**CO2 sorption and diffusion in Fluorinated polymers for carbon transport application**

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**1.Introduction**

Polymeric materials play a relevant role in the protection for gas transport equipment (such as pipeline, pumps, vessels, compressor..), and they can thus be used in the value chain of Carbon Capture and Storage (CCS), which is considered as the most viable solution to limit the CO2 emission in the atmosphere, with the potential to be applied at short-medium times [1]. Among the various classes of polymers, fluorinated material look promising for their potential application for CO2 transport, either in pipelines or in ship vessels, due to their excellent thermal and chemical resistance [2,3].

This work explores the sorption and diffusion properties of three different fluorinated polymers (PVDF, PTFE and PVF) when they are exposed to Carbon Dioxide, since their industrial applicability is related to their barrier behaviour and their intrinsic mechanical response. In fact, industrial carbon transport chain requires to deal with dense CO2 phases, either in its supercritical or in liquid state, which can affect the performance of the materials due to a physical change in their structure.

**2. Methods**

The materials characterized in this study for the CO2 sorption are three commercial grades of fluorinated-based polymers (Table 1): polyvinylidene fluoride (PVDF), poly-(tetrafluoroethylene) (PTFE) and Polyvinyl fluoride (PVF).

The sorption experiments have been performed at 35°C in a fixed volume and variable pressure system, temperature controlled by a thermostatic bath. The sample is inserted into a cell and connected to a pre-chamber volume where the gas is loaded to the desired pressure. The CO2 solubility in the polymer is then evaluated by considering the pressure variation during the gas absorption in the sample. The gas diffusivity in the polymer matrix is then calculated for each sorption step considering the Fick’s law of diffusion.

The experimental results of CO2 solubility in PVDF, PTFE and PVF have been modelled via thermodynamic model (Lattice Fluid equation of state [4]), whose optimization parameters for the three materials are reported in Table 1, obtained by the resolution of phase equilibrium problem, aiming to be able to predict both gas sorption and transport under different operating conditions. The ultimate goal of this work is indeed to inspect penetrant-polymer characteristic interaction and the polymer behaviour.

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| **Polymer** | **ρ [g/cm3 ]** | **Thickness [µm]** | **App Tg [°C]** | **App Tm [°C]** | **T\* [K]** | **p\* [MPa]** | **ρ \*****[kg/L]** |
| polyvinylidene fluoride (PVDF) | 1.77 | 50 | -35 | 180 | 630 | 620 | 1.79 |
| poly-(tetrafluoroethylene) (PTFE) | 2.20 | 50 | 120 | 330 | 629 | 388 | 2.16 |
| Polyvinyl fluoride (PVF) | 1.44 | 50 | 40 | 200 | 670 | 660 | 1.42 |

**Table 1.** Material properties and optimization parameters (T\*, p\*, ρ\*) for Lactice fluid EoS model [5]

**3. Results and discussion**

The results of the experimental CO2 sorption in commercial PVDF, PTFE and PVF at 35°Care illustrated in Fig. 1 as a function of the pressure. The solubility behaviours observed are linear in all cases, with PVDF showing the larger uptake, followed by PVF and PTFE which results to have the lower solubility.

Their behaviour is then described by the thermodynamic Lactice fluid EoS model (continuous lines), which is able to represent the experimental results, and can be used for predictive purposes at lower temperatures and/or larger pressures. Figure 1b reports the diffusivity coefficient obtained from transient CO2 sorption. In such fluorinated polymers, the diffusion coefficient increases by increasing the CO2 concentration, following an exponential law with CO2 mass fraction, as a direct consequence of the plasticization of the polymer matrix.

 (a) (b)

**Figure 1**. CO2 solubility (a) and diffusivity (b) in PVDF, PVF, PTFE as obtained from sorption experiments and comparison with thermodynamic model for gas sorption

**4. Conclusions**

This experimental work characterizes the CO2 sorption behavior in three commercial polymers PVDF, PTFE and PVF, potentially suitable as materials for CO2 transport process, in view of their use in CO2 transport to ensure the safe deployment of CCS. From the experimental CO2 sorption data at room conditions, following a rigorous physically sound model, it is possible to evaluate thermodynamic and kinetic parameters, such as Solubility, Diffusivity and Permeability. That allows the penetrant-polymer interaction and the effect of dense phase CO2 on polymer-based materials to be understood, as well as proving essential performance information for targeted applications.

Moreover, by fitting those sorption data through a thermodynamic model, based on EoS, it is possible to describe and predict the molecular behaviour of these commercial polymers in wide temperature and pressure ranges, including super-critical conditions, relevant for CO2 transport application, and to evaluate their future use in industrial applications.

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