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Focus Review

Mesoporous Materials

Xerogel Coatings Produced by the Sol–Gel Process as Anti-Fouling, Fouling-Release Surfaces: From Lab Bench to Commercial Reality

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Abstract: We show the large environmental and practical impact of nanochemistry innovation by telling the story of how the sol–gel hybrid coating technology was subtly adapted to meet the urgent demand for clean antifouling marine coatings for vessels of widely different size, composition, and operation requirements.

1. Introduction

In the marine, lake and fluvial environments, bacteria, diatoms, algae and invertebrates rapidly attach to any submerged metal, wood or polymer surface causing increased hydrodynamic drag.[1] Depending on water temperature, microfouling bacteria naturally present in sea, river and lake water colonize onto immersed surfaces and form a biofilm composed of a conditioning film, microfouling alga, and marine bacteria within 1 h (Figure 1). A layer of the macrofouling alga *Ulva* settles and adheres prior to the adherence and growth of the calcareous organisms such as tubeworms and barnacles. Within a month macrofoulers such as algae, barnacles, tubeworms and mussels will have colonized the unprotected surface.

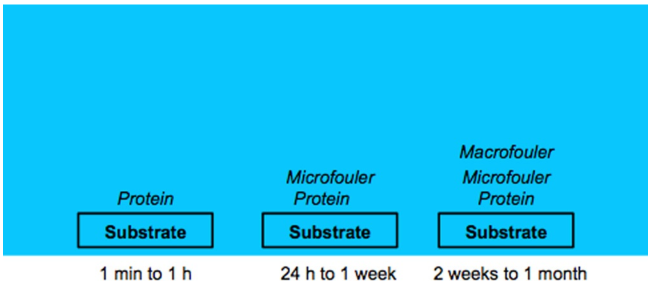

Figure 1. The settlement progression of a clean surface immersed in fresh or salt water.

Biofouling is also responsible for the decreased performance of sensors, cameras, and other optical devices from fouling interfering with signals/imaging, as well as for the decreased flow capacity and performance of water intakes.

After six months a ship without antifouling paint will rapidly need to use 40% more fuel due to additional hull drag from fouling.[2] As fuel consumption accounts for up to 60% of the operating costs of a ship, more than 900 million liters of marine antifouling (AF) paint are used worldwide yearly[3] (a Figure growing at >5% annual rate, with growth mainly located in Asia).[4]

The costs of biofouling are significant also for the environment. Besides the ubiquitous release of large amounts of biocides (pesticides and copper compounds), undesirable migration of fouling organisms from one ecosystem to another takes place via shipping.

In 2008, the international Convention[5] banning the use of effective but environmentally damaging coatings containing tributyltin (TBT) formulated in copolymer paints with cuprous oxide,[6] came into force. The Convention prohibits the use of toxic tin biocides and, in principle, establishes a mechanism to prevent the potential future use of other harmful substances in antifouling systems.

Providing a nontoxic alternative to biocidal antifouling coatings, foul release (FR) coatings reduce the ability of fouling organisms to adhere to the surface, while the movement of the surface through water results in removal of weakly bonded foulers by shear stress.[7] Patented by Milne in 1975 the original silicone poly(dimethylsiloxane) elastomer (PDMSE) formulation was commercialized in the early 1980s in the US as low-modulus FR thick (>150 μm) coating for large ships cruising at over 15 knots.[8]

Besides the high cost of silicones, especially of fluoropolymer-modified silicones, low efficacy of these coatings for vessels cruising at lower speeds, or remaining idle for prolonged periods, has generally limited their utilization on larger scale. Only in the last few years, intense research activities mainly carried out at marine coating suppliers has resulted in a number of new, successful FR coatings going beyond their traditional limitations;[9] and now, the current (2015) share of FR coating applications on ship hulls exceeds 10%, with all major antifouling marine coatings now including elastomeric foul release paints in their product portfolio (in 2009, this Figure did not exceed 1%).

In this context, we have described the emerging strategies for the development of environmentally friendly AF/FR systems based on biocidal and non-biocidal hybrid xerogel coatings,[10] concluding that the sol–gel technology is a mature platform for the development of new marine coatings for both the prevention of biofouling as well as to enhance the hydrodynamic properties of boat and ship hulls.

Herein we discuss in detail how the sol–gel hybrid nanocoatings technology has been practically applied to meet the urgent demand for clean antifouling marine coatings, providing an eminent example of the innovation invoked by Ozin and Cademartiri in 2010, who concluded that nanochemistry was bound to enter a productive phase in which the new discoveries of nanoscience would result in new materials that really solve problems of large economic and environmental relevance.[11]

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In the following, we summarize achievements using a multifunctional xerogel coating (tradenamed *AquaFast*) providing protection against biofouling and enhanced foul release properties to vessels composed of widely different materials, including fiberglass, metal and wood, in both fresh water and then in the marine environment, further showing how chemical ingenuity is actually leading to rapid improvement of the original formulation.

2. AquaFast

The first successful FR sol–gel coating was *AquaFast*, namely an organically modified silica-based hybrid xerogel obtained by hydrolytic polycondensation of *n*-octyltriethoxysilane (C8) and tetraethoxysilane (TEOS) in 1:1 molar ratio prehydrolyzed in aqueous isopropyl alcohol [Eq. (1), unbalanced, in which R is the *n*-octyl group]:[12]

$$Si(OEt)_4 + RSi(OEt)_3 + H_2O \xrightarrow{PrOH} [R\text{-}SiO_nH_m(OEt)_q]_p + EtOH \quad (1)$$

The *AquaFast* xerogel coating turns out to have a surface energy of 21.5 $mN\,m^{-1}$, namely in the 20–30 $mN\,m^{-1}$ region of minimal bioadhesion in the curve of adhesion strength versus surface energy (Figure 2), namely Baier's "theta surface" elegantly defined as "that characteristic expression of outermost atomic features least retentive of depositing proteins, and identified by the bioengineering criterion of having measured CST between 20 and 30 $mN\,m^{-1}$").[13]

In this region, bioadhesion of microfoulers is minimized due to the formation of weak boundary layers between the surface and the adhesive proteins of fouling organisms. Indeed, *AquaFast* produced in small (100 liter) batches at Telluride East (in the US) since 2006 has been applied with a roller as 20 μm thick coating to the hull of over 100 boats in Lake Ontario (North America) providing prolonged reduced settlement of algae and barnacles.[9]

The release of fouling species from the hard (elastic modulus 10^2–10^4 MPa) and thin (10–60 μm) silica-based xerogel coatings, we have explained elsewhere,[13] is dependent upon shear. Contrary to flexible silicones, indeed, glassy ORMOSIL xerogel thin films cannot undergo deformation. Furthermore, beyond huge elastic modulus, the ORMOSIL xerogel surfaces have also very low roughness (10^{-9}–10^{-10} m, several orders of magnitude lower in comparison to the 6×10^{-5} m roughness of commercial silicone coatings). Reduced roughness is *more* significant when compared to surface energy in determining the strength of adhesion of diatoms to these surfaces.

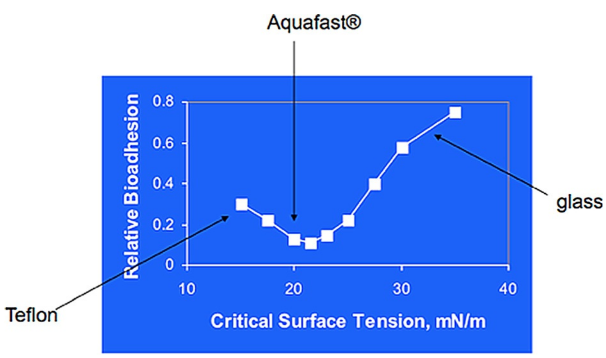

Figure 2. Critical surface tension can often be predicted by water contact angles. *AquaFast* is in the zone of minimal bioadhesion.

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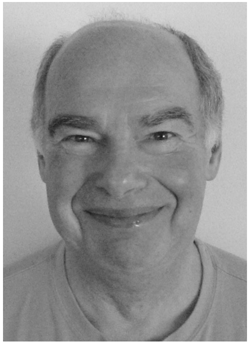
Michael R. Detty is the current Chair of the Department of Chemistry at the University at Buffalo where he has been a Professor since 1995. His research interests in the broad field of environmentally benign chemistry span from ecofriendly antifouling coatings through solar hydrogen and solar electricity. The AquaFast coating is one of his joint research achievements.



Mario Pagliaro is a chemistry and solar energy scholar based at Italy's Research Council. His research group's achievements encompass a large body of publications, 20 books and the organization of the yearly SuNEC and FineCat international meetings. A Fellow of the Royal Society of Chemistry, Mario is the co-founder of Sicily's Solar Pole.

In general, along with *i)* surface energy, *ii)* elastic modulus and *iii)* nanoscale roughness are the two other main surface properties determining the settlement and the ease of removal of biofouling.[1] The sol–gel processing using organically modified silica (ORMOSIL)[14] coatings allows one to independently tune the three parameters above affording FR coatings meeting advanced performance requirements.[10]

Indeed, many organically modified precursor silanes with alkyl or fluoroalkyl groups, were used to prepare two component ORMOSIL-based coatings and study their AF/FR behavior toward adhesion of bovine serum albumin (BSA), settlement of barnacle larval cyprids, and attachment and release of the diatom *Navicula perminuta*.[15] The fluorocarbon, aminopropyl, and hydrocarbon groups provided a range of surface chemistries and surface energies (γ_S from $\approx 19\ \mathrm{mN\,m^{-1}}$ to $> 53\ \mathrm{mN\,m^{-1}}$), with the fluorinated surfaces showing, as expected, the lowest surface energies.

The adhesion of BSA to all the xerogel surfaces was weaker in comparison to adhesion to PDMSE standard. Furthermore, adhesion of BSA to the xerogels mimicked the Baier curve with adhesion being stronger to surfaces with lower *and* higher values of γ_S.

Barnacle cyprids showed the strongest adhesion to surfaces with higher surface energies, while diatoms showed the strongest adhesion to surfaces of lower surface energy. Finally, *Ulva* sporelings were easily removed from hydrophobic (low-surface energy) surfaces (Figure 3). On the other hand, removal of the diatom *Navicula perminuta* is easier when surfaces are hydrophilic (higher energy, Figure 4).

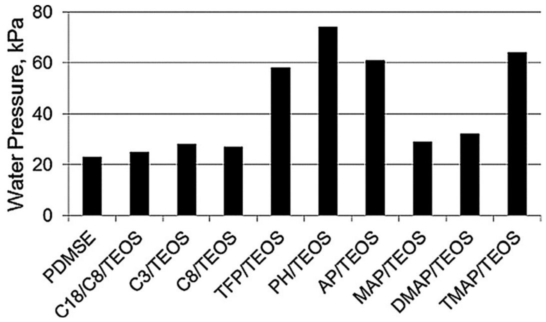


Figure 3. The water-jet pressure to give 50% removal of 7 day *Ulva* sporeling growth from xerogel surfaces plotted as a function of water wettability as defined by the static water contact angle, θ_{Ws}. [Reproduced from Ref. [15], with kind permission].

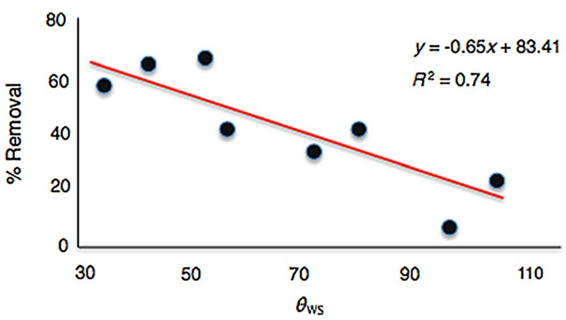


Figure 4. The diatom *Navicula perminuta* is linearly correlated with the static water contact angle (θ_{Ws}). [Reproduced from Ref. [15], with kind permission].

