Influence of additives on CO_2 transport in PEEK-WC membranes

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Introduction

The addition of plasticiser agents to a polymer matrix can be considered an efficient way to modify its transport properties. Furthermore these components are suitable to improve the elastic character of the original polymer, to facilitate the multilayer structures preparation, lowering also the cost of the final composite material. In many cases the insertion of small amounts of these additives is the only possibility for a proper combination of an inorganic filler with a glassy polymer in order to tailor its performance for specific gas separations avoiding the adhesion problems at the interface.

Carbon dioxide is one of the main responsible of the greenhouse effect and membrane technology based on polymer materials represents one of the methods more promising for CO_2 separation and recovery. Aim of this work is the combination of the two aspects above described: how CO_2 transport changes after the addition of a plasticizer to a glassy polymer matrix.

Materials and methods

As reference polymer PEEK-WC, an amorphous poly-ether-ether-ketone modified soluble in different organic solvents and therefore suitable to prepare membranes by phase inversion techniques, was used. The choice of this polymer is justified by its high glass transition temperature and very good thermal and mechanical properties combined to interesting gas separation performance [Zhang et al., 1987; Golemme et al., 1994].

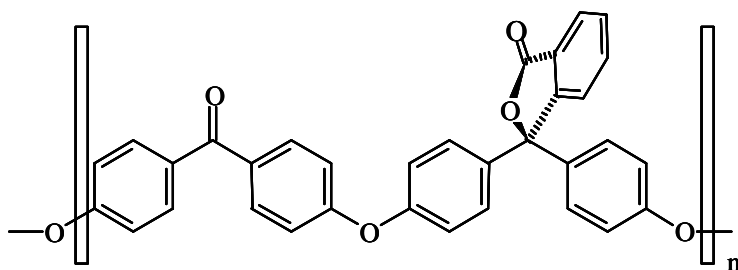In figure 1 the chemical structure of this polymer is reported.

Figure1. Chemical structure of PEEK-WC

Poly-α-pinene (PαP) and poly-β-pinene (PβP) are terpenic resins suitable to improve the handling of stiff materials, with potential applications in the food packaging field [Torchia et al., 2004], while triethylcitrate (TEC) is one of the most common plasticizers used in different applications. Membrane samples used in this study were prepared by casting of a 15 wt% PEEK-WC and additive solution onto a glass plate. Chloroform, the solvent used for all different PEEK-WC-based films, was allowed to evaporate slowly for two days in air at room temperature, then the membranes were dried in a oven under vacuum for at least 12 h at 80°C

in order to remove the residue solvent still contained inside the membrane after the dry phase inversion process.

Permeation rate tests on flat dense membranes were carried out in a 15-65 °C temperature range by using an experimental set-up constituted by a cell thermostated in air, where the upstream and downstream sides are separated by the membrane supported on a macroporous steel disk, fed by means of pneumatic controlled valves with CO_2 from a cylinder (purity level 99.999 vol %). Also the two symmetric parts of the cell are tightened by a pneumatic system controlled via software. The operating principle of the test unit is a pressure measurement (manometric method) and the pressure in feed and permeate sides of the cell is monitored by using two pressure transducers.

Time lag method was applied to determine the CO_2 diffusion coefficient through the PEEK-WC films, with and without additives, according to the simplified equation $D = \dfrac{l^2}{6 \cdot \vartheta}$, obtained considering the expression of the total amount of diffusing substance which permeates through a membrane, initially at zero concentration, in time t, as $t \rightarrow \infty$. [Crank, 1975]. Permeability coefficients were calculated from the slope of time-pressure curve in steady state condition.

Some CO_2 sorption tests were carried out on thick samples (about 200 µm) by using a Mc Bain balance. The equipment is constituted by a chamber, containing the membrane sample hang to a quartz spring, thermostated by a water jacket and a pumping system to evacuate the whole apparatus (chamber, connections and tubes). A rotary pump realises the primary vacuum (up to $5 \cdot 10^{-3}$ mbar), then a diffusive pump completes the operation, increasing the vacuum level in the system to 10^{-6} mbar. This value was assumed as reference for the zero in the sorption tests. The gas is fed to the chamber from a cylinder by means of a short line; a feed-back controller regulates the gas amount inside the chamber on the basis of the pressure measured into the same chamber and compared with a set-point value. The increase of the weight of the membrane sample, completely evacuated at the beginning of the experiment, is observed on a cathetometer equipped with a calibrated scale. Desorption tests were carried out extracting the gas by using the system above described from the sample at fixed equilibrium pressure and temperature values.

Results and discussion

All the additive materials, despite of their differences, determine a change in the mechanical properties of the PEEK-WC, in the morphology of the membranes and in transport properties of the pure polymer.

The surfaces of all membrane samples result completely defect-free at a magnification of 20000 times; the cross section micrographs show an isotropic dense structure for pure PEEK-WC and low additive concentration samples (5 wt %). The presence of additive clusters, due to phase separation phenomena during the solvent evaporation, is observed for PαP and PβP loaded samples when the additive concentration overcomes the 5 wt %. The addition of TEC up to 20% does not reveal any anisotropy or cluster formation inside the membrane structure. Higher TEC concentrations produce voids uniformly distributed within the films.

