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Biomimetic Fouling Control

Thesis submitted by

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ABSTRACT

Any man-made structure immersed in the marine environment rapidly becomes fouled, with significant economic consequences. Solutions to fouling have generally used toxic paints or coatings which have damaging effects on marine life. The subsequent phasing out of these antifoulants has sparked a search for non-toxic antifouling alternatives, including the development of technologies based on natural biofouling defence models (biomimicry). The biomimetic approach to antifouling is the focus of this thesis, with an emphasis on physical fouling defence mechanisms in molluscs. Surface microtextures have been identified as potential fouling deterrent mechanisms in molluscs and have been recorded on the blue mussels *Mytilus galloprovincialis* and *M. edulis*. The aim of this thesis is to develop biomimetic fouling control using marine molluscs as a natural model.

To determine physical defences the surface texture of a range of marine bivalves and gastropods from the Great Barrier Reef was characterised and many unique micro-topographical patterns discovered. Laser scanning confocal microscopy was used to quantify the surface roughness parameters for 36 selected species. This is the first example of the characterisation of natural marine surfaces in terms of mean roughness and waviness profiles, skewness, anisotropy and fractal dimension. The wettability of the selected species was also determined. Subsequently, the 36 species were assessed for fouling resistance over three months and fouling resistance and removal was correlated with the surface roughness parameters generated. Key roughness parameters, in particular skewness, fractal dimension and hydrophobicity, were identified for species specific fouling resistance and also fouling removal. Total fouling cover was positively correlated to fractal dimension and negatively correlated to skewness. Algal cover was negatively correlated to hydrophobicity, Spirorbid tubeworm cover was positively correlated to fractal dimension, and percent fouling removal was positively correlated with mean waviness.

To establish the role of surface microtexture in fouling deterrence, biomimics were created for three bivalves, *Mytilus galloprovincialis* and *Tellina plicata*, which have differing microtopographical patterns, and *Amusium balloti*, which has a smooth

surface. Smooth biomimics were significantly more fouled than microtextured biomimics. The fouling resistance of microtextured biomimics diminished after 6-8 weeks, in contrast to natural shells which maintained their fouling resistant properties for 3 months. The extended fouling resistance of natural shells supports a multiple defence strategy of the surface-bound periostracum, with the proteinaceous nature of the coating providing a defence against microfouling. A theory is proposed that microtextured biomimics only deters macrofouling larvae and that microfoulers that are smaller than the size of the microtexture fill the textures and negate its effects.

This theory is termed 'attachment point theory', whereby larval attachment is influenced by the number of attachment points with settling larvae preferring the maximum number of attachment points to enhance successful adhesion and recruitment. To test attachment point theory, microtextured films of varying texture widths (2-512 µm) were developed and attachment to the microtextures by a range of micro- and macro-fouling organisms was determined. Diatoms attached in significantly higher numbers on textures smaller than the width of the diatom cell. In contrast attachment was reduced on textures slightly smaller than the cell width, clearly supporting attachment point theory. Attachment by macrofouling larvae and algal spores to microtextures also supported the theory. Larvae and spores generally settled in higher number on the texture larger than the spore/larval size. Attachment points for settling larvae are identified as important mechanisms in fouling deterrence, or attachment, with the critical factor being the ratio of the width of settling organism to that of the microtexture.

The findings of fouling resistance on micro-rough surfaces were explored further to incorporate nano-scale surface roughness. This novel antifouling mechanism combines micro- and nano-scale roughness to a hydrophobic surface to create superhydrophobicity. A range of surfaces incorporating micro- with nano-scale roughness, and nano-scale roughness alone, were tested against a range of micro- and macro- fouling organisms. Nano-rough surfaces alone significantly deterred all tested organisms. In contrast micro-scale with nano-scale roughness either attracted or repelled larvae. From the mixed preferences recorded on the choice bioassays, factors other than hydrophobicity play a significant role in the selection of a surface on. All coatings were superhydrophobic (> 155º) but differed in roughness and produced very different settlement responses. The consistently high level of deterrence by the nano-scale surface supports a theory of nano-bubbles at the surface of these coatings as an antifouling mechanism. The confirmation of this theory requires further collaborative investigation between physicists, chemists and biologists, but is a significant outcome.

Overall, the research presented has elucidated a number of novel approaches to biomimetic fouling control and developed novel theories for the mechanisms of action of natural surface-mediated fouling defences. These results also contribute to the development of promising alternatives to toxic antifouling technologies and provide unique approaches to significant new developments in micro- and nano-surface technologies in the field.

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