to the permeability becomes less important. In fact for both glassy polymers a CO₂/N₂ selectivity ranging from 40 to 15 moving from low to high temperature limits is almost wholly achieved in virtue of differences in solubility, since the diffusion of the two species is practically equivalent.

Conclusions

The gas transport properties in isotropic non-porous membranes based on three amorphous polymers were experimentally determined. Diffusion coefficient of different permanent gases in homogeneous glassy and rubbery polymer membranes, prepared according to the dry phase inversion technique, was calculated by the time-lag method, at a low feed pressure.

Polysulfone and PEEK-WC are characterized by similar permeation rates and selectivity values; also gas diffusion coefficients behave equally as a function of the temperature. However, the absolute values of D in PSf are two times higher than in PEEK-WC.

With reference to the rubbery polymers, the increase of styrene concentration (21 → 30 wt.%) in SBS determines a decrease of permeability and a higher sensitivity to temperature changes. Nevertheless, the gas sequence in terms of permeation and diffusion rates remains the same independently on styrene content.

From the comparison among glassy and rubbery polymers results that less permeable species are more significant influenced by temperature changes; however in the elastomers the diffusive contribution to the gas transport is less important, even if the absolute value of D can be two order of magnitude higher than in glassy polymers.

References