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Marine biofouling – a sticky problem

or

Gluing in seawater

Within the sea, a hard solid surface is something rare and therefore very attractive to a wide range of organisms that need something to adhere to. Many marine algae and invertebrates are dependent on a solid surface for their reproduction and survival. A hull of a ship or other human structures in the sea is therefore most welcome, providing the organisms a new hard surface to colonize. And they do, very fast and with an efficiency that is remarkable. Within a few weeks in warm water, if the circumstances are good, a thick layer of up to 1 dm of different kinds of organisms can be found. Obviously it takes longer in cold water. Colonizing new surfaces is something necessary for many marine organisms, but boat owners do not appreciate it, to speak mildly. A hull fouled by organisms such as algae, mussels, barnacles, and tubeworms becomes very rough. The roughness of the hull increases the drag and causes the ship to be slowed down. The drag increases the consumption of fuel to retain the speed. This has both economic and environmental implications, the latter because of an added emission of above all CO_2. In the end, the ship will become almost impossible to manoeuvre. These problems are by no means new, and there are almost 2000 years old recipes on how to prevent fouling on ships (Figure 1). So what are the strategies for the future of this continuous battle between man's reasons for sea transportation and marine organisms?

*Figure 1. The problem with marin biofouling has existed as long as man has utilized the sea. (By permission from KFS/Distr.Bulls). "Raise your swords!", "It is time to attack!!" – "I **hate** scraping the ship in spring!"*

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Marine glues

More than 2 500 organisms have been found on man-made surfaces in the marine environment all over the world. Most of them are unicellular such as different

Figure 2. A blue mussel secured to a surface with its byssus threads. The byssus threads are made of proteins that give both strength and elasticity at the same time. Within the anchoring patch, there are proteins that glue to the surface and connect the surface with the byssus threads and keep the mussel at place. In contrast to other fouling organisms, the blue mussel can deliberately release itself from its threads and find a new, more suitable place to live. (With permission, Professor Herbert Wait, Univeristy of California, Santa Barbara, USA.)

bacteria or diatoms (unicellular algae with a silica case). These micro-organisms are the first to colonise a hull. They attach themselves by producing mucilaginous substances, which create a slimy surface. This layer of slime can easily be felt when touching something that has been left in seawater for some time. The brownish colour of the slime comes from the diatom shells.

Atop of the slime (also called a biofilm), larger organisms are then colonizing the surface. Due to their appearance, they are divided into soft foulers and hard foulers. Algae, sponges, anemones, tunicates and hydroids are examples of soft foulers while barnacles, mussels, and tubeworms are hard foulers. All these organisms use specific glues to attached them to the surface. Interesting is that the glues are all different from each other. The mussel glue is not the same as the barnacle glue or the algal glue. They are chemically unrelated and adhere and cure by different mechanisms. From an evolutionary perspective, the ability to glue has been invented several times. This indicates that the ability to produce a glue is a vital trait for many species having free-swimming larval forms and a sessile adult life, where they do not normally move from the chosen and fixed spot. The quality of the glue is also important – it should be stable enough to prevent the organism to be washed away.

