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SciVerse ScienceDirect
Procedia Engineering 44 (2012) 468 – 469
Procedia Engineering
www.elsevier.com/locate/procedia

Euromembrane Conference 2012

[OC45]

Carbon dioxide sorption and plasticization of thin glassy polymer films tracked by gas permeability and optical methods

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Thin glassy polymer films respond to highly-sorbing penetrants, such as CO_2, quite differently than thick films. Studies focused on CO_2 permeation behaviour have revealed that, for thin films, CO_2 permeability at constant CO_2 pressure goes through a maximum followed by a continual decrease in permeability owing to physical aging (Figure 1). This behaviour was not observed for thicker films over comparable experimental timescales. Thick and thin glassy polymer films can be compared in the context of gas permeability, but lack of substantial means of obtaining thin film sorption data has historically prevented adequate comparison of thick and thin films in the context of gas solubility. In this work, spectroscopic ellipsometry is used to obtain simultaneously the film thickness and CO_2 sorption capacity for thin glassy polymer films, allowing a more comprehensive look at CO_2 permeability, sorption, and diffusivity as a function of both CO_2 pressure and exposure time. The ellipsometry results suggest that thin film sorption behaviour is substantially different than that of thick film counterparts. Partial molar volume is determined from sorption-induced swelling data. Fractional free volume and diffusivity are calculated as a function of CO_2 pressure. Dynamic ellipsometry experiments show that refractive index minima, fractional free volume maxima, and CO_2 diffusivity maxima correlate well with observed CO_2 permeability maxima observed for thin Matrimid® films (Figure 2). The permeability and optical data support the claim that plasticization and physical aging are competing processes but that aging dominates over long time scales. The CO_2 diffusivity behaviour over time is most affected by the competing effects of plasticization and aging, and the evolution of CO_2 diffusivity is shown to be the main contributing factor to changes in CO_2 permeability at constant pressure.

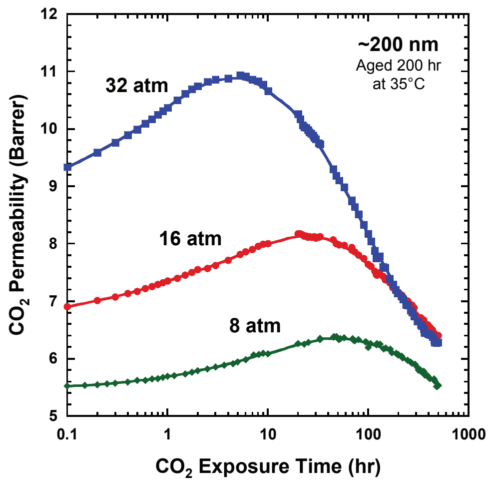

Figure 1: Effect of long-time CO_2 exposure at constant pressure upon CO_2 permeability for Matrimid® thin films with similar thickness and prior thermal history.

doi:10.1016/j.proeng.2012.08.452

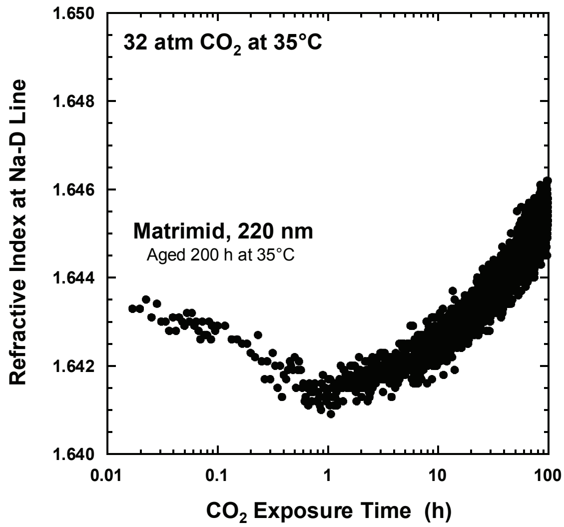

Figure 2: Effect of long-time CO_2 exposure at constant pressure upon the refractive index of a 220 nm Matrimid® thin film aged 200 h at 35°C.

Keywords: physical ageing, plasticization, carbon dioxide, thin films