Colloids and Surfaces A: Physicochem. Eng. Aspects xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Amphiphobic coatings for antifouling in marine environment

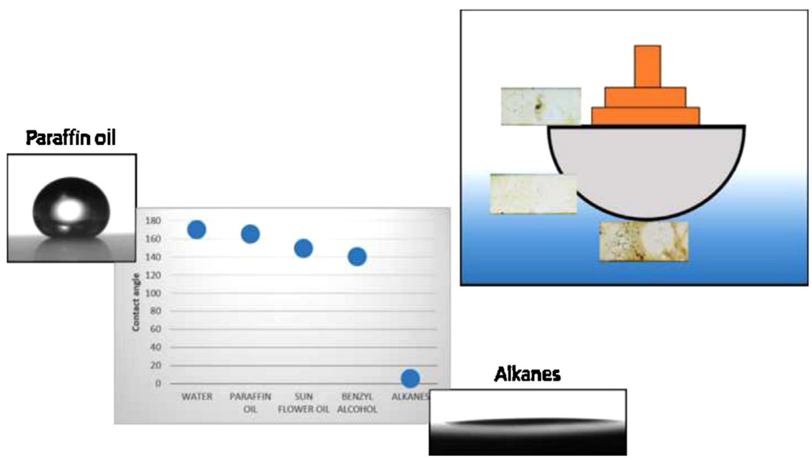
Francesca Cirisano, Alessandro Benedetti, Libero Liggieri, Francesca Ravera, Eva Santini, Michele Ferrari*

CNR—Istituto per l' Energetica e le Interfasi, 16149 Genova, Italy

HIGHLIGHTS

- Easy preparation and application of amphiphobic coating for marine environment.
- Wearing and temperature resistance for longer term application.
- Easy removability of early stages biofilm for antifouling.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 November 2015
Received in revised form 22 February 2016
Accepted 15 March 2016
Available online xxx

Keywords:
Coatings
Amphiphobic
Marine environment
Superhydrophobic
Oleophobic
Wearing

ABSTRACT

Highly hydro and oleophobic materials applied to needs of the marine environment represent a relatively young field achieving growing interest as innovative solution, where technological and ecological aspects allow to be merged, taking into account the limitations imposed by international laws in terms of environmental protection.

In this work a superhydrophobic (SH) coating for seawater applications has been characterized and tested in both laboratory and field conditions, since investigations in real seawater are crucial to evaluate the behaviour of SH surfaces because of a complexity not reproducible in laboratory. Taking into account the real conditions where the surface can operate oleophobicity can be investigated in presence of organic and inorganic pollution. The amphiphobic surface has been also studied to simulate those applications where the surface undergoes to thermal stress like pipelines and desalination plants affected by biofouling.

The preliminary wearing test shows the effective resistance to a continuous low velocity impact of micrometric particles of the coating investigated here.

Finally, time durability in field tests has been studied as a function of immersion angle in real seawater environment to investigate the role of the coating on early stages of biofilm growth.

1. Introduction

The contact of seawater with materials causes major, undesired chemical-physical alterations like mainly change in surface

* Corresponding author.
E-mail address: m.ferrari@ge.ieni.cnr.it (M. Ferrari).

http://dx.doi.org/10.1016/j.colsurfa.2016.03.045
0927-7757/

topography and chemical composition induced by the growth of biological layers at solid-liquid interfaces (the so-called biofouling) holding to corrosion phenomena and drag reduction of vessels. The resulting effects are the enhancement fuel consumption during navigation and material deterioration. These effects regard ship hulls and materials used in other applications like marine sensor, pipelines in power or desalination plants, inducing high maintenance costs regarding different maintenance procedures [1,2].

In this direction, it is important to develop innovative solutions merging technological and ecological aspects taking into account limitations imposed by international laws in terms of environment protection [3–5]. In this respect, superhydrophobic materials applied to marine environment are a relatively young field achieving growing interest [6,7].

A superhydrophobic surface shows extraordinary non-wetting properties due to the simultaneous existence of specific topographical patterns (micro-nano roughness) and low surface energy compounds [8,9]. As a matter of fact, this kind of surfaces exhibit large water contact angle (CA), CA >150°, and low sliding angle (SA), SA <5°. Water drops easily roll off the surface producing a self-cleaning action [10]: while moving they easily remove dust and dirt particles.

Thus, superhydrophobic surfaces (SHS) can act as a protecting defence against water in different applications such as antifouling coatings, membrane for oil separation, waste-water treatments, optical windows including anti-corrosion [11,12], anti-fouling [13] and drag reduction for ship's hull [14,15], anti-bacteria of medical equipment [16,17] and anti-water condensation and heat transfer [18].

