Metal-Organic Framework-Inspired Metal-Containing Clusters for High-Resolution Patterning

CNF Project Number: 2751-18

Principal Investigator(s): Christopher Kemper Ober
User(s): Emma Hester

Affiliations(s): Department of Materials Science and Engineering, Cornell University

Primary Source(s) of Research Funding: Office of Naval Research (ONR)

Contact: cko3@cornell.edu, egh66@cornell.edu

Research Group Website: https://ober.mse.cornell.edu/index.html

Primary CNF Tools Used: Molecular Vapor Deposition (MVD), Atomic Force Microscope (AFM)

Abstract:

In order to treat surfaces for resistance of a wide range of marine organisms, surface chemistry, physical properties, durability, and attachment scheme must all be considered in the synthesis and design of a coating. By synthesizing a hydrophobic polymer backbone and modifying it to contain different functional groups with varying degrees of hydrophilicity, it is possible to achieve an overall amphiphilic material that is resistant to settlement and will promote removal of certain marine species. Surface characterization of these thin films suggests that buffered and zwitterionic species are capable of interfering with calcareous and non-calcareous foulers.

Summary of Research:

PS-PVMS is a block copolymer that was synthesized to high purity using a method previously established by the Ober group [1]. The polymer contains a vinyl group that is reactive and is later utilized in thiol-ene click chemistry in order to attach different chemical functionalities that are thought to be useful in generating antifouling and foul resistant surfaces. The following buffers were synthesized (Figure 1) with corresponding water contact angles. Generally speaking, the goal is to have more hydrophilic character as most foulers are more attracted to hydrophobic materials. In this case, however, it was found that the more hydrophobic materials better resisted fouling.

The process of coating the slides starts with molecular vapor deposition of a thin single layer of APTMS on piranha cleaned slides. This prepares the substrate for the following layers: Ma-SEBS, SEBS, and finally, the PS-PVMS modified antifouling coating. (Figure 2). With the addition of each layer, water contact angle is once again measured prior to addition of the following layer. Ma-SEBS and SEBS are thermally annealed to the surface post drying in a 120°C oven for 12 hours, which helps with thermal stability and increases the durability of the materials in the water. The final layer is then spray coated on to the surface. Synthetic methods adapted from [2-4].

AFM was used to characterize the surface morphology of each of the coatings. AFM gave a better idea of the uniformity of the coatings (Figure 3). In the images it was noted that ImZ-PVMS had some crater-like formations. It is not totally clear what caused this, but it is important to note as this can impact the results of fouling. One theory is that because the permanent zwitterionic imidazole group contains two opposite charges within a close proximity to one another, it is possible that intermolecular entanglement becomes higher resulting in an overall rougher surface [5].

References:

[1] Zhang, Z.; Chaudhuri, K.; Kaefer, F.; Malanoski, A. P.; Page, K. A.; Smieska, L. M.; Pham, J. T.; Ober, C. K. Controlling Anti-Penetration Performance by Post-Grafting of Fluorinated Alkyl Chains onto Polystyrene-block-poly(vinyl methyl siloxane). ACS Applied Materials and Interfaces 2024, 16(15).

[2] Leonardi, A. K.; Medhi, R.; Zhang, A.; Düzen, N.; Finlay, J. A.; Clarke, J. L.; Clare, A. S.; Ober, C. K. Investigation of N-Substituted Morpholine Structures in an Amphiphilic PDMS-Based Antifouling and Fouling-Release Coating. Biomacromolecules 2022, 23, 2697–2712.

[3] Leonardi, A. K.; Ober, C. K. Polymer-Based Marine Antifouling and Fouling Release Surfaces: Strategies for Synthesis and Modification. Annu. Rev. Chem. Biomol. Eng. 2019, 10, 241–264.

[4] Leonardi, A. K.; Zhang, C; Düzen, N.; Aldred, N.; Finlay, J. A.; Clarke, J. A.; Clare, A. S.; Segalman, R.; Ober, C. K. "Amphiphilic nitroxide bearing siloxane-based block copolymer coatings for enhanced marine fouling release", Appl. Mater. Int., (2021), 13(24), 28790-28801

[5] Lin, C. H.; Luo, S. C. Zwitterionic Conducting Polymers: From Molecular Design, Surface Modification, and Interfacial Phenomenon to Biomedical Applications. Langmuir 2022, 38(24), 7383-7399.

