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A Modern Approach Towards Efficient Antifouling Coating Technologies

Nikolaos D. Papadopoulos[1]*, Paraskevi Vourna[1], Pinelopi P. Falara[1] and Polyxeni Vourna[2]

[1]BFP Advanced Technologies, 11633, Athens, Attiki, Greece

[2]Institute of Communication and Computer Systems, School of Electrical and Computer Engineering, National Technical University of Athens, 9 Ir. Polytech. St., Zografou, 15780, Greece

***Corresponding author:** Nikolaos D. Papadopoulos, 33 Damareos Str., 11633, Athens, Attiki, Greece

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Abstract

Marine fouling is a worldwide problem with various economic and environmental threats. Most current antifouling technologies suffer from poor performance. It is evident that more efficient antifouling technologies under both static and dynamic conditions have to be developed. These should effectively combine diverse characteristics and functions. The incorporation of conductive and electrically anisotropic moieties into water soluble resins may prove a drastic solution to this on-going problem.

Keywords: *Antifouling paints, Biofouling, Conductive coatings, Electrical anisotropy*

Discussion

Biofouling poses major technical, scientific and economic challenges to various maritime sectors. Within the marine environment, any surface in contact with seawater suffers from biofouling. The biofilm can form in as little as 48 hours [1-3] giving rise to macrofouling, i.e., the attachment of marine organisms, such as algae and barnacles to the hull of a ship, which compromises performance of the vessel. Fouling on ships' hulls decreases speed and maneuverability and significantly increases fuel consumption [4]. Hard (calcareous) fouling especially, can result in power loses exceeding 85% and ultimately, engine failure.This natural phenomenon constitutes a huge economic problem for marine industries, as it raises the costs related to materials' maintenance and repair [5-7], since dry-docking for cleaning is more frequently necessary.

There are also unintended ecological effects when a bio-fouled ship moves between ports, since non-indigenous species are transferred from one region to another.Biofouling of the ship's reefs is directly related to the roughness of its reefs. It has been calculated that for each increase in reef roughness by 10-20 μm, the friction resistance increases by 0.5% for ships at high speeds. In general, the surface roughness of the reefs is increased by mechanical detachments or structural defects [8].

Thus, the development of innovative low-drag antifouling coatings for the hulls of ships, vessels, and speed crafts is essential [9-13]. Numerous attempts have been made to develop efficient antifouling coatings, which exploit recent adcances in biology, physics, marine chemistry and materials science. More specifically, biological methods [14] involve the use of a variety of enzymes or metabolites, secreted by cells, as substitutes for traditional biocides. The organic secretions inhibit the growth of their competitors and are biodegradable. This approach however has, up to now, limited success, since crucial technical obstacles, such as designing of an appropriate coating matrix or balancing of the effectiveness and lifespan of the coating still remain. Moreover, it is difficult to predict the impact of metabolites and enzymes on the marine environment if these are broadly applied to ships. Furthermore, with regards to the physical methods employed in antifouling coatings, electrolysis of seawater, with the coating acting as the anode, is perhaps the most common one. When such equipment is available on ships, hypochlorous acid (HClO), ozone bubbles, hydrogen peroxide or even bromine can be produced. Because of their strong oxidizing ability these compounds spread all over the ship's hull and eliminate fouling. However, due to large voltage drop across the surface, steel corrosion is intensified and efficiency of these systems is limited.Traditionally, chemical biocides have been regarded as the standard approach to control marine biofouling. Compounds such as tributyltin oxide ($C_{24}H_{54}OSn_2$) and tributyltin fluoride ($C_{12}H_{27}FSn$) are incorporated into polymeric matrixes to produce antifouling paints for ships' hulls. When the International Maritime Organization (IMO) banned the use of effective but environmentally damaging coatings containing TBT in 2008, the development of non-toxic coatings became more important than ever [15]. Due to the lack of effective alternatives, biocidal antifouling paints, such as those based on copper, which are considered as a transition between toxic and non-toxic coatings, have dominated the antifouling paint market. Copper oxide has been recommended by the Environment Protection Agents (EPA) as a suitable replacement of TBT, since it can be bound in water with other substances and thus, its toxicity is reduced. However, materials for marine applications have to comply with new stricter rules with regards to protection of environment, aquatic organisms and human health [16]. Therefore, that nonbiocidal antifouling coatings are in high demand.

Besides toxicity of its ingredients, a well-designed antifouling coating should adequately address issues, such as efficiency of antifouling performance and application costs. With regards to antifouling efficiency, it has to be noted that this is an unambiguous prerequisite under both static and dynamic conditions. Unfortunately, current antifouling paints fail to perform sufficiently under static conditions, with the majority of them having a useful lifetime of just 30-40 days. With regards to application costs, they should also include the cost of surface priming (and perhaps the cost of tie coating) as well as the cost of removing older paint coats. In addition, complexity of the method used to apply the coating should not be neglected. Finally, the special characteristics of the coating used, such as the drying time or the number of coating layers required in order a functional thickness to be obtained should be also taken into account in order to accurately evaluate sustainability and potential economies of scale. It should be also noted that seawater parameters, such as salinity, temperature and pH fluctuations, substantially affect the ability of microorganisms, algae, and plants to adhere and settle on a surface [17,18]. For example, pH variations affect solubility of biocides and the rate of corrosion of the coating [6]. Annual fluctuations and seasonal changes in temperature significantly affect the reproductive cycles of the microorganisms, and consequently the species of the growing microorganisms, the rate of corrosion and the extent of the biofouling [19]. Therefore, an efficient antifouling coating should be fully functional under a broad range of conditions [20].

It is evident that more efficient antifouling technologies have to be developed. A promising alternative are antifouling nanocomposites based on conductive and electrically anisotropic antimicrobial nanostructures, which can effectively combine the primary advantages of the various methods within a single multifunctional approach. In further analyzing the above concept, a short introduction on conductive polymers should be made. More specifically, electric conductive polymers have been employed in the manufacture of protective coatings, mainly against corrosion of metals. It has been also reported that, such polymers may also find use as additives in antifouling paints [21]. Towards this prospect, the most significant obstacle is that their electronic conductivity slowly decreases due to the dissolution in water of anionic dopants. Thus, antifouling efficiency also decreases. It has been reported [22] though, that when conductive polymers are doped and/or mixed with certain nanostructured materials, such as TiO_2 or ZnO they exhibit perfect electrochemical reversibility for long periods of time. It has been also recommended that they can be used as a copper alternative for electrolyzing seawater. Among possible candidates, polyaniline (PAni) in its doped form is the most promising one. Its low price, facile synthesis process, unique conductive properties and high thermal stability make PAni a highly attractive anti-foulant. The antibacterial activity of PAni is based on various factors, such as the length of its long polymer chain, the low molecular weight, and the presence of amino groups [23]. It has been found [24] that paints formulated with Pani, which was doped with HCl, and zinc biocides were effective against marine fouling for more than twelve months; longer that the period used by common commercial paints. In its doped form PAni is also able to protect steel against corrosion by an anodic protection mechanism, owing to the formation of a layer consisting of iron oxides. In the case of coating failure, doped Pani is also able to regenerate the metal oxide layer. This feature is of crucial importance, since application of all modern antifouling coatings presents a serious drawback: the necessity of using a primer coat and sometimes, a second coat, namely a tie coat, prior to application of the antifouling paint. Undercoats provide mechanical robustness to the entire coating's structure, but their main functionality is to provide anticorrosion protection to the steel substrate. It goes without saying that the application of a single durable coating providing both antimicrobial and anticorrosion properties would be a truly breakthrough in the maritime coating technology.

In addition, when PAni is combined with TiO_2 especially, synergistic phenomena may enhance both conductivity and antimicrobial performance of the coating. The latter is promoted by the photocatalytically active TiO_2 mineralogical form, i.e. anatase. In this case, visible light adsorbs on the coating's surface leading to generation of H_2O_2. The latter disintegrates shortly into H_2O and O_2, therefore poses no threat to the environment. In addition, the large surface area of nanosized materials means that the development of coatings with low amounts of photocatalysts is achievable. In addition, such coatings may possess an amphiphilic behavior, since they can combine within adjacent heterogeneous nanoscale regions the low surface energy and the resistance to protein adsorption of Pani with the high surface energy and foul-release properties of TiO_2 nanoparticles.

Anti-fouling properties may be further enhanced by the incorporation of carbon nanofibers (CNFs) or graphene oxide (GO) sheets within the coating's matrix. Nanomaterials of acrbon allotropes have shown promise for electrochemical biofouling reduction due to superior conductivity and cytotoxicity arising from generation of reactive oxygen species [14]. Their nanosize allows facile dispersion in a wide range of matrices, as well as a reduced material demand, while exhibiting strong antibacterial activity. In addition, they can act as fillers providing mechanical reinforcement to the coating's matrix. Cylindrical carbon structures with sub-micrometer diameters and lengths within the 30-100 μm range can be readily prepared. A modern antifouling approach may thus result by externally decorating polyaniline nanorods with magnetite nanoparticles and then magnetically align the resulting nanocomposite out of the coating's plane, which is defined by the structural growth orientation of carbon allotrope sheets or plates. The latter can be further modified with anatase nanoparticles, in order to develop a conductive and photocatalytically active matrix with enhanced in-plane antimicrobial and antifouling performance. The resulting nanostructure can then be easily incorporated into a soluble polymer matrix by wet chemical methods.

