

# Biomimetic Strategies

## in Antifouling Coatings

by Maria Salta

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The lotus leaf (Qingdao, China), with its hydrophobic nature and self-cleaning ability, has been the focus for several bio-inspired applications.

### Introducing Biofouling: The Challenge

Marine biofouling is the colonization of aquatic organisms on manmade structures such as ship hulls and platforms, and has been of major concern since the inception of naval fleets. The aim in modern ship coatings is primarily directed towards minimizing the hull roughness caused by biofouling, as a higher roughness leads to increased drag and subsequently to excessive fuel consumption. Reducing marine biofouling is therefore analogous to reducing fuel emissions and the high costs associated with fuel production. Biofouling has an impact in a range of marine operations such as sensors, aquaculture, energy systems and oil platforms.

Because of the need to replace antifouling paint systems at specific intervals (approximately every five years), biofouling also impacts on the through-life costs. This necessitates the removal of fouling and previously applied coatings before subsequent repainting, incurring manpower, material and drydocking costs. It is true to say that naval vessels do not dock solely to remove fouling build-up, but the failure to remove attachments in a timely fashion seriously impacts on performance, i.e., reduces speed and manoeuvrability, increases the risk of noise signatures, and increases fuel costs. Importantly, the environmental issue of alien species translocation between the world's

harbours due to shipping can affect local marine biodiversity and have detrimental effects on the ecosystem as a whole.

Despite the high variability of environmental conditions and the wide diversity of organisms involved, the formation of biofouling is observed to follow a reoccurring sequence: after the initial step during which the submerged surface undergoes biochemical conditioning from the surrounding water, pioneer bacteria will eventually attach to the surface (in a process implicating physical, chemical and biological parameters), and progressively form a multiple species biofilm, often commonly referred to as “slime.” The complexity increases if microalgae (especially phytoplankton such as diatoms) and fungi are involved. This initial part of the fouling process is known as “microfouling.” The subsequent attachment and growth of spores of macroalgae and/or larvae of various micro-invertebrates constitutes “macrofouling.” Although the mechanisms involved are not yet fully understood, microfoulers, or at least some of the bacteria and diatoms involved, have been reported to regulate macrofouler settlement, especially via chemical cues, and often serve as a food source.

Since the late 1960s-early 1970s, effective protection against marine fouling of naval



An example of alien species (invasive species) where the Japanese oysters have outcompeted the local species in Den Helder, Netherlands.

vessels has been achieved through the use of organotin systems, with a durability of around five years. Their use, however, has become a major issue since the breakdown products of tributyltin (TBT) in seawater were identified as inducing serious biological damage to marine invertebrates. This impact on the environment resulted in the application of TBT paint systems being completely banned by the International Maritime Organization in 2008. As a consequence, considerable international effort has been devoted towards developing environmentally friendly technologies capable of providing the required degree of protection from marine fouling along with adequate coating adhesion and endurance.

### **The Solution: Biomimetic Approaches**

In the marine environment, a wide variety of species appear to remain fouling-free over extended periods of time and illustrate antifouling abilities by several means, e.g., the use of chemical and physical defences, but also symbiotic relationships between host (e.g., algae) and epibionts (other organisms that live on them) that prevent fouling. The impediment of biofouling in a natural way, as observed in marine organisms, has triggered the scientific

interest in, and led to the examination of, marine natural systems as a possible route for novel antifouling technologies. The term biomimetics as the word signifies (from the Greek  $\betaίος$ =bio=life and  $μίμησις$ =mimesis=to imitate) is used to describe technologies that are in this way inspired by nature. Biomimetics have often resulted in models for numerous engineering-related applications in order to overcome scientific challenges and in the same context, bio-inspired antifouling technologies make a strong candidate to resolve the problem of bio-fouling in an environmentally friendly manner.

### **Biomimetics: Chemical Defences**

Nearly 20,000 natural products have so far been described that originate from marine organisms. Sessile marine organisms (e.g., sponges, soft corals and seaweeds) as well as microorganisms are known to elaborate chemical defence mechanisms against predation and epibiont growth. The excreted metabolites might repel or inhibit fouling organisms and can act enzymatically by dissolving the adhesives of the fouling organism and/or act as biocide. Since the early 1980s, a great number of marine natural extracts have been assayed against organisms



implied in the biofouling process and several reviews dealing with their potential use as novel antifouling biocides have been realized. The most successful story is that of the red algal species *Delisea pulchra*, which produces secondary metabolites, halogenated furanones, exhibiting antifouling properties. Interestingly, it was observed that in *D. pulchra*, furanones are encapsulated within specialized glands located at the surface of the alga. These secondary metabolites were found to be released from the algal surface at such concentrations (ranging from 10 to several 100 ng.cm<sup>-2</sup>, depending on the furanone) that the settlement of microfouling in both field and laboratory assays was largely reduced.

