Polymer-Metal–Organic Framework Mixed-Matrix Membranes for Gas Separation Applications

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Abstract

Metal–organic frameworks (MOFs) represent the largest known class of porous crystalline materials ever synthesized. Their narrow pore windows and nearly unlimited structural and chemical features have made these materials of significant interest for membrane-based gas separations. Mixed-matrix membranes (MMMs) formed by incorporating MOF particles into polymers have attracted significant attention because these composite systems can potentially surpass the separation performance of pure polymers alone. However, performance improvements are often unrealized because of poor interfacial compatibility between the MOF and the polymer, which results in interfacial defects. From a practical perspective, strategies are needed to address these defects so that MMMs can be deployed in real-world separation processes. From a fundamental perspective, strategies are needed to reliably form defect-free MMMs so that transport models can be applied to estimate pure-MOF property sets, thereby enabling the development of robust structure–property relationships. To address these interfacial challenges, this thesis describes a developed method to surface functionalize MOFs with nanoscopic shells of covalently tethered oligomers through various imidization routes. Upon embedding these post-synthetically modified (PSM) MOFs in high molecular weight polymers, defect-free MMMs were formed, revealing synergistic improvements in both permeability and selectivity due to enhanced interfacial compatibility. Additionally, pure-MOF permeabilities for various gases were predicted by the Maxwell Model. The PSM technique developed initially was further developed to address its generalizability to various MOFs, oligomer surface reactions, reaction conditions, and polymer compositions, providing robust guiding principles to form MMMs with excellent polymer–MOF interfacial compatibility. Finally, the potential of a novel MOF, MFU-4, as a filler in MMMs for $CO_2/H_2S/CH_4$ separation was studied by dispersing the MOF in high molecular weight polymers. To validate a CO_2-driven gate-opening mechanism proposed by other researchers earlier, a systematic temperature study of diffusion, sorption, and permeation through an MFU-4/polyimide MMM was carried out. Separation performance of the MMM did improve with decreasing temperatures, however, no obvious evidence of the gate-opening mechanism was found under the conditions tested.