Within this approach chemical antifouling mode of actions can be coupled to mechanical ones through triggering of fur-like phenomena. More specifically, PAni nanotubes (or nanorods) can be filled with magnetite NPs to align them, by a weak magnetic field, in an out-of-plane configuration, during curing of the coating's resin. Magnetic orientation has advantages over the use of an electric field because magnetic forces are non-contact, do not cause chemical changes and are not sensitive to pH changes. The aim of such modification is to confer to the matrix a foul-release activity, too. It has been demonstrated [25] that fiber coatings containing piles of flexible thorns, such as polyamide, can provide a strong antifouling effect due to their fur-like surface, which enables tiny swaying movements in water and therefore detachment of fouling organisms by tidal currents and waves. Although fiber dimensions are in the mm range, it was found that the control of fiber's stiffness, which is directly dependent on the thickness to length ratio, is the critical parameter in enhancing antifouling properties. Therefore, the same mode of action can be also exhibited by nanofibers or nanorods, provided that a functional ratio of nanotube diameter and length is found. Our team is currently working on the discovery of such optimum ratios of PAni tubes, which have been functionalized by magnetite nanoparticles and embedded on graphene oxide matrices modified by anatase nanoparticles. The out-of-plane configuration of PAni tubes may have a similar functionality role to the thorn-like structure of common fiber coatings. Towards this end, a fundamental requirement is the utilization of a soluble paint matrix. Soluble matrixes are characterized by the fact that the binder is dissolved in water; therefore, the coating's thickness is decreased during immersion and PAni nanorods are gradually revealed. The above mechanism is similar to the primary mode of action of common self-polishing antifouling paints.

Due to the aforementioned arrangement, the problem of biofouling can be addressed at its root, i.e. before the onset of primary biofilm formation. In particular, the first stages of colonization can be prevented due to the high in-plane conductivity, evoked by modified GO sheets. The photocatalytically active TiO_2 nanoparticles can further contribute to the in-plane anti-fouling ability of the coating. At the same time, the developed electrical anisotropy enables charge dissipation, thus limiting electrostatic attractions and preventing early adsorption of bacteria and microorganisms through their negatively-charged outer membrane.

As the coating's binder dissolves an increasing part of vertically aligned PAni nanorods is revealed. As a result, the coating's out-of-plane conductivity becomes increasingly important. Colonization is now effectively addressed through direct contact of microorganisms with the PAni nanorods. Beyond a certain limit, the exposure of most of the nanorods makes them flexible and prone to microscopic oscillatory movements in the water, which facilitate the detachment of macrofouling under the influence of tidal currents and waves. The above mechanism provides a second anti-fouling defence based on foul-release properties. The importance of this mechanism is obviously smaller compared to the chemical antifouling mode of action and valid only in dynamic conditions However, it can prolong the useful lifetime of the coating, especially when its initial antifouling efficiency starts to fade. Even more importantly, an additional mechanism of action is present when surface biofouling is already there. The afore-mentioned process constantly exposes a fresh coating's surface; thus, the antifouling behavior of the coating remains sufficient for long periods of time.

The development of antifouling coatings based on the above approach has industrial potentiality. Nanotubes of PAni can be readily synthesized by the template free method. First, carboxyl-modified aniline dimers are prepared. Subsequently, they are functionalized by magnetite nanoparticles with diameters in the 10-30 nm range developed by ultrasonic (20 kHz) co-precipitation of iron (II) and iron (III) precursors. Then, polymerization of functionalized dimers follows. Furthermore, modified graphene oxide sheets can be prepared by sonication of an acidified graphene oxide colloidal emulsion in the presence of titanium isopropoxide $Ti[OCH(CH_3)_2]_4$. The graphene oxide emulsion can be prepared by the modified Hummers method. The above nanocomposites can be directly added to aqueous dispersions of commercially available water-soluble resins in order to produce the antifouling paint. The latter can be easily applied to solid substrates, such as naval steel by traditional spraying methods, e.g., airless spraying.

Our research team is currently conducting a series of tests in the Mediterranean coastline to evaluate real-field performance of such nanocomposite coatings. The experimental verification of the above approach will allow for the development of an environmentally friendly coating with long lifespan and robust performance, possessing both antifouling and foul release properties. Preliminary studies have shown enhanced functionality, which is attributed to the synergistic effects of antimicrobial attributes with anisotropic electrical conductivity. Moreover, the developed coatings have a distinct advantage over state-of-the-art competition: they can be applied directly to metal substrates providing anticorrosive properties without the use of primers.

The successful implementation of the afore-mentioned strategy into marine paints could provide an eco-friendly and efficient alternative to contemporary antifouling technologies. It could also considerably reduce the time required for compliance certification procedures according to international standards and facilitate fast implementation of similar technologies in other industrial sectors as well.

Conclusions

It seems that no antifouling technology alone can yield the performance required to address biofouling under a variety of conditions, either static or dynamic. Environmentally friendly nanocomposite materials which combine conductive, electrically anisotropic and antimicrobial functions and can be incorporated into water soluble matrices is a highly promising approach. The resulting antifouling paint exhibits both antifouling and foul release properties and can be applied directly to metal substrates without the use of a primer providing anticorrosive protection to the underlying surface. It is also expected to be cost efficient, not only in terms of being economical to apply and maintain, but also in terms of saving fuel costs, reducing out-of-operation time for the marine vessel and requiring minimal drydocking.

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Conflicts of Interest

All authors declare no conflicts of interest in this paper.

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