An important factor that contributes towards the exploitation of marine algae as natural resources against biofouling is that these organisms are cultivable, relatively easy to harvest and that the extract yield is relatively high. Hence, algal extracts represent cost effective alternative antifouling compounds and are an attractive source for a commercially viable product. Algae are often sedentary and thus act as biomimetic solutions for static ship operational profiles. Some algae can tolerate exposure out of the marine environment (e.g., during low tides) and a ship's hull would be an analogue of this exposure at the waterline of the splash zone. Marine organisms are able to synthesize new compounds to maintain the antifouling effect, but such an option is not available to the paint formulator.

Despite the wide range of promising natural products deriving from algae, they are becoming less effective models for bio-inspired antifouling technologies against biofouling. This is mainly because developing antifouling compounds from marine natural products is considerably restricted by the regulatory environment for chemicals in coatings. Also, secondary metabolites are complex molecules and the active compounds



In-situ microscopy showing natural biofilm (“slime”) in real-time colours formed on a plastic surface after a month. These biofilms can be as thick as a few hundred micrometres and can directly affect a ship's hydrodynamics by increasing its drag as it moves into the water.

involved in inhibition have frequently been difficult to identify, posing a problem in creating structural analogues for incorporation into antifouling coatings.

### **Biomimetics: Physical Defences**

The other major environmentally friendly antifouling mechanism possessed by several marine organisms is via physical/mechanical means, mainly through ingenious topographic arrangements on their surfaces. This is the case for a great spectrum of marine organisms ranging from mammals (skins of killer whales, pilot whales, dolphins and porpoises) through to fish (e.g., sharks), crustaceans (e.g., crabs) and molluscs (e.g., mussels and oysters). One of the most investigated model surfaces from the marine world is the shark's skin, as sharks require low drag in order to develop high speeds during prey catching. Indeed, the shark's skin is characterized by repetitive microstructured diamond shaped ridges which may help by reducing the drag through the increase of the water flow along the shark's skin as it swims. Effectively, this allows the shark to move faster, while preventing biofouling accumulation. These riblet structures can range from 30 μm to 300 μm according to the species. A technology



Example of biofouling growth on buoys that support instruments for oceanographic work.

inspired by the shark's skin, named Sharklet AF™, was achieved by designing similar patterns using silicone (polydimethylsiloxane) at a variety of sizes that were scaled down from the ones found in nature. Interestingly, some of the designs managed to reduce barnacle larvae settlement by 97% and spores

of seaweed (*Ulva*) by 62%. Observations of shark skin patterns showed that surfaces with less points of attachment were more successful in preventing settlement. Although these are very promising results, the patterns were optimized to the size ranges of the specific biofouling organisms tested. This illustrates

the difficulty in taking biofouling as a whole, as organism sizes range from a couple of micrometres (bacteria) to a few hundreds of micrometres (larvae and spores). Nevertheless, ongoing investigation of shark skin pattern sizes and combinations may show improved performance in the future.

Oysters and mussels have also been the focus of research for their potential antifouling properties deriving from their surface properties. These are attributed to microstructures formed by the top layer of the shells, the periostracum, which has been shown to inhibit biofouling. Interestingly, juvenile oysters with intact periostracum appeared to inhibit boring by other organisms, while older oysters (more than one year old) did not prevent boring which was related to eroded periostracum. The same principle was observed for mussels which were found to form straight and sigmoidal micro-ridges on their shells. The replication of the mussel's surface texture has been attempted and tested against several biofouling organisms in the lab. Interestingly, the results were very similar to those found for shark's skin; that is, both microfoulers and macrofoulers exhibited increased settlement and attachments on surfaces with a high number of attachment points. By developing topographies with lowest number of attachment points, the settlement and growth of larvae and spores of fouling organisms can be decreased and the release of fouling from surfaces increased.

Recently, a bio-inspired paint has been developed that is flocked with fibres mimicking the seal's coat (SealCoat). This paint is claimed to remain foul-free from macrofoulers for up to five years; however, no published literature provides scientific data to confirm this. Although SealCoat exploits an interesting concept, it has to be noted that seals intensively groom their hairs when out of the water, therefore mechanically removing dirt off their coat. Moving away from the traditional paint application, a new bio-inspired approach, called Thorn-D®, challenges biofouling by

creating a self-adhesive foil mounted with millions of micro-fibres that vibrate constantly by the water's movement. This movement, mimicking thorn-looking fibres observed on marine living surfaces, appears to discourage settlement of macrofoulers such as barnacles, mussels and algae. These last two fibre-inspired approaches may provide a non-toxic antifouling solution to the long-standing biofouling issue; however, there is no clear understanding of the effect on the vessel's drag when covered with fibres and whether increased friction eventually underpins the beneficial antifouling effects.

