Modular Chemical Functionalization of External Surfaces of Porous Metal-Organic Framework Filler Particles for Optimization of Interfacial Properties in Mixed Matrix Membranes

The following two research objectives were formulated to optimize the interface between polymer and particles in MMMs and improve MMM separation performance. Develop modular methods for attaching chemical moieties to the exterior surfaces of MOF filler particles in order to control the interactions between the polymer and the particle. Then, prepare MMMs using the chemically-modified MOF filler particles; characterize polymer particle interface using a suite of characterization methods; and evaluate MMM performance as a function of MOF external surface modification.
Benefits:
The team has developed new methods for finely controlling the external surface chemistry of porous MOF particles and has demonstrated how this chemistry influences polymer-MOF interactions within a MMM. Further, they have demonstrated how MOF external surface chemistry can influence MMM physical properties and performance in gas separations. These intellectual outcomes will allow for optimization of polymer-particle interfaces for gas separation applications, in particular the separation of CO\textsubscript{2} from flue gas streams. Additionally, the developed tools, materials, and understanding can benefit multiple areas of research that focus on the design and development of MMMs for applications ranging from molecular separations to personal protection to controlled release of molecular therapeutics.

Accomplishments:
The team has established a facile methodology for systematically tuning the exterior surface of UiO-66, which relies on a simple, one-step modification strategy using commercially available benzoic acid derivatives and no additional reagents. They prepared a suite of narrow particle-size distributions and subsequently controlled the identity and density of functional groups on the external surface of these particles. In one case, they demonstrated how this strategy can be used to stabilize suspensions of MOF nanoparticles in a hydrophobic solvent. They then demonstrated how the amine-functionalized particle could enhance the performance of MMMs based on PIM-1 and MEEP80. The ability to independently tune particle size and surface chemistry in this way opens the door for high through-put iterative studies aimed at optimizing MOF particles for various applications including gas separations (MMMs) and drug delivery.

NETL Collaboration:
Both the PI and the lead student researcher (Patrick Muldoon) attended bi-weekly meetings at NETL that focused on the preparation, testing, and development of MOF-based mixed-matrix membrane materials. The researchers interfaced and communicated weekly with several NETL researchers who were in charge of polymer preparation and membrane testing. Team members regularly supplied NETL with MOF particles for incorporation into membranes.

Relevant Publication: