



## Design, development and first validation of “biocide-free” anti-fouling coatings



M. Barletta<sup>a,b,\*</sup>, C. Aversa<sup>a,b</sup>, E. Pizzi<sup>a</sup>, M Puopolo<sup>a</sup>, S. Vesco<sup>a</sup>

<sup>a</sup> Dipartimento di Ingegneria dell'Impresa, Università degli Studi di Roma Tor Vergata, Via del Politecnico 1, 00133, Roma, Italy

<sup>b</sup> Dipartimento di Ingegneria, Università degli Studi Roma Tre, Via Vito Volterra 62, 00146, Roma, Italy

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### ABSTRACT

New antifouling (AF) coatings were designed and manufactured exploiting the proven foul-release (FR) properties of amphiphilic systems and comparing them with fully hydrophobic and hydrophilic systems. The novel strategy implied a simple synthesis route that involves exclusively the chemistry of polyurethanes. The system was indeed constituted by a corrosion resistant polysiloxane-polyester hybrid resin as binder, rich in highly reactive hydroxyl groups that make the polymer associable to the polyol of a polyurethane couple. Hydrophilic and hydrophobic moieties were introduced in the form of lateral chains of isocyanate hardeners. The system resulted easily implementable due to the combination of commercially available raw materials and the rapid kinetic of the reaction.

This method was used to prepare amphiphilic, as well as fully hydrophilic and hydrophobic systems, which were spray coated on construction steel samples. The coating wettability was analysed on all samples through the measurement of wetting hysteresis, highlighting the amphiphilic behaviour of the formulations. The highest amphiphilic character was detected on the hydrophilic reference sample, probably due to the highest mobility of PEG-ilate chains under this configuration. Anti-fouling properties were determined by the evaluation of the retention rate of two alive Mediterranean marine organisms, *Mytilus Edulis* and *Ulva Intestinalis*, on the surface of samples. A further test was carried out to evaluate the AF/FR properties against a natural protein probe, namely egg white. The test carried out with natural organisms proved the suitability of all the proposed strategies to the implementation of effective AF/FR marine paints. The egg white test assessed that the highest efficiency in AF/FR activity was detained by the fully hydrophobic systems. The observation of the surface of the samples by SEM in back scatter modality revealed that the chemical patterning of the hydrophobic scenario could play a significant role in the development of such behaviour.

### 1. Introduction

Design and implementation of antifouling paints for applications in the marine segment are mostly devoted to the achievement of new eco-friendly, non-toxic products, able to substitute traditional AF/FR paints based on noxious organotin composites [1]. One of the most promising eco-friendly approaches is represented by the implementation of structures able to disorientate the adhesion mechanisms of gluing proteins, exploiting the principle of finely patterned surfaces where domains of different chemical, physical, and topographical characteristics alternate [39].

The alternation of peaks and voids in a regular patterned topography was indeed found to be effective against the adhesion of marine species (*Ulva linza* sporelings) [2] and bacteria (*Staphylococcus aureus*) [3] that adhere on their substrate through the application of cell

elongation mechanisms.

Carman et al. [2] prepared a surface whose micro-topography mimicked the microstructure of fast moving sharks' skin by the use of photolithographic technology. The spacing between two ridges was designed to be smaller than the diameter of the globular protein used as gluing element by the organism selected for the test (*Ulva linza*). The ridges induce the protein to elongate its tertiary structure as they were perceived as a unique continuous substrate. Nevertheless, the voids occurring between the ridges molecule cannot be filled by functionalities on the protein, providing a reduced area of adhesion. This kind of structure was found to be effective also against the deposition of a *Staphylococcus aureus* over a period of 21 days by Chung et al. [3]. Long et al. quantified the antifouling properties of such kind of systems correlating topographical characteristics with AF/FR properties [4].