### **Biomimetics: A Few Examples from the Land**

Another desirable characteristic for an antifouling coating system is a self-cleaning effect. In nature, this is observed in the lotus leaf with its superhydrophobic and low adhesion nature. Specifically, the lotus leaf exhibits hierarchical micro-scale bumps covered with waxy nanostructures. This texture/wax combination allows air pockets to form at the solid-liquid interface, offering a self-cleaning effect aided by rain drops taking with them the dirt as they smoothly roll off the leaf. A recent attempt to use the combined effect of low surface energy and self-cleaning characteristics lead to the investigation of rice leaves and butterfly wings. In rice leaves, a self-cleaning effect is used to avoid fouling that would otherwise prevent photosynthesis. For butterflies, a similar principle allows maintenance of wing colouration and flight control, achieved by the observed hierarchical scales and microgrooves on their wings. These two systems appeared successful against bacterial colonization in laboratory experiments (especially for the rice leaf), making them interesting antifouling candidates which however have yet to be tested in real-life conditions of the sea.

### **Conclusions and Future Directions**

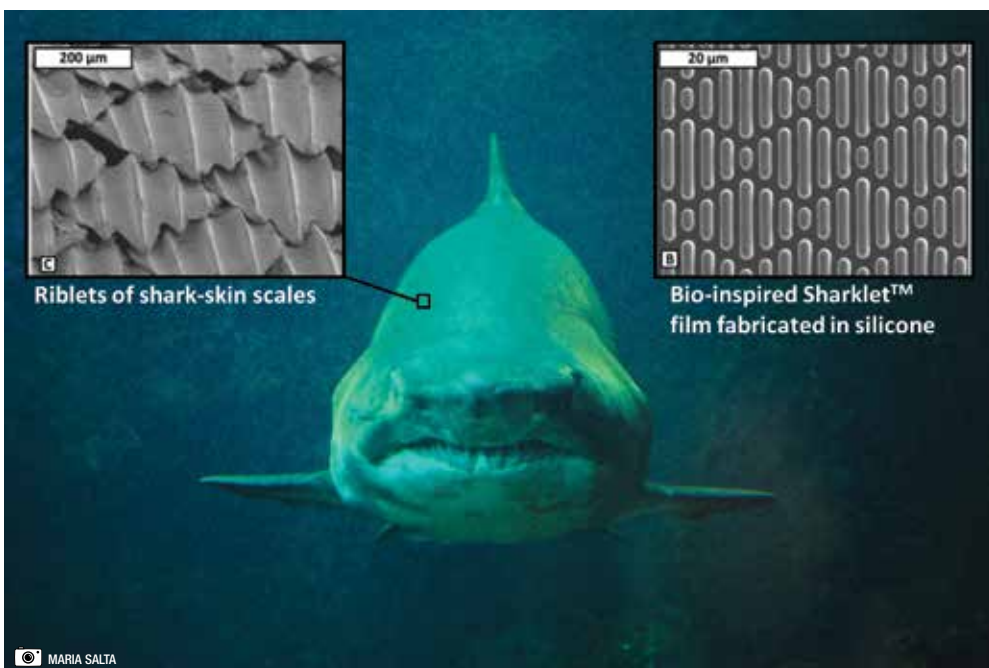
I would like to end this essay by acknowledging the fact that most marine organisms utilize a combination of mechanical, chemical, and physical





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Example of biofouling growth on a docked vessel in Venice, Italy.



Mimicking the shark's skin (left insertion), the bio-inspired Sharklet™ has been developed (right insertion) – adapted from Scardino and de Nys [2011]. *Biofouling*, Vol. 27, pp. 73-86.

mechanisms to deter biofouling. For instance, some species will use surface renewal to shed their top surface layer and along with it the fouling organisms (e.g., algae), while metabolites are being released by their crusts to chemically enhance their defence. This kind of observation has made it clear that a combined approach such as topography corroborated by non-toxic chemistry will lead to a more successful antifouling technology, ideally against a range of biofouling organisms. An important aspect in antifouling research is to gain a better understanding of the overall biofouling processes which are poorly understood. Specifically, biofilm formation is the first step towards establishing the entire biofouling community; therefore, considerable effort should be placed in investigating these microorganisms. Recent advances in molecular tools can uncover unprecedented information on biofilm dynamics and attempt to answer questions such as “which bug sticks to which antifouling surface.” This will eventually lead us to better manage novel antifouling technologies.

Despite repeated efforts, finding a universal physical antifoulant may be a hard task and

the most promising results are often temporal, lasting a month or less when tested in the field. However, as Dr. Andrew Scardino brilliantly put it: “Nature has successfully managed this challenge and we should graciously accept guidance, and be inspired, in understanding and developing the most sustainable marine technologies to control biofouling.”



Maria Salta is a marine biologist (focusing on environmental microbiology) and oceanographer working on projects ranging from coral conservation to plankton ecology and ecophysiological responses of microorganisms to high CO<sub>2</sub> levels. Over the past seven years, Dr. Salta has been funded by the European Defence Agency and the European Union to work on the discovery of environmentally friendly antifouling coatings by exploring and mimicking natural systems. Having been based in the Engineering Sciences Department at the University of Southampton for seven years, she has been applying her knowledge in marine natural systems to conduct translational research by fabricating novel bio-inspired antifouling surfaces. Dr. Salta has recently been assigned the post of lecturer in Environmental Microbiology (University of Portsmouth) where she will continue focusing on bio-inspired solutions to environmental issues.