AGING OF POLYMERS OF INTRINSIC MICROPOROSITY STUDIED BY SORPTION AND PERMEATION

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Key Words: physical aging, polymer of intrinsic microporosity, gas sorption, vapor permeation.

Polymers of intrinsic microporosity (PIMs)[1] seem to be effective materials for gas and vapor separations.[2] However, gas separation efficiency of PIMs can be strongly influenced by the material aging process connected with the changes of PIMs inner structure.[3] With respect to potential industrial applications, the investigation of such changes and their effect on gas and vapor transport is necessary. In this work, we present a detailed study of i) CO_2 sorption in PIM-1 *via* momentary measurements during four years and ii) methanol permeation in PIM-1[1] and EA-TB-PIM[2] *via* continuous and momentary experiments. Sorption experiments were performed gravimetrically using a self-developed apparatus equipped with McBain's spiral balances. In this case, PIM-1 membranes were pre-treated (soaking in ethanol with consequent drying at different temperatures) in order to study the influence of temperature on PIM-1 aging. Methanol permeation experiments were performed using a differential flow permeameter with H_2 and He as carrier gases. Permeation experiment were performed with PIM-1 and PIM-EA-TB methanol treated membranes. CO_2 sorption measurements revealed that, assuming the validity of the solution-diffusion model, the decrease of permeability during aging can be attributed directly to the decrease of diffusivity, whereas solubility is time independent in the studied period of four years. Although higher preparation temperature led to the initial drop of diffusivity, this process stabilized separation performance of PIMs over time (Figure 1). MeOH permeation experiments confirmed previous findings from CO_2 tests, that the permeability decrease during the aging is a diffusivity controlled process. Moreover, it was found that the momentary permeation data can be mathematically transferred to continuous data, which are more relevant for applications but more difficult to measure. The nature of aging process was studied by infrared spectroscopy. We have found that aging of PIMs does not influence their chemical structure and; therefore, they undergo only the so called physical-aging.

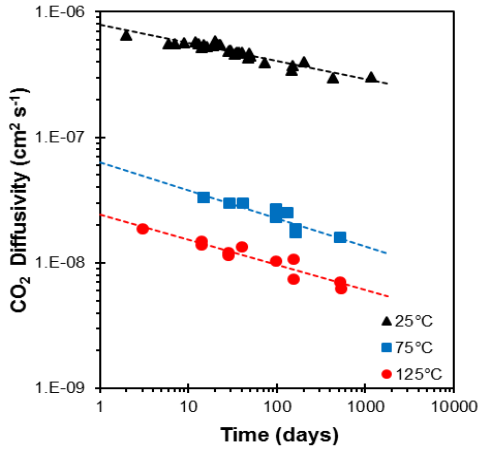

Figure 1 – Time dependency of CO_2 diffusion coefficient in PIM-1 during physical aging. Temperature refer to the different treatment history of samples.

Acknowledgement: Parts of the work leading to these results have received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement no. NMP3-SL-2009-228631, project DoubleNanoMem. The financial support of the Czech Science Foundation (Grant No. P106/10/1194 and 13-32829P) and financial support from specific university research (MSMT 20-SVV/2016) is greatly acknowledged.

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