Reducing Biological Adhesion to Silicones: New Mechanisms Indicated by Contact Angle Anomalies

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Statement of Purpose: The goal of the work reported here was to utilize contact angle measurements to examine how certain modified silicone coatings effectively interfere with bioadhesive strength of biological fouling in fresh, brackish, and sea water, as compared with unmodified silicone controls. There are many similarities in the mechanisms of biological deposition, attachment, and adhesion in the internal aqueous environment of our bodies and the external environment of oceans, rivers, and other waterbodies. Key differences include kinetics of events, macromolecular and cellular concentrations, and ionic strength. Interfacial events, as determined by physical/surface chemistry, however, are remarkably consistent. Methyl silicone coatings reduce the tensile forces sustained by attached biofouling to low, but non-zero, values, prompting this successful search for coating modifications that further reduce biofouling retention strengths (Truby et al. 2000).

Methods: Observations of droplet stability (or lack of stability) on sample surfaces were recorded for each of 12 diagnostic fluids. The diagnostic fluids used for contact angle measurements possess chemical functionalities that are similar to those present on peptides comprising adhesive proteins. Types of instability included droplet creep, Marangoni effect (Mendes-Tatsis & Agble 2000), and coating swelling. All of the coatings were confirmed to be polysiloxanes by MAIR-IR spectroscopy. NHLBI reference PDMS (unfilled) was included as a control for the contact angle analyses. Four coatings were selected from an extensive field program (Kavanagh et al. 2003) for the contact angle study: (1) RTV11 control, a $CaCO_3$-filled PDMS elastomer (GE Silicones); (2) RTV11 amended with 10 wt% of DMSC15 (Gelest; Tullytown, PA), a hydrophilic (carbinol-terminated) PDMS oil; (3) RTV11 amended with 10 wt% of SF1147, an organic silicone oil (decylmethyl-siloxane) (GE Silicones); and (4) silica-filled silicone elastomer base, amended with 10 wt% of SF1147. Panels were retrieved from the field (fresh, brackish, and seawater sites) and gently cleaned of macrofouling, before air-drying and shipping for post-exposure analysis. The panels also were cleaned in the lab to remove any loose debris and biological films.

Results/Discussion: All of the silicone coatings in the study fell within Vogler's adsorption index zone (Vogler et al. 1993), guaranteeing that bio-adsorption would occur. They also fell within "Baier's window" (i.e. critical surface tensions, CST, between 20 and 30 mN/m; later refined to be between 20 and 27 mN/m) (Brady & Singer 2000; Meyer et al. 1994), predicting minimization of bioadhesion in the presence of mechanical shear forces. Thus, while it is certain that components (e.g. proteins) adsorbed to the coatings, the adhesive strength of the adsorbed material was very low.

Instabilities observed for particular diagnostic fluids on the different coatings indicated different potential mechanisms for further reductions in biological adhesion. The control RTV11 increased in surface activity during the immersion period, consistent with mild surface chain scission and hydrolysis of the surface. Coatings with additives that most effectively reduced biofouling (field measurements) showed both initial and persistent contact angle anomalies for the test liquid, thiodiglycol, suggesting lower-shear biological release mechanisms based on diminished bioadhesive crosslinking by interfering with hydrogen- and sulfhydryl bonds. In all cases, the hydrocarbon fluids caused swelling of the pre- and post-exposure silicone elastomeric coatings.

The coatings evaluated in this study were very similar in terms of surface chemical and physical properties --- including mechanical properties (Newby & Chaudhury 1997). It is not surprising, then, that concepts of minimization of generalized bioadhesion (Baier et al. 1968; Dexter et al. 1975) developed from studies with a much wider range of materials (e.g. fluorocarbons, silicones, polyamides, metals, ceramics) fall short of the mark in predicting performance among a relatively narrow range of already-selected “easy release” silicone elastomers. On the other hand, contact angle data that “fall off the line” for determination of CST (i.e. those involved in solubilization, swelling, or wicking) are sources of additional useful information about a surface. Instabilities of particular fluids can point to mechanisms of fouling-release coating efficacy (Meyer et al. in press).

Conclusions: Whereas critical surface tension data did not well-discriminate among the easy-release test coatings, comprehensive contact angle analyses did reveal at least two additional fouling inhibition mechanisms: (a) hydrolysis and fragmentation of superficial silicone polymer and (b) the presence of elutable agents working against sulfhydryl-crosslinking bioadhesives.

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Acknowledgments: This work was supported by a subcontract from GE Corporate R&D (DARPA contract N00014-96-C-0145). NSF grant #EEC9712629 (UB) supported undergraduate research fellows.