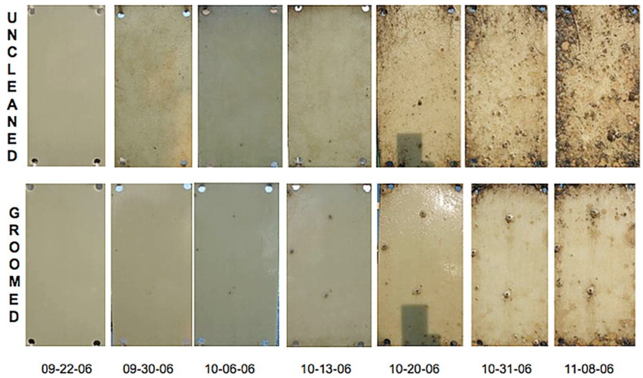


Figure 5. Static immersion testing in salt water (Melbourne, Florida). The submerged, durable and smooth surface is resistant to the glycoprotein that fouling organisms secrete, hence making it difficult for them to adhere strongly to the surface. [Image of Prof. M. R. Detty, reproduced with kind permission].

In general, the water-borne transparent *AquaFast* paint is easily and efficiently applied at ambient temperature, requiring no pretreatment coat for bonding to different substrata, affording uniform, uncracked and smooth painted surfaces.

For example, the 1:1 C8/TEOS colorless coating was applied by paint brush to the 4" x 8" fiberglass samples displayed in Figure 5. The upper panel was allowed to collect fouling in sea water over the time period shown, while the bottom panel was lightly groomed at the indicated time points.

3. AquaFast Pro

The removal of diatom stains from hull surface coated with *AquaFast* is less successful when compared with the removal of algae. The versatility of the sol–gel nanochemistry approach to tune not only the hydrophilic-lipophilic balance (HLB) of the coating, but also its nanoscale homogeneity, however, provides a second generation xerogel series capable to achieve foul release performance of broader scope.

In detail, it is enough to add 1 mol% of long-chain alkyl-modified silane (*n*-octadecyltrimethoxysilane, C18) to the original *AquaFast* formulation to create a surface topographically and chemically *inhomogeneous* with 100–300 nm wide pores (Figure 6b, AFM investigation done in air), with the hydrocarbon moieties distribution (the polymethylene chains in the C18 chain) concentrated at the organosilica pore's surface,[16] as shown by the FTIR microscopic analysis of the 1:49:50 C18/C8/TEOS coating (Figure 7b).

This subtle finding is in full agreement with previous structural studies on C18-modified ORMOSIL xerogels in which the alkyl tails are fully extended in a crystalline-like conformation at the material's inner surface.[17]

Said addition of small percentage (1 mol%) of C18 to the original *AquaFast* formulation results in greatly enhanced removal of barnacles (Figure 8). While both hydrophobic and hydrophilic surfaces fail, the new formulation (tradenamed *AquaFast Pro*) employed in the removal of barnacles has performance similar to that of a standard 500 μm thick silicone

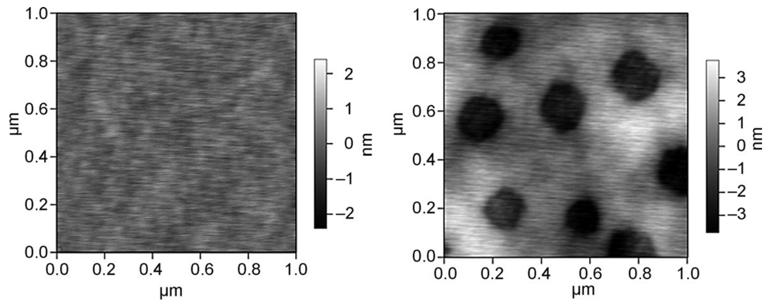


Figure 6. AFM images of 50:50 C8/TEOS coating show a uniform surface (left). The AFM images of 1:49:50 C18/C8/TEOS coating (right) show a porous surface with 100–300 nm wide pores that are 3–5 nm deep. [Reproduced from Ref. [16], with kind permission].

PDMSE coating (*Silastic T2*, tradename of a platinum-catalysed hydrosilylation cured silicone).

