SILICONE POLYMER FOR ANTIFOULING/FOULING RELEASE MARINE COATING APPLICATION

Seok-Bong Choi,[*,1] *John Jepperson,*[1] *Johnson Thomas*[1], *Laura Jarabek,*[1] *Bret Chisholm,*[1] *and Philip Boudjouk*[2]

[1]Center for Nanoscale Science and Engineering
1805 Research Park Drive, North Dakota State University
[2]RCATT, 1735 Research Park Drive, NDSU
Fargo, ND-58105, Tel: (001) 701 231 5326.
Sb.Choi@ndsu.edu

Introduction

Biological fouling of surfaces exposed to an aquatic environment such as ship hulls and offshore marine structures is a serious problem. For example, biofouling on ship hulls reduces ship speed, maneuverability, and range, which impede mission performance[2]. Fouling, thus, has serious consequences for high ship fuel consumption by as much as 30 – 40% and necessitates extensive maintenance, which raises the overall costs of operation.

Traditionally, two parallel lines of coatings research and development aimed at reducing bio-fouling have predominated: biocide containing coatings and low surface energy, "non-stick", foul-release coatings. Each of these approaches has produced elements of success but continue to have serious problem areas, which demand solutions. Interestingly, while aimed at solving the same problem, these two lines of R & D have had a minimum of overlap.

Biocidal coatings contain metal or organic compounds (e.g., organotin or copper compounds) toxic to fouling entities and hence, deter settlement on the hull surface. Unfortunately, in spite of high effectiveness of these coatings at reducing hull fouling,[1] the application of biocidal coating materials has been significantly diminished by the International Maritime Organization due to the unfavorable environmental problems.

Non-toxic fouling-release coatings[2] do not inherently protect against fouling settlement, but as the ship moves through the water the shear forces on the hull allow for some degree of fouling removal and self-cleaning. The most common formulations center on highly fluorinated polymers or the silicones based coatings at foul release[7]. Although these coatings do ease fouling release and removal, their inadequate adhesion to the substrate, durability, and high cost has limited their deployment in the field.

Hence, the development of an effective, non-toxic alternative to biocidal and / or easy release coatings in urgently needed. The synthesis, coating preparation and fouling resistance of these coatings for ocean test are reported here.

Experimental

Synthesis and formulation of coating materials: The aim of this study is to investigate the efficacy of chemical incorporation of biocides into the siloxane coating materials for ship hull coating application. Thus, we expect that this coating surface obtained could show dual function mechanism in order to reduce the microfouling (bacterial biofilms, slime, Ulva, bryazoans, diatoms, etc.) and macrofouling (e.g. barnacles, muscles, tubeworms, etc.) materials on ship hull with minimum environmental impact.

Triclosan (5-chloro-2-(2, 4-dichlorophenoxy) phenol) is a broad spectrum antibacterial/antimicrobial agent used in various personal care and consumer products such as shampoo, toilet soap, deodorants, toothpaste, footwear and plastic ware. In this study, Triclosan was attached via covalent linkage to silicones to minimize its release into the environment.

The biocide Triclosan was modified with alkenyl or (meth)acrylate moieties and incorporated into a silicone backbone through well known hydrosilation reaction as depicted in figure 1.

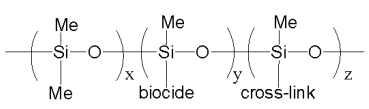

Figure 1. General structure of silicone resins

Results and discussion

The multi-nuclear NMR studies show effective tethering of biocides with various linear and cyclic silicone backbone. Synthetic control over the incorporation of crosslink functionalities within the polymer resin allows tuning of the surface of the coating and of mechanical properties. Resins synthesized were cured using vinyl terminated polydimethylsiloxane for hydrosilyl functionality, amines for epoxy cross linking functionality or moisture cure for alkoxysilyl cross linkage.

The physical characteristics of coating materials such as surface energy, tensile modulus, glass transition temperature have been tailored in order to determine the correlation between the chemical structure and antifouling / fouling release performance. Also chemical structures of some coatings were characterized by FT-IR analysis.

Resistance and release performance of coatings against macro foulant, barnacle, was tested by static immersion test in the Indian River Lagoon at the Florida Institute of Technology. The performance of coating against barnacle was validated with international copper ablative reference coating for the comparison of antifouling performance and the INTERSLEEK 425 for the easy release performance. Preliminary results showed that the coatings prepared from biocide incorporated silicones significantly reduced macro fouling.

Interestingly, our results show that the antifouling performance of the coating is deeply related to not only the biocidal activity but also the bulk modulus of silicone even though for the coatings containing tethered biocide. It was postulated that for high modulus coatings, biocide may be trapped and unavailable to prevent macro-fouling in the highly cross linked polymer matrix, whereas for extremely low modulus coatings, barnacles appear to cut through the coatings and grow on the anti-corrosive primer coating.[3,4]

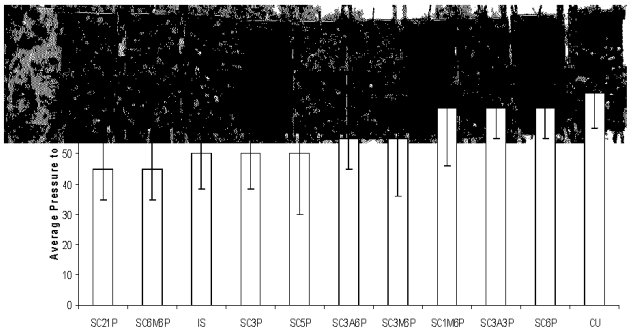

Figure 2. An example of coating panels shown antifouling and fouling release properties for barnacles and slims.

Conclusions:

The preparation, characterization, and bio-testing of biocide incorporated silicone coatings for marine applications have been conducted. Derivatives of the biocide, Triclosan (5-chloro-2-(2, 4-dichlorophenoxy) phenol), were used to covalently attach the biocide moiety to a silicone backbone. The synthetic process allowed for control of the resulting coating's mechanical properties as well as antifouling / fouling release performance in laboratory and ocean site testing. The test results showed significantly reduce macro fouling with sustained fouling release characteristics for the coatings produced.

Acknowledgements:

Financial support from the Office of Naval Research through ONR grants # N00014-04-1-0597 and the scientific assistance from all members of CNSE scientists are gratefully acknowledged.

References

[1] Katranitsas, A.; Castritsi-Catharios, J.; Persoone, G., *Marine Pollution Bulletin* **2003**, *46(11)*, 1491.
[2] Thorpe, A. A.; Nevell, T. G.; Young, S. A.; Tsibouklis, J. *Applied Surface Science* **1998**, *136(1/2)*, 99-104.
[3] Thomas, J.; Choi, S-B.; Fjeldheim, R. and Boudjouk, P. *Biofouling*, **2004**, *20*, 227.
[4] Boudjouk, P.; Choi, S.-B.; Ready, T.; and Thomas, J. Patent PCT application. **2005**, WO2005030405.