The patterning of surface chemistry and polarity also emerged as an

\* Corresponding author at: Dipartimento di Ingegneria dell'Impresa, Università degli Studi di Roma Tor Vergata, Via del Politecnico 1, 00133, Roma, Italy.  
E-mail address: [barletta@ing.uniroma2.it](mailto:barletta@ing.uniroma2.it) (M. Barletta).

efficient anti-fouling strategy [5–13].

A gluing protein features a mobile 3D structure and the simultaneous presence of hydrophilic and hydrophobic amino acids in its primary structure. Such feature is ascribable to the capacity of the protein to adapt its surficial polarity to the character of the substrate and ensure a stronger adhesion. This mechanism can easily fail if the protein simultaneously experiences hydrophilic and hydrophobic domains alternating over an amphiphilic surface, rearranging in a distorted fashion. Under this spatial configuration, the protein features a lower adhesion [5]. At the same time, an amphiphilic surface combines anti-settling properties of hydrophilic surfaces and anti-adhesion properties of low-energy surfaces [6].

The technology required for the implementation of amphiphilic surfaces is by far more economical and accessible than the technology required for the implementation of a topographic anti-fouling system. Indeed, it mainly coincides with the technology required for the implementation of traditional coatings even if the synthesis of raw materials often represents the “bottle neck” of this process. Martinelli et al. [7] evaluated the radical polymerization for the manufacturing of an amphiphilic block co-polymer having Poly(dimethyl siloxane)propoxyethyl 4-vinylbenzoate or 4-(triethyleneglycol monomethyl ether)-2,3,5,6-tetrafluoro-styrene as repetitive units, featuring hydrophobic and hydrophilic character respectively. The synthesis required 40 h at 65 °C for the polymerization in addition to the time required for the trans-esterification of the precursors. Analogous operative settings were found with the procedure of atom-transfer radical polymerization described by Hussain [8] for the synthesis of PEG-ilate/fluorinate amphiphilic block co-polymer. The introduction of commercially available surfactants reduced to one the number of steps of the grafting procedure due to employment of an alternating “surfactant block” and “neutral block” structure. Yet, the whole process necessitated a reaction time of 78 h at 100 °C.

The use of the silane chemistry represents a step forward in the simplification of the coatings formulating process. Indeed, the synthesis routes of the main branched grafted polymer, namely xerogels, does not require complex technical arrangements, with the exception of a stirring system [14]. A number of commercially available functionalized silanes can be used for the customization of the final product.

Mosaics of domains featuring different polarities were firstly obtained alternating moieties having different intensities of hydrophobicity character [9–11]. Sokolova et al. and similarly, Gunari et al. found that a xerogel obtained by the alternation of C8/C18 alkyl silanes, Triethoxy(1H,1H,2H,2H-perfluoro-1-octyl)silane and TEOS (Tetraethyl orthosilicate) was more efficient than PDMS in the foul-release of barnacles, establishing that the 3D structure arising from a possible segregation of components at determined concentrations did not influence the AF/FR properties of the system. Finley et al. [12], and Detty et al. [13] evidenced how the introduction of silanes with a marked hydrophilic behaviour (PEG-ilate silanes [13]; amino-terminated silanes [12]) gave a massive improvement of antifouling properties against *Ulva linza* sporelings and diatoms in analogous xerogels.

The chemistry of polyurethanes features many advantages over the chemistry of silanes including a lower cost of raw materials and a higher mechanical resistance. These two aspects were indicated as the most critical issues in the technology transfer of the chemistry of silanes to the paint industries [13]. Nevertheless, this option was not fully investigated yet in the manufacturing of antifouling coatings.

Vaidya et al. [40] manufactured segmented polyurethane where PEG-ilate diols-terminated and fluorinate diols-terminated succeeded along the chain, exploiting the reactivity of isocyanates as bridging molecule. The synthesis of diols did not require the application of extreme conditions, even though a mild heating (temperature ranging between 25 and 75 °C) and the fluxing of protective atmosphere were required. Nevertheless, the curing step could be not carried out at ambient temperature. The system resulted effective against fouling caused by soil and oily substances but was not evaluated against protein

and marine organisms [40].

