Carbon dioxide sorption and plasticization in glassy polymers studied at the molecular level

S. Neyertz[1], N.F.A. van der Vegt[2] and D. Brown[1]

[1]LEPMI, UMR 5279, CNRS - Grenoble INP- University of Savoie - University J. Fourier, LMOPS - Bât. IUT, University of Savoie, Savoie Technolac, 73376 Le Bourget-du-Lac Cedex, France
[2]Center of Smart Interfaces, Technical University of Darmstadt, Petersenstrasse 32, 64287 Darmstadt, Germany

Polyimides are of great interest as dense membranes for gas separation since they combine excellent mechanical, thermal, and chemical stabilities with a large range of selectivities.[1] Their permeabilities with respect to small gas penetrants such as oxygen O_2 or carbon dioxide CO_2 are partially governed by the basic dianhydride and diamine motives and the resulting chain chemical structures. However, it is well-known that other parameters influence membrane permeation over the processing stage. Among those, the so-called "skin-effects" are related to the differences between the core and the surface layers of a membrane.

While gas permeation in polyimides has been extensively studied from an experimental point-of-view, there are still in comparison relatively few realistic molecular dynamics (MD) simulations in the literature, with the model densities being in very close agreement ($\leq$ 1-2%) with experimental values. A fully-atomistic and complex representation is required for the glassy polyimides. In addition, MD timescales are much shorter than the typical polymer relaxation times, and specific techniques have to be used to generate pre-relaxed starting chain configurations. Even so, such bulk models, which can be considered as being representative of the membrane core, cannot possibly take into account the skin effects. Recent advances have thus also been made in the preparation of inhomogeneous atomistic films with actual interfaces, which can be considered as being representative of the membrane surface layers.

In this work, we report comparative MD simulations of O_2 and CO_2 transport in a series of both bulk and membrane polyimide models. The matrices under study are ODPA-ODA for O_2 and three fluorinated 6FDA-based polyimides for CO_2.[2-6] Bulk models were generated using the well-documented hybrid pivot Monte Carlo-molecular dynamics (PMC-MD) single-chain sampling procedure,[5,7,8] in which MC pivot moves of rotatable torsions are regularly attempted and the change in local energy is evaluated based on Flory's hypothesis. Membrane models with explicit polymer surfaces were obtained by applying a wall-compression technique designed to mimic the experimental solvent-casting process.[5-7,9,10] The latter exhibited the typical features of surface layers, *i.e.* flattened chain configurations, lower density, surface roughness, and increased mobility at the interfaces.

Following the preparation of the pure polyimide matrices, gas molecules were first inserted into the bulk models. Different concentrations of O_2 showed that the penetrant did not induce any plasticization of the ODPA-ODA matrix. On the other hand, high concentrations of CO_2 (Figure 1a) clearly led to a conditioning of the 6FDA-based matrices over the limited timescale available to MD simulations. As such, the fluorinated polyimides were loaded with CO_2 in increments of 2% up to ~30% in order to mimic an experimental uptake curve. This was then followed by a progressive desorption phase. Issues associated with solubility such as sorption and desorption isotherms, volume changes, plasticization and hysteresis, void spaces or preferential interactions were characterized. The mechanisms underlying gas motion were also studied. The diffusion coefficients were obtained using the recently-developed "Trajectory-Extending Kinetic Monte Carlo" (TEKMC) method,[2,3] which is based on the analysis of the actual trajectories of gas molecules generated by the MD simulations. Providing that enough of the percolating paths through the polymer system are revealed during the limited atomistic MD simulation, TEKMC can, at negligible computing costs, extend the timescale of the penetrant mean-square displacements by several order of magnitudes. It thus allows the prediction of the penetrant self-diffusion coefficient for systems such as the ones studied here where the Fickian regime is difficult to reach with MD simulations.
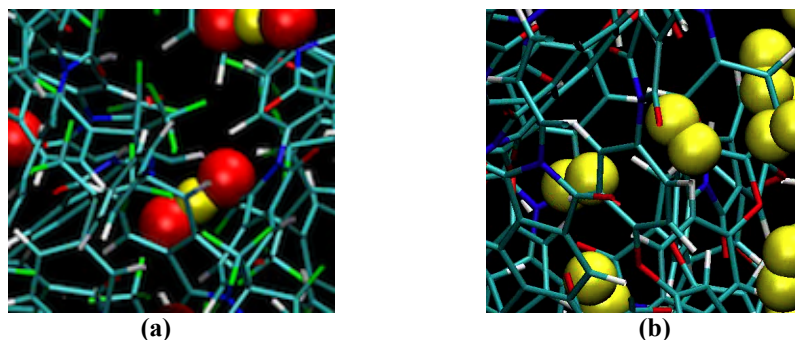
(a)   **(b)**

Figure 1:   **(a)** CO_2 molecules in a bulk 6FDA-6FmDA matrix and **(b)** O_2 molecules at the interface of an ODPA-ODA matrix

In order to complement the bulk model studies, gas sorption and diffusion at the polymer interface were addressed using the aforementioned membrane models. O_2 transport at an ODPA-ODA surface (Figure 1b) was studied under different conditions of applied external gas pressure. The concave uptake *vs* pressure behavior for low-solubility penetrants was well reproduced and the initial gas uptake was found to be linked to two distinct mobility modes. Due to a strong chemical potential gradient, the penetrants first undergo a rapid adsorption at the polymer surface, which results in a complete saturation of the interfacial region and the establishment of a dynamic equilibrium with the gas phase. This is followed by a second slower and diffusion-limited uptake mode. Although the O_2 uptake *vs* pressure curves could be well described by the popular dual-mode (DMS) sorption model,[11] no evidence of two different populations of sorbed species was found at the molecular level. Boltzmann-weighted probability densities of test-particle insertion energies were described by single Gaussian distributions, thus supporting the site-distribution (SD) model.[12,13] We will also present new results obtained for the sorption and diffusion of CO_2 in 6FDA-based membrane models with explicit surfaces. In addition to the bulk *vs* surface layer characterizations, this will allow us to compare the behaviour of a non-plasticizing gas such as O_2 with that of a plasticizing gas such as CO_2 in the vicinity of a polymer membrane surface.

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