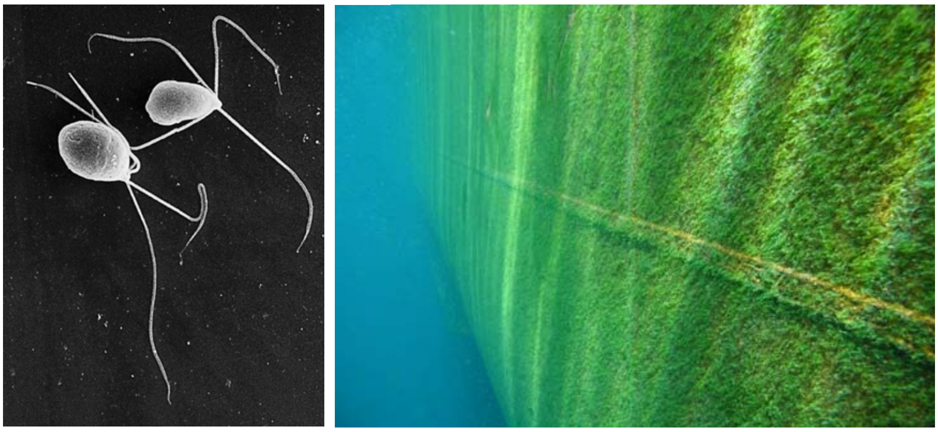

Figure 3. The left picture shows zoospores from Enteromorpha sp. When the spores have attached to a surface, they release their glue and the spores get imbedded and germinate. The picture to the right shows a ship hull that is fouled by Enteromorpha sp. The algal growth reduces the speed and increases the fuel consumption. To prevent algal growth, antifouling paints contain different kind of algaecides. (With permission; Dr. M.Callow, Univeristy of Birmingham, UK och Mr. Johnny Elias-son, Solt-Nielsen, NLNL)

On top of the slime (also called a biofilm), larger organisms are then colonizing the surface. Due to their appearance, they are divided into soft foulers and hard foulers. Algae, sponges, anemones, tunicates and hydroids are examples of soft foulers while barnacles, mussels, and tubeworms are hard foulers. All these organisms use specific glues to attached them to the surface. Interesting is that the glues are all different from each other. The mussel glue is not the same as the barnacle glue or the algal glue. They are chemically unrelated and adhere and cure by different mechanisms. From an evolutionary perspective, the ability to glue has been invented several times. This indicates that the ability to produce a glue is a vital trait for many species having free-swimming larval forms and a sessile adult life, where they do not normally move from the chosen and fixed spot. The quality of the glue is also important – it should be

stable enough to prevent the organism to be washed away.

Some mussels (e.g. the blue mussel) adhere through threads that are anchored to the substrates. These byssus threads are tenacious proteins that are produced in a gland within the mussel and secreted via the mussel foot. During the secretion, the glue is fluid but in contact with seawater and the substrate, the proteins harden and are then able to anchor the mussel to the preferred substrate. What is interesting with the blue mussel is that in contrast to most other species, the mussel can release the byssus threads from the gland and set itself free only to fix itself to a new spot (Figure 2).

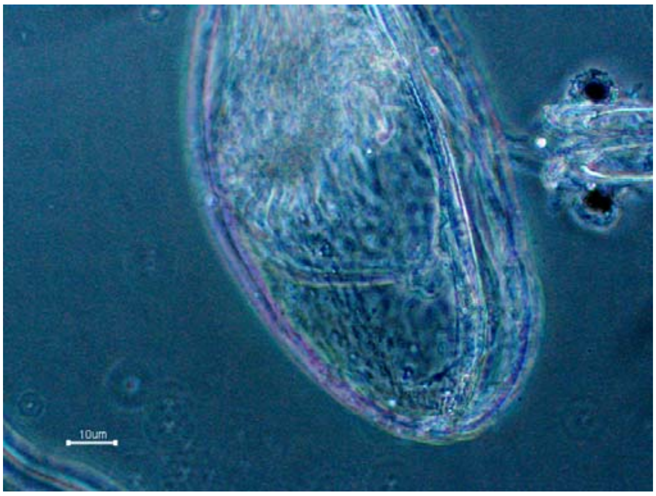

Figure 4. A cuticle shell left behind from a metamorphosed cyprid larva. On the right side of the picture there is a pair of eyes attached to the optical nerves. The compound eyes are not essential for the sessile barnacle, only for the cyprid larval stage. The sessile adult barnacles have instead light sensitive organs for shadow reflexes.

Algal glue, like glue from the green alga *Enteromorha sp*., is composed of glycoproteins. The glue is located within the algal spores. When the spores hit a surface, it secrets the glue and by a self-aggregating mechanism, it forms an adhesive pad surrounding the spore. The glue then cures by an unknown mechanism and becomes insoluble (Figure 3).

Barnacles are perhaps the most notorious foulers and the worst to deal with. They start their lives as nauplius larvae that feed on plankton and after five series of moults they become something quite different, the cyprid larvae. This very special phase in the barnacle life cycle is characterised by a single quest, finding a surface to settle. They do not even eat. When the right place for settling is found, the cyprid stands on its head and releases the glue through its antennas. Thereafter, the metamorphosis begins and the cyprid larva is transformed to the adult sessile stage (Figure 4). During the metamorphosis the animal loses all traces of eyes. In the sessile phase of the life cycle they are no longer needed and have no value for the survival or continued life of the animal.