In other studies of amphiphilic systems, polyurethanes were terminally modified by reaction with citric acid, malic acid, or lactic acid, and introduced as amphiphilic additives to functionalize a polyphenylsulphone membrane [15]. PEG-modified polyurethanes were also adopted as hydrophilic domains on a polyvinylidene fluoride surface [16] which constituted the hydrophobic moiety of the amphiphilic system described by Lü and collaborators. This modification, applied to a material usually adopted for the manufacturing of membrane filters, ensured a longer duration of the membrane due to slower staining of the surface on the proteins side. A similar approach was undertaken by Huang et al. [17] to confer antifouling properties to polyether sulphone membranes used as filters in blood analysis. In this case the PEG-ilate polyurethane was blended with the matrix polymer. The flexibility of polyurethanes also allowed their modification as hydrophobic moieties in a silica/polyurethane hybrid amphiphilic coating on PET, by plasma deposition [18]. The study demonstrated the achievement of a super-amphiphilic behavior of plasma-treated PET, however possible application as anti-fouling surface were not yet studied. Nevertheless, the use of plasma technology constitutes a remarkable limit to the exploitation of this technology for large-scale applications.

To the best of our knowledge, no study reports the implementation of purely polyurethane coatings as amphiphilic coating systems using a simple traditional coating technology.

This study first reports an easy process for the fabrication of an antifouling coating aimed to applications in the marine industrial segment. The proposed methods exploited the availability of a wide range of commercial polyurethane hardeners, featuring a different wettability, to modify the polarity of a hydroxyl-rich polysiloxane-polyester hybrid coating. Hydrophobic hardeners and hydrophilic PEG-ilate hardeners were selected as hardeners that react through their isocyanate groups with the hydroxyl groups on the resin. The coating was then characterized, together with its hydrophilic and hydrophobic reference samples, in terms of wettability and anti-fouling properties.

## 2. Experimental

### 2.1. Materials

Amphiphilic coatings and the corresponding reference samples were obtained blending –OH rich hybrid polyether-polysiloxane resin and isocyanate hardeners featuring hydrophobic and hydrophilic groups. Silikotop E901 (Evonik, Essen, Germany) was selected as –OH rich resin, while Bayhydur 3100 (Covestro, Leverkusen, Germany) and Desmodur N 3900 (Covestro, Leverkusen, Germany) were selected as hydrophobic and hydrophilic hardeners respectively. Silikotop features an –OH content of 200 mg KOH/g, while the isocyanate content of hardeners, Bayhydur 3100 and Desmodur N 3900, featured isocyanate content of 17,4% w.t. % o and 32,5% w.t. respectively. The amphiphilic sample was obtained using a blend between hydrophilic and hydrophobic hardeners for the curing of the coating. The hydrophilic reference sample and the hydrophobic reference sample were obtained curing the system with solely hydrophilic hardener or solely hydrophobic hardener each time respectively. The amount of isocyanate was calculated to have every –OH functional group react with one molecule of hardener, meaning the hardener bears three isocyanate functionalities. The reaction was catalysed through the addition of dibutyltin dilaureate (Sigma Aldrich Italia, Milano, Italy). Butyl acetate, purchased from Sigma Adrich Italia (Milano, Italy), was used as thinner for all the formulations. The precise composition of each formulation is reported in Table 1.

Antifouling polyurethane varnishes were applied on an epoxy primer, (Adherpox, Veneziani, Italy) applied on sand blasted Fe E 340 steel slabs. Anti-fouling properties of the samples were compared with the performance of a traditional, one-pot, non-anti-vegetative painting product: Unigloss from Veneziani Yachting (Boero, Genova, Italy). The

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