Microporous Polymer–Metal Organic Framework (MOF) Hybrid Materials for Separations

by

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Membrane-based separation holds significant promise for reducing the high energy consumption associated with traditional thermal-based separation processes in the chemical industry. Recent advancements in microporous materials, such as polymers of intrinsic microporosity (PIMs) and metal-organic frameworks (MOFs), have demonstrated performance improvements over conventional polymers. Mixed-matrix membranes (MMMs) have emerged as a potent strategy, combining the processability of polymers with the superior separation properties of MOFs to create high-performance membranes. Additionally, the integration of MOFs into polymers can mitigate stability issues such as plasticization, swelling, and physical aging. This thesis investigates MMMs based on PIM-1 and its derivatives, along with UiO MOFs, for gas and organic solvent-based separations. The studies focus on enhancing polymer–MOF interfacial compatibility, understanding penetrant transport, and addressing key challenges in MMM design and fabrication.

A longstanding challenge with MMMs fabrication is poor polymer–MOF compatibility, leading to particle agglomeration and non-selective interfacial voids. To address this, the strategy of decorating polymers and MOFs with compatible functional groups was explored. By studying UiO-66-NH_2 MOF and carboxylic acid-functionalized PIM-1 (PIM-COOH), it was demonstrated that MMMs with compatible functional groups exhibit enhanced polymer–MOF interaction and plasticization resistance. To further understand transport within these MMMs, self-diffusivities of gases were measured using pulsed-field gradient nuclear magnetic resonance and compared to macroscopic diffusivities obtained from permeation and sorption analysis. The PIM–MOF material platform was also extended to solvent-based separations. To understand solvent transport through microporous polymers, intrinsic properties of swollen polymers were obtained both experimentally and computationally, and these properties were correlated with solvent transport metrics. Finally, MMMs composed of PIM-COOH and UiO MOFs with systematically increasing pore apertures were evaluated for their solvent nanofiltration performance. Key challenges such as MOF instability and non-ideal polymer–MOF interfaces were identified. In summary, this thesis delves into the structure-property relationships of microporous materials for gas and solvent-based separations, offering insights that can guide the future design of advanced composite membranes for challenging separations.

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