The barnacle cyprid glue is produced, within special glands, out of unique proteins with no resemblance elsewhere. The curing process is still unknown.

Antifouling paints

Marine biofouling has been a problem as long as we have used the sea for trading, fishing or transportation. To protect the ship hull, many ideas have evolved throughout the years - mainly to create a poisonous hull by painting with tar or using iron or copper sheathing to protect the wood. With the introduction of iron hulls, copper sheathing became impossible. The iron hulls corroded because of the galvanic currents

Figure 5. When the antifouling paint is not effective anymore, a ship can become as severely fouled as shown in the picture. With this amount of attached biological material, the ship is neither safe nor suitable for transportation. (With permission, Johnny Eliasson, Stolt-Nielsen, NL).

between the hull and the copper sheathing. Painting the hull with something poisonous became necessary. The evolution of marine antifouling paints started in the 19th century and usually copper ions were incorporated into paints as the active antifouling substance, but lead, mercury, and arsenic were common as well. In 1970s, a new paint was introduced containing tributyltin (TBT). The TBT-paints were a great technical achievement and regarded as the final solution against marine biofouling. TBT acts as a broad-spectrum biocide and can be incorporated into paints in such a way that it leaks and effectively inhibits fouling on a hull for up to five years (Figure 5).

In late 1970s, it was found that TBT had big environmental impacts, especially noted were the reproductive failures in molluscs like oysters and dog whelks. Oysters also got thicker shells and the whelks became sterile (females developed male sexual characters: imposex). Especially alarming were the reports that high levels of TBT were found not only in bays and inlets but also in the open ocean. A very marked bioaccumulation could also be found in many food chains. Possibly TBT was one of the worst contaminant that we, the humans, had exposed to the marine environment.

Not until 2001 the International Maritime Organisation (IMO) of the United Nations started to introduce regulations on the usage of TBT as an antifouling agent on ships and it is to be banned completely by the year 2008. (Since 2003 TBT is not allowed on boats smaller than 12 m in Sweden.) Every ship must then carry a certificate stating which kind of paint has been used, and harbour authorities may check this by taking a sample from the paint on the hull for testing.

What can be used instead of TBT - and how can new antifouling paints be developed?

To prevent fouling – the way nature does it

All biological surfaces in the marine environment, from those on algae to sea turtles and whales, are exposed to biofouling. During evolution different strategies and chemical defenses have been developed to protect the various species. Several sponges, corals, sea squirts, algae and bacteria have developed chemical defences where special molecules are secreted onto the exposed surfaces or embedded in them. Other animals have a surface structure which makes it difficult for zoospores or larvae to attach themselves. A further method is used by most fishes – to continuously secrete mucous over their scales so the surface becomes slippery enough to prevent fouling.

A lot of efforts have been made to find and use these natural substances or molecules that nature itself has invented as antifouling agents. Some have been identified and successfully used in the laboratory, but problems arise when they are mixed with the paint. The active agent should be gradually and slowly released to the surface to have a long-term effect, which is not easy to achieve. Also, the agents have to have special surface-chemical characteristica.

Many of the substances found in nature are too complex or expensive to synthesize in large quantities or they are too poisonous to use extensively. Thus, the task to mimic what nature does is indeed difficult.

A natural substance which is used in antifouling paints today is capsaicin – although as yet in a small scale. Capsaicin is found in Spanish pepper and influences certain neurons to release transmittor substances which can cause a burning pain and itching in man. Many organisms are sensitive to capsaicin and therefore try to avoid surfaces treated with it.

