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Aging of polymers of intrinsic microporosity tracked by methanol vapour permeation

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Abstract

The initially very promising transport properties of glassy high free volume polymers deteriorate rapidly over time. In this work, we focused on this aging phenomenon in two polymers of intrinsic microporosity (PIMs), namely PIM-1 and PIM-EA-TB. To identify the main mechanisms involved, we studied the time-declines of permeability and diffusivity of methanol vapours in flat membranes with approximately equal thicknesses. The permeation measurements were carried out using a continuous flow permeation method with carrier gas, where the methanol vapours were held at constant activity 0.2 at 25°C. Two different experimental modes were used: (i) continuous experiments that consisted of one long experiment with a duration of over 650 hours for each polymer and (ii) momentary experiments that consisted of a vast number of short (*ca.* 6 hours) consecutive measurements of transient permeation. The observed decreases of methanol permeability due to aging were more intense in the case of continuous mode for both polymers. In other words, the aging was *ca.* 1.3 times faster in the continuous mode in comparison with the