For applications in real seawater, a superhydrophobic coating has to survive long-term exposures to water, sand impact, mechanical scratch/abrasion and fouling growth. The aspect of the fouling growth has been addressed in our previous work, dealing with a facile fabrication of a superhydrophobic surface [19] and its preliminary characterization. In particular, we had investigated the behaviour of the SHS in a real seawater environment and the corrosion behaviour evidencing the evolution within 3 weeks of electrochemical parameters and surface wettability [20,21].

Biofouling is a process consisting in biocolonization of surfaces immersed in natural seawater. Macromolecules adsorb within minutes/hours determining the formation of the so called 'conditioning film' [22]. This layer contributes to further bacteria and diatoms adhesion (days) constituting the biofilm, followed by the subsequent arrival ad colonization of macro organism (macrofouling) [23,24].

Along with the formation of biological layers, in real seawater environments mechanical wearing like abrasion by suspended particles can be regarded as another possible source of damage occurring on topographical patterns of a SH surface. The integrity of micro-nano textured topography is essential for the presence of air pockets in the Cassie-Baxter non-wetting state [25]. The physical damage of this structure can lead to undesired progressive pinning of water droplets and, eventually, to the loss of superhydrophobicity.

In addition, surfaces are often easily wetted by oily liquids, leading to organic contamination and loss of water repellence. To avoid this problem an oleophobic/superoleophobic surface is preferred [26–28], and, regarded in combination with the superhydrophobicity, as a more suitable solution for a wider use in many fields.

The preparation of surfaces with such behaviour is a wide research topic [29–31], nevertheless, many of these coatings require a too expensive preparation, exhibit very short lifetime and often are limited to small surface, reducing their use for a real employ. Some works are devoted to the durability of these surfaces with different techniques: abrasion by sand paper [32], sand particle impacting [33], continuous drop impact [34] and immersion in solution [35] are referred. Nevertheless, in general, the investigation of surface robustness was limited to a short time (minutes, hours) [31,36].

This work is devoted to the investigation of a coating for underwater/seawater applications as a possible tool to control biofouling growth and friction drag. The coating was easily prepared by spray allowing the possibility to use it for applications that require frequent maintenance. Characterization was performed by CA measurements, profilometry and water bouncing, laboratory investigations were performed including wettability tests after thermal treatment and wearing tests, in order to emphasize the oleophobic behaviour. Finally, the growth of biofouling growth and its removability has been studied in seawater exposing the samples to the natural photoperiod up to 4 weeks with different angles.

2. Materials and methods

2.1. Surface preparation and characterization

The surfaces were prepared by a mixed organic-inorganic coating, fluoropolymer blend and fumed silica nanoparticles, as described elsewhere [37]. High purity grade water, produced by a MilliQ (Milli-Pore) ion-exchange purifier with a microfiltration stage, was utilized for the contact angle (CA) measurements. The coating was applied on a glass substrate by spraying a dispersion of silica particle/fluorinated polymer coating on the substrate. The spray was used at the distance of 5 cm at the pressure of 3 bar.

For the evaluation of wetting properties of the surface, CA measurements were carried out by the ASTRAview tensiometer (developed at CNR-IENI [38]) at room temperature. In order to check the homogeneous deposition of the film data were collected in at least 3 different positions of the surface.

The surface structure of samples was investigated with 3D Confocal and Interferometric Profilometry (Sensofar S-NEOX, Spain) in order to evaluate the roughness. The profilometry was chosen to permit large surfaces scan, such as the samples used in this work and for its ease of use.

The as prepared surface was tested to study its oleophobicity. For this purpose different organic liquids, hexane, paraffin oil, benzyl alcohol, sun flower oil, petroleum and lubricant were used. These solvents were chosen for their different properties such as viscosity or surface tension and as example of a real possible contaminant. In addition, the samples have been studied observing the impact of water bouncing on the SH surface with the use a camera Fujifilm Finepix HS10 (1000 fps). A stainless steel capillary, with a diameter of 0.21 mm, was connected to a syringe to produce water drops of about 5 mm^3 from a height of 25 mm (tip to surface).

The amphiphobic behaviour was tested with thermal treatment and immersion in stirred solution with suspended solids, in order to understand the behaviour in conditions more similar to a real employ.

2.2. Thermal treatment

The thermal test was performed in a furnace in air atmosphere. The temperature was increased at a constant rate of 5°/min up to 200 °C and maintained constant for 60 h. Successively, the samples were extracted from the furnace and cooled down at room temperature. Furthermore a cyclic test was done. The samples were heated until 200 °C for 2 h, then cooled at T room and repeated for 10 times. The temperature of 200 °C [39] was selected in order to avoid the thermal decomposition of the fluoropolymer. This test was also a possible accelerated aging test for application where is required a thermal treatment