To prevent fouling – the human way

1. To develop slippery surfaces

The idea behind technologies preventing fouling is to invent such a slippery surface that the fouling organisms can not adhere, and if they still do, they are to be washed away by the hydrodynamic forces when the ship moves through the water. Such a slippery surface can be made out of silicon elastomers with an addition of silicon oil. There are now several products on the market based on this new technology. They are all biocide free and since they are even smoother than ordinary paints, they reduce drag and as a consequence thereof, a silicon coating saves fuel. The drawback is

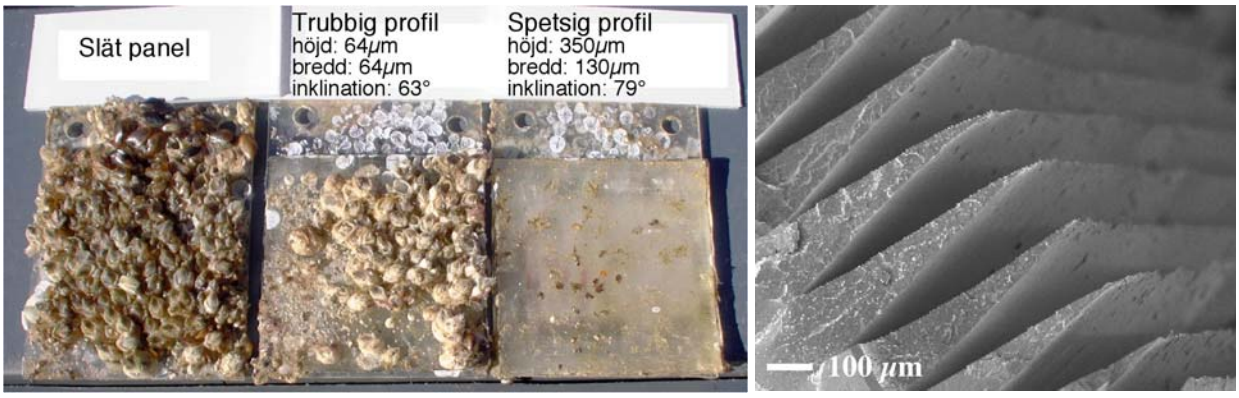

Figure 6. A field experiments evaluating micro-textured surfaces. A surface with pointed riblets prevents barnacle attachment. The picture to the right shows micro-textured surface with pointed riblets in high magnification. (With permission, Dr. Kent Berntsson, Tjärnö Marinbiologiska Laboratorier, Sweden.)

that these types of coatings have low mechanical strength and can easily be damaged. They are also expensive, difficult to apply, and can only be used by boats in frequent traffic with a speed over 18 knots. But for fast boats in frequent traffic, the silicon based paints are a very good alternative.

Intensive research on silicon elastomeres is ongoing and financed by the American Office of Naval Research

(ONR). The goal is to make the material more strain tolerant and also usable for speeds below 18 knots. Another task is to improve the adhesion of the silicon paints to the hull, while still keeping the exterior surface as slippery as possible.

2. To develop structured surfaces

From nature we have learned that some surfaces have less fouling organisms than others. One explanation is that there is a special surface structure that is less attractive to, *e.g.*, balanid larvae. How such a surface may look has been described by researchers at the Tjärnö Marine Biological Laboratory in Sweden. A special mini-striation of the surface was found to prevent attachment of balanid larvae (Figure 6).

3. To develop selective methodologies

The idea behind selective activity is that by knowing the biology and chemistry behind the adhesion of fouling organisms, it will become possible to inhibit fouling without using toxic compounds such as TBT or copper. It is the same approach as behind the development of new pharmaceutical drugs. These selective compounds shall only interfere with attachment and without toxic effects, neither on target animals such as barnacles or mussels, nor on non-target animals such as fishes or marine mammals. Thus, it is obvious that one compound cannot be found to have the desirable affect on all fouling organisms – one has to decide on which ones to investigate. Thus the question becomes restricted from “How do we prevent marine fouling?” to, *e.g.*, “How does a balanid larva attach to a surface?”

