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14. ABSTRACT

A series of styrene/butadiene polymers were combined with up to 90 wt% UiO-66(Zr) to form mixed-matrix membranes with varying physical properties. Notably, polystyrene-block-polybutadiene membranes retained both the processability and flexibility of the native polymer component and the porosity, chemical tunability, and adsorption performance of the native MOF.

15. SUBJECT TERMS

metal-organic frameworks, mixed-matrix membranes, toxic industrial chemicals

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Report Title

Final Report: MOF-based Mixed-Matrix Membranes for Hazardous Chemical Capture

ABSTRACT

A series of styrene/butadiene polymers were combined with up to 90 wt% UiO-66(Zr) to form mixed-matrix membranes with varying physical properties. Notably, polystyrene-block-polybutadiene membranes retained both the processability and flexibility of the native polymer component and the porosity, chemical tunability, and adsorption performance of the native MOF.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper

TOTAL:

Number of Manuscripts:

Books

Received	Book

TOTAL:

Received	Book Chapter

TOTAL:

Patents Submitted

Metal-Organic Framework-Polymer Mixed-Matrix Membranes and and a Preparation Method Thereof

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Jessica C. Moreton	1.00	
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Seth M. Cohen	0.00	No
FTE Equivalent:	**0.00**	
Total Number:	**1**	

Names of Under Graduate students supported

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Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

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Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

Statement of the problem studied

The goal of this project was to identify polymers that form stable, flexible, and well dispersed mixed-matrix membranes (MMMs) with metal-organic frameworks (MOFs). Polymers were sought that had good interactions with the MOF particles such that the polymers acted as strong binders, giving MMMs with high loadings of MOF particles and whose properties were dominated by those of the MOFs.

Summary of the most important results

The most important results obtained are well summarized in the manuscript draft provided with this final report that will be submitted to *Chemical Communications* shortly. These results were obtained primarily by Ms. Jessica C. Moreton, a 3rd-year graduate student working on this project, with assistance from Michael S. Denny, Jr. a more senior (5th-year) graduate student that initiated the project on MMMs in my laboratory.

As summarized in the manuscript draft, three polymer binders were explored: pure polystyrene (abbreviated **PS**, M_w = 35,000 g/mol), a polystyrene and polybutadiene block copolymer (**SBS**, M_w = 97,000 g/mol), and a random copolymer of styrene and butadiene (**SBR**, M_w = 270,000 g/mol). The polymers were chosen for because they are commercially available and have well established processing conditions and broad industrial uses. **PS** can be melted, extruded, and foamed, providing a plethora of form factors for a MOF-based MMM. Styrene/butadiene copolymers are broadly used as binder-type elastomers that could offer flexibility to a MMM.

Films of **PS**, **SBS**, and **SBR** could be readily formed by casting a polymer solution onto a substrate and removing the solvent by evaporation. These MOF-free membranes displayed varying physical properties from highly brittle (**PS**) to tacky and stretchable (**SBR**), indicating that a range of MMM physical properties could be obtained with these polymers. Given the few examples of polystyrene/MOF MMMs in the literature, a thorough investigation of these polymers in combination with MOFs was undertaken. For the MOF component, UiO-66(Zr) was used as a model system for forming MMMs. UiO-66(Zr) particles with diameters of ~200 nm with a truncated, rounded octahedral habit were used for this study. The MOF particles were characterized by scanning electron microscopy (SEM), powder X-ray diffraction (PXRD), and porosity was assessed by N_2 sorption.

MMMs were fabricated by preparing two solutions, one with the MOF component and the other with the polymer component. Mixing the two solutions and casting a combined MOF and polymer solution (a viscous MOF/polymer 'ink') onto an aluminium foil substrate, followed by draw-down coating (500 µm blade height), and heating to remove the solvent by evaporation gave the best films. Upon drying in a 55°C oven for 15 minutes the films could be delaminated from the substrate upon cooling.

All MMMs showed excellent retention of the MOF crystallinity as assessed by PXRD. Cross-section images obtained by SEM show retention of the MOF particle morphology within the membranes as well, further confirming that no significant changes to the structure of the MOF occur upon incorporation into the MMM. Importantly, no apparent macrovoids were observed in the SEM images, suggesting good adhesion between the MOF and the polymer. In contrast to earlier studies published from our group using PVDF as the polymer component, N_2 sorption analysis revealed all membranes with <70 wt% MOF to be non-porous. At ≥70 wt%, the surface area of the MOF is partially recovered and type I isotherms are observed that are characteristic of native UiO-66(Zr).

Physically and mechanically, the MMMs resemble their pure-polymer counterparts. At the thicknesses studied (roughly 50-100 µm) **PS** MMMs were extremely brittle, while **SBR** versions were plastic and deformed readily upon delamination; only films with high MOF loadings (70%) in **SBR** kept their shape upon physical manipulation. **SBS** MMMs delaminated easily and held up well to bending and manipulation at all MOF contents tested. Mechanical testing on **SBS** MMMs reveal a tensile strength maximum at 50 wt% MOF, although all MMMs up to 70 wt% MOF showed a higher tensile strength than the pure polymer. There is a decrease in elastic modulus seen with increased MOF loading from 50 wt% to 70 wt%, consistent with other polymer/filler systems and the process of 'chain rigidification' that occurs as filler content increases in an organic/inorganic MMM system. However, as with ultimate tensile strength, all MMMs tested maintained higher elastic moduli than the native polymer.

Given the overall mechanical superiority of **SBS** MMMs, further studies were conducted to assess the chemical reactivity and accessibility of the MOF within this membrane. The chemical reactivity of the MMM was assessed by postsynthetic modification (PSM) and exchange (PSE) reactions. MMMs fabricated from 80 wt% UiO-66(Zr)-NH_2 were immersed in neat acetic anhydride for 1 d at 55 °C, washed with copious amounts of solvent, and analysed by ^1H NMR. A ~47% conversion of UiO-66(Zr)-NH_2 to UiO-66(Zr)-AM1 was observed, which is comparable to that achieved with the native MOF. PSE experiments were carried out with UiO-66 MMMs immersed in solutions of 2-aminoterephthalic acid at room temperature for 5 d, followed by copious washing. PSE was also successful, achieving ~17% exchange of terephthalic acid for the amine-functionalized linker.

Overall, this project demonstrates that SBS is a viable alternative polymer binder to PVDF for forming MOF-based MMMs. This expands the scope of polymers that can be used to transform MOFs into more useful, processable form factors.

Bibliography

See attached manuscript draft: J. C. Moreton, M. S. Denny, Jr., and S. M. Cohen* "*High MOF loading in mixed-matrix membranes utilizing styrene/butadiene copolymers*" **2016**, in preparation for submission to *Chemical Communications*.