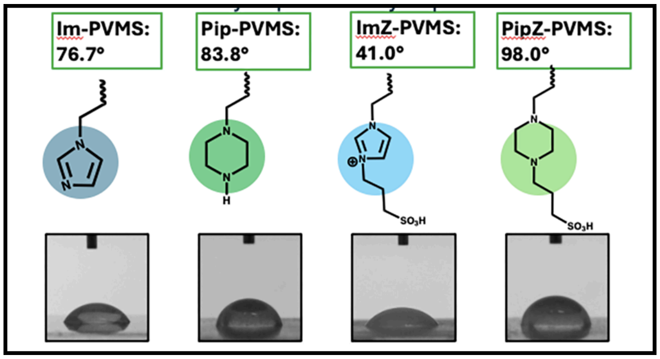

Figure 1: Four buffers were synthesized and attached to a PS-PVMS backbone via thiol-ene click chemistry. Once adhered, corresponding water contact angles were measured to gauge effectiveness of reaction and to test surface presence.

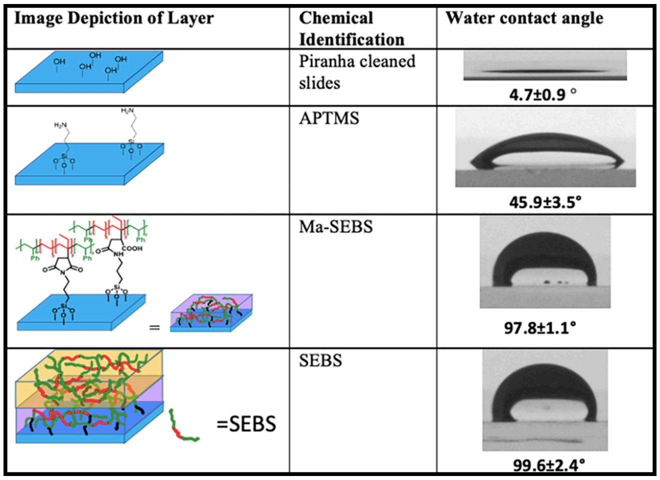

Image Depiction of Layer	Chemical Identification	Water contact angle
	Piranha cleaned slides	4.7±0.9 °
	APTMS	45.9±3.5°
	Ma-SEBS	97.8±1.1°
	SEBS	99.6±2.4°

Figure 2: Visual depiction of each layer and water contact angles post adhesion/thermal annealing.

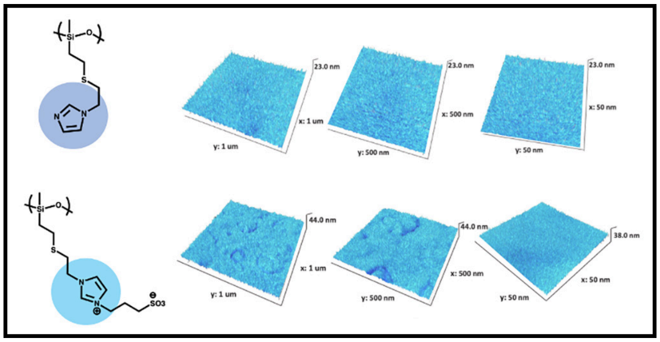

Figure 3: Imidazole family of buffered PS-PVMS AFM surface characterization.

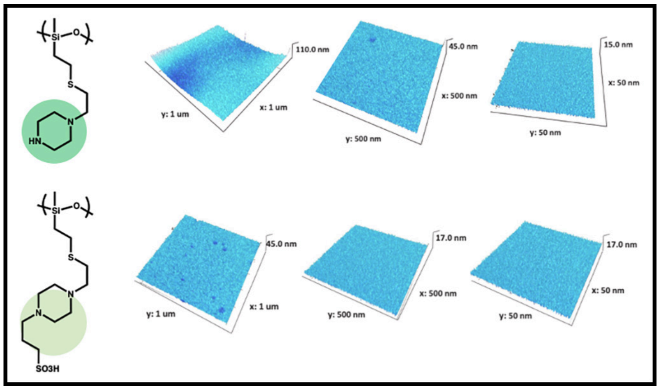

Figure 4: Piperazine family of buffered PS-PVMS AFM surface characterization.