In other words, even though 50:50 C8/TEOS (*AquaFast*) and 1:49:50 C18/C8/TEOS (*AquaFast Pro*) have nearly identical surface energies and elastic modulus, the different nanoscale topographies result in greatly enhanced release of barnacle from the inhomogeneous C18/C8/TEOS surface.

This outcome is similar to that observed with silicone low modulus materials (all with an elastic modulus of 1 MPa), typically applied as thick (150–500 μm) FR coatings, whose second generation fluoropolymer-based product specified for vessels with speeds of 10 knots and above,[18] combines at the nanoscale the low surface energy effect of hydrophobicity *and* the resistance to protein adsorption characteristic of hydrophilicity, eventually providing an amphiphilic surface with improved FR characteristics against micro- and macrofouling organisms.

On June 2013 a large ship in was thus coated with 3 m×3 m patches of *AquaFast Pro*. The coating survived one season on the North America Great Lakes and showed largely reduced fouling relative to the untreated hull, opening the route to forthcoming commercialization.

4. Perspectives and Conclusions

Undertaking research on marine antifouling in the US about a decade ago, our goal was to design a fouling-resistant and fouling-releasing coating effective for both fast-moving ships and ships in dock, being at the same time environmentally friendly and affordable. Knowledge following intense research on xerogel-based hybrid coatings,[19] suggests that these thin glassy xerogel coatings would be mechanically much more stable (superior wear- and chemical resistance) and of longer duration compared to organic polymers, including fluorinated silicones.

The outcomes of these prolonged efforts are *AquaFast* and *AquaFast Pro*, namely two environmentally benign ORMOSIL-derived coatings that cure at low temperature providing reduced settlement of algae and barnacles due to minimal bio-

