## Effect of Water vapor in polymer with Intrinsic Microporosity for carbon capture applications

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The present study investigates the impact of relative humidity on the permeability and selectivity of three polymers with intrinsic microporosity (PIM), namely PIM-EA-TB, PIM-SBF, and AO-PIM-1. To that aim single gas permeation tests were conducted at 25°C and 1 bar with nitrogen and carbon dioxide with different humidity levels, from 0 up to 80%. The effect on polymer ageing was also considered, while water sorption was measured independently to correlate relative humidity to the water content in the membrane. Results indicate that water vapor strongly affects the permeability of the three materials. On one side, a drastic decrease of CO<sub>2</sub> permeability, higher than 90%, was observed for all the polymer increasing the gas relative humidity. In addition to that, in the case of PIM-EA-TB and PIM-SBF, permeability was not completely recovered after test due to irreversible changes caused by aging. After three permeation runs the permeability of dry CO<sub>2</sub> decreased, from 2285 to 249 Barrer and from 4070 to 1150 Barrer for PIM-EA-TB and PIM-SBF respectively. In AO-PIM-1, on the other hand, dry gas permeability remained substantially unchanged even after exposure to water vapor. The same behaviour was also observed in sorption experiments which showed a strong decrease of water uptake in subsequent tests for PIM-EA-TB and PIM-SBF while smaller reductions were observed for AO-PIM-1. CO<sub>2</sub>/N<sub>2</sub> selectivity was in the order of 10 and 25 for the PIM-EA-TB and PIM-SBF and remained substantially unchanged during the tests, while for AO-PIM-1 a more than two-fold increase was observed, from about 40 to more than 100, when relative humidity was increased from 0 to 80%. This increase, coupled with a CO<sub>2</sub> permeability still higher than 200, allowed this polymer to surpass the 2019 Robeson's plot for the  $CO_2/N_2$  gas pair.

Keywords: PIMs, Humid gas permeation, Water vapor sorption, Carbon capture

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