www.elsevier.com/locate/memsci

Nanosecond-Time-Scale Reversibility of Dilation Induced by Carbon Dioxide Sorption in Glassy Polymer Membranes

Sylvie NEYERTZ, David BROWN

PII: S0376-7388(16)30406-9
DOI: http://dx.doi.org/10.1016/j.memsci.2016.08.003
Reference: MEMSCI14653

To appear in: *Journal of Membrane Science*

Received date: 18 May 2016
Revised date: 13 July 2016
Accepted date: 3 August 2016

Cite this article as: Sylvie NEYERTZ and David BROWN, Nanosecond-Time Scale Reversibility of Dilation Induced by Carbon Dioxide Sorption in Glassy Polymer Membranes, *Journal of Membrane Science*, http://dx.doi.org/10.1016/j.memsci.2016.08.003

Nanosecond-Time-Scale Reversibility of Dilation Induced by Carbon Dioxide Sorption in Glassy Polymer Membranes

Sylvie NEYERTZ*, David BROWN

[1]Univ. Savoie Mont Blanc, LEPMI, F-73000 Chambéry, France

[2]CNRS, LEPMI, F-38000 Grenoble, France

*Corresponding author: sylvie.neyertz@univ-smb.fr, postal address: LEPMI(LMOPS), CNRS UMR 5279, University Savoie Mont Blanc, Bât. Hélios/INES, Savoie Technolac, 73376 Le Bourget du Lac Cedex, France. Tel.: +33 4 79758697, fax: +33 4 79758614

ABSTRACT

Many models have been proposed to describe the sorption isotherms of small gases in glassy polymers at equilibrium. However, the sorption kinetics to reach this equilibrium are dependent on the nature of the penetrant and the swelling of the matrices. In the present work, large-scale molecular dynamics (MD) simulations are used to describe CO_2 sorption-induced dilation kinetics at very short time scales in 6FDA-6FpDA polyimide membranes. The latter are subjected to two cycles of CO_2 sorption and post-degassing relaxation, which mimick the sorption-degassing experiments with large integral pressure steps. The glassy membranes dilate during sorption, mainly because of an increase in the longitudinal strain. Upon degassing, they systematically relax to a metastable state, with some residual extra-volume and improved solubility for the penetrant, which depends on the swelling behaviour history. These subtle changes agree with the qualitative model based on variations in the relative fractions of Fickian and relaxational dilation sites as a function of the swelling history. Both sorptions also exhibit differences at very short times, with a enhanced void-space and concentration of CO_2 sorbed along with a lower