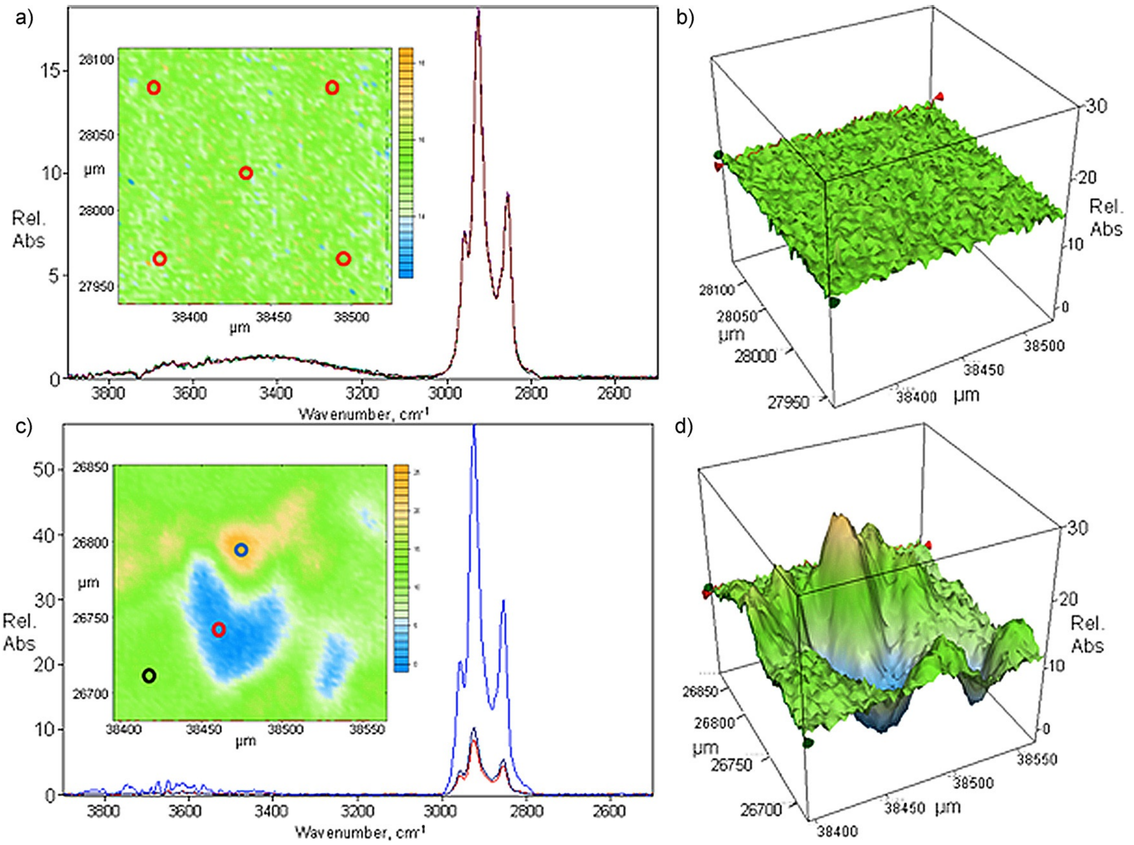


Figure 7. IR microscopic analysis of the 50:50 C8/TEOS coating shows a uniform surface (top), but reveals a nonhomogeneous distribution of the alkyl moieties in the 1:49:50 C18/C8/TEOS coating (bottom). [Reproduced from Ref. [16], with kind permission].

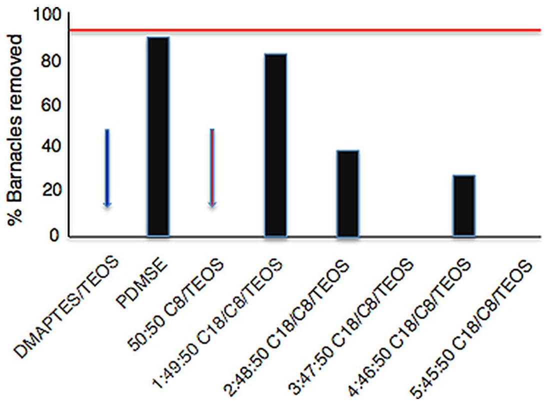


Figure 8. Removal of *Juvenile* barnacles (5–7 mm basal plate) from surfaces coated with different sol–gel and elastomeric coatings. [Reproduced from Ref. [16], with kind permission].

adhesion, which in its turn is due to low critical surface energy *and* to optimally tailored topographical and molecular inhomogeneity; while efficient removal of partly formed biofouling by shear is ensured by the exceedingly large modulus of these uniquely hard, glassy coating.

Besides containing no biocides (pesticides or metals), the colorless and transparent xerogel coatings can be applied via roller, brush or spraying to many types of surfaces, including cameras[20] and solar panels, lasting several seasons rather than one season as it happens with traditional antifouling paints. For comparison, in the case of recreational boats, traditional biocidal paints are typically renewed every 12–18 months, while the *AquaFast* xerogel coating on small boats can be reapplied after 3 years continuing to give similar performance.[9]

From an environmental viewpoint, in contrast to conventional paints using toxic biocides and large amounts of volatile organic compounds (VOCs) as solvents, water-based FR sol–gel paints do not contain harmful biocides and make a limited use of VOCs mainly present as ethanol, isopropanol or related small chain alcohols of limited toxicity.

Low surface energy, hard sol–gel coatings are advantageous from both technical and scope viewpoints. Technically, silica-based xerogel coatings are one order of magnitude thinner than elastomeric coatings, thus requiring lesser material. Furthermore, the pre-hydrolyzed water-based silane paint is perfectly suited to easily coat and protect from biofouling hulls composed of widely different construction materials (i.e. steel, wood, fiberglass, aluminum), independently of vessel's size and cruising speed. This means that both large vessels, cruising as slower speeds, and faster small crafts can be protected with *AquaFast* at affordable cost, offering an alternative to FR paints based, for instance, on fluoropolymer silicone that in the US retail, under various tradenames, for about $800 per gallon (110/liter, not including the cost of application).[21]

Today, silica-based protective coating formulations from today's affordable alkoxysilanes are reliably manufactured by numerous companies worldwide.[19] Adding to the list of hybrid silicas nanocoatings, marine foul-release coatings *AquaFast* and *AquaFast Pro* are now produced by Canada's company (SiliCycle, Quebec City)[22] as alternative to traditional antifouling marine paints.

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Keywords: antifouling · mesoporous materials · nanochemistry · ormosil · sol–gel coating

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