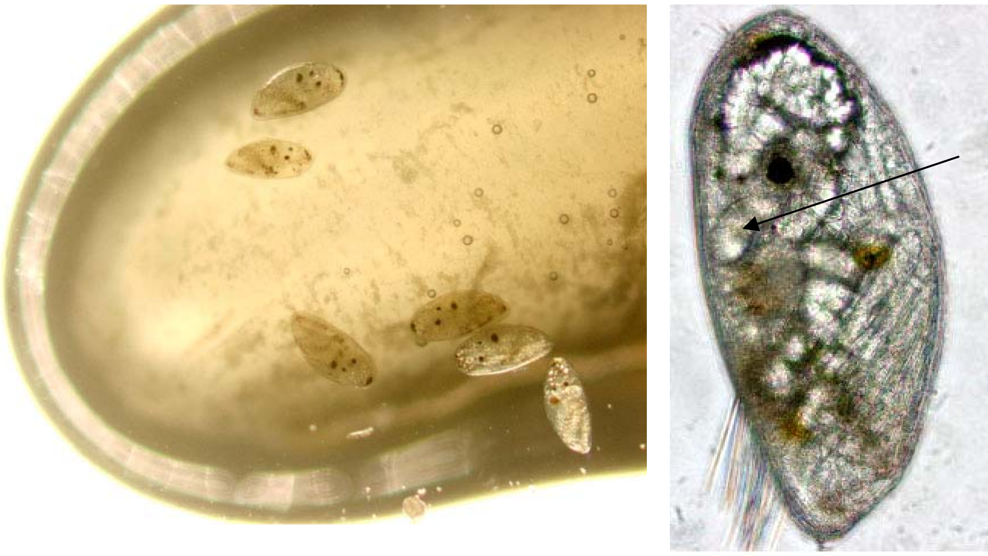

Figure 7. A cypris larva looks as a rice grain with legs, although much smaller. The picture to the left shows a rice grain compared to half-millimetre long larvae. The picture to the right shows a 200 times magnification of a larva. The arrow is pointed at the cement gland that stores the gluing protein.

Research on balanoids

In Nordic waters balanoids create the most serious problems regarding fouling on ships or marine installations. Because of this much research at the Gothenburg University is devoted to the general biology of balanoids – from genetic studies to the behaviour of the larvae.

The strategy should be to find non-toxic ways to prevent larval attachment, either to stop glue production or release or to disturb sensory functions and thereby the normal behaviour of the larvae (Figure 7). Investigation of the nervous system of the larvae and how different functions and behaviour are regulated then becomes natural targets. Nervous transmittors are obvious molecules to investigate and one, dopamine, is of particular interest. In humans it regulates many functions, especially in the brain. In balanoid larvae it is responsible for the release of glue from the antennal glands (and possibly also other functions). Since there are a number of ways to inhibit the dopamine function, this is obviously one research direction to follow. If such a substance is included in paint and can gradually be released, then this will prevent the balanid larva to attach to the painted surface. The effect is only temporary, so the larva will be able to glue to another surface afterwards.

Figure 8. A ship's hull with barnacles. When a ship looks like this, it is too slow and consumes too much fuel. The ship will become too expensive to use for transportation and at the same time, increases the emission of green house gases. (With permission, Johnny Eliasson, Stolt-Nielsen, NL)

The catemines are another example of such a group of substances. The catemines are pharmaceutical compounds that are also able to inhibit barnacle settling without being lethal. To inhibit settlement, concentration as low as a couple of ng/l is needed, but to kill the barnacle larva, 100 000 times higher concentration must be added. The effect of catemine is also reversible. It means that the inhibition of settling is not permanent and the larvae can settle elsewhere, as long as that surface is not treated with catemine. One catemine has also been proven to function as a barnacle deterrent when incorporated into a paint formulation.

Parallel to such research it is equally important to conduct research on possible side-effects of the molecules or compounds being investigated. They must not have a broad effect on the marine environment and they must not be long lasting. (This is similar to the demands on the pharmaceutical industry).

Summary

Marine fouling is an old problem for shipping and other marine activities all around the world (Figure 8). It contributes to increased fuel costs and a higher release of carbon dioxide from boats and ships. It causes increased weight, strain and corrosion on installations in the sea, and it is also a powerful way of spreading species to new parts of the world oceans (via ships).

To safeguard marine-related industries in a longer perspective it is important to manage the fouling problem without destroying the marine environment. This is an important task considering the multitude of organisms that inhabit marine hard surfaces. Ideally we have to find a combination of substances (agents, molecules) and technological methods that will protect both the marine environment and the industries involved.

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