Each additive, according to its concentration and affinity for the polymer, determines some changes in CO_2 transport properties with respect to the values observed for this species through the pure polymer membranes in the temperature range investigated in this study. A low concentration ($\leq$ 10 wt%) of TEC, the component more similar to PEEK-WC, does not modify the diffusion coefficient (D) of carbon dioxide with respect to pure PEEK-WC. As the

TEC concentration increases, D rises overcoming the value measured for PEEK-WC at high temperature. An analogous trend is observed for PβP, that is the species less similar to PEEK-WC. In this case the differences become remarkable at concentration of 10 wt%.

Concentrations of PαP $\leq$ 10 wt% do not change significantly the diffusion coefficient also at high temperature. However, higher additive amounts cause an important decrease in D (-30%) for temperature values less than 25 °C, whi le diffusivity values close to those of the pure polymer are measured at high temperature.

Apparent activation energy for CO_2 diffusive process was calculated plotting the logarithmic of diffusion coefficient (cm^2s^{-1}) versus the reciprocal of the absolute temperature (K). Thus it is possible to evaluate the influence of a temperature change on the kinetic term of the CO_2 transport. In the figure 2 some representative results for PEEK-WC loaded samples are reported.

A similar analysis developed for the permeation rate has demonstrated how this parameter is extremely influenced by the presence of the additive. Again at low concentration ($\leq$ 5 wt%) no significant differences result; as the additive concentration increases a generalised decrease of the permeability is measured. The level of this variation is much more evident than that observed for the diffusion coefficient. For example for samples characterised by diffusivity values close to PEEK-WC, reductions in permeability up to 30% are measured, while diffusivity differences of 20% are combined to permeability changes of about 50%. Thus the main contribution to the change of the permeation rate must be ascribed to the solubility coefficient.
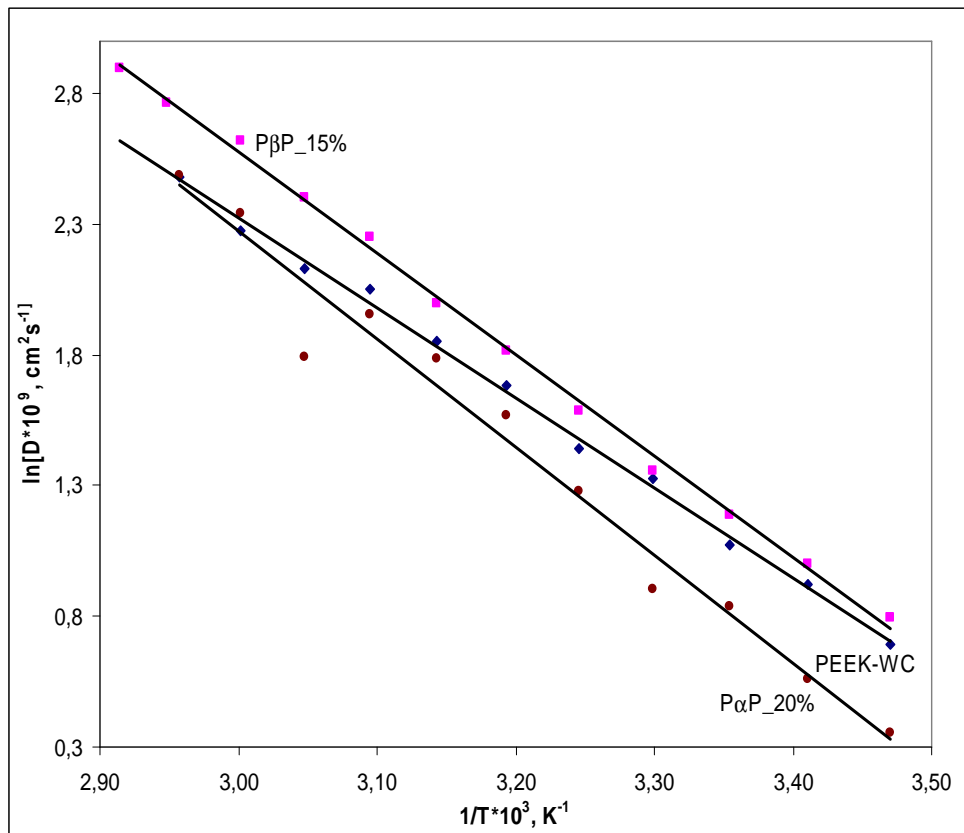

Figure 2. Arrhenius' plot of CO_2 diffusion coefficient vs. the reciprocal of absolute temperature

Sorption/desorption tests confirm how CO_2 solubility is significantly influenced by the presence of these additives, particularly at low temperature values.

Conclusions

In this study the influence of three different additives (TEC, PαP density=0.96 gcm^{-3}, PβP density=0.98 gcm^{-3}) on the carbon dioxide passage through membranes prepared with a modified polyaryletherketone (PEEK-WC) is investigated.

The CO_2 diffusion coefficients measured using time lag method in a wide temperature range (15-65 °C) are not significantly influenced a t very low concentration independently from the additive type; the differences increase as the concentration rises and result more significant for the additives less compatible with the polymer.

Apparent activation energy of the diffusion process for all samples was calculated, suggesting as a proper addition of a specific component could be used to take into account advantageously the influence of the operating temperature.

CO_2 permeation rate is significantly affected by presence of additive demonstrating the importance of solubility term to the global transport of carbon dioxide according to the results of sorption/desorption tests carried out to evaluate changes in the CO_2 uptake as different amounts of the additive were added to PEEK-WC-based films.

References

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