Exploring sustainable alternatives for gas separation: testing and molecular screening of membranes from biopolymers and green solvents

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Abstract:

The gas separation performance of biopolymers is still scarcely characterized, mostly because of their poor thermomechanical properties and high crystallinity which is associated to low permeability.
In this work we characterized the gas transport in a poly(hydroxybutyrate-co-hydroxy valerate) (PHBV) random copolymer, that has a relatively low crystallinity and good mechanical properties, combined with a renewable origin, biodegradability and biocompatibility. In the study we also compared several solvents for membrane casting, with different toxicity levels. We found that dimethyl carbonate allows to produce polymer films with transport properties similar to those obtained with the more toxic chloroform, and also allows to stabilize the crystallinity of the samples over time. PHBV films show a size-sieving gas separation behaviour, as the permeability decreases significantly with the gas kinetic diameter. However, the strong energetic interactions of CO_2 with the polymer matrix, confirmed by the Flory-Huggins model, induce a marked solubility-driven CO_2/N_2 and CO_2/CH_4 selectivity, lying between 26 and 46,which could make the material suitable for CO_2 removal processes. The solubility-based separation is particularly promising because it is founded on energetic interactions rather than on the polymer morphology, in particular its crystallinity. Therefore, a modification that would allow to lower the polymer crystallinity would also enhance the permeability without negatively affecting the selectivity. The results were compared to other biodegradable polymer commercially available, like Polylactic acid (PLA) which show similar performance but slightly lower selectivity, and placed in a Robeson's plot for the CO_2/N_2 and CO_2/CH_4 separation.
To accelerate the deployment of sustainable materials for gas separation applications, we performed a molecular screening of a wide range of copolymer formulations based on the poly hydroxy alkanoate (PHA) chemistry, which allowed to identify the biopolymer membranes that are potentially lying on the Robeson's upper bound for the CO_2/CH_4 couple.

Keywords: gas separation, biodegradable membranes, green solvents, molecular simulations