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Design, manufacturing and testing of anti-fouling/foul-release (AF/FR) amphiphilic coatings

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ABSTRACT

In this study, innovative strategies for the manufacturing of anti-fouling/foul-release (AF/FR) coatings based on the implementation of amphiphilic surfaces by the chemistry of silanes and polyurethanes were evaluated. The newly developed process for the synthesis of amphiphilic resins involved the introduction of hydrophobic functionalities by the sol-gel reaction of a fluorinate-alkyl bearing silanes (FTSi). Conversely, the introduction of hydrophilic PEG-ilate functionalities was alternatively implemented by the sol-gel reaction with PEG-ilate silanes (PEGSi) or PEG-ilate isocyanates. These synthesis processes were possible thanks to the adoption of a peculiar hydroxyl-rich hybrid resin, consisting in a polysiloxane resin modified by polyester domains. Manufacturing of the formulations was a rapid process (shorter than 3 h), and easily implementable thanks to the sole use of commercially available raw materials. The synthesis did not require any special technical arrangement such as reflux conditions, autoclave or inert atmosphere. The effectiveness of the synthesis was evaluated by FTIR analysis, while the amphiphilic character of the surfaces was ensured by wettability test against water. AF/FR properties were tested under severe conditions using a protein test probe (i.e., the so called "egg white" test) that well simulates the substances secreted by the bio-fouling organisms to adhere. All the samples tested showed amphiphilic character, with most of them featuring excellent AF/FR properties.

1. Introduction

Bio-fouling of ship hulls caused by marine organisms and algae is responsible for higher fuel consumption of vessels. Maintaining a clean hull is, therefore, extremely important [1]. Many strategies of coating were developed in the past to promote the removal of the marine biofilm deposited on hulls, between two cleaning cycles. Most of these strategies rely their anti-fouling activity on the use of noxious biocide substances, namely organo-tin and organo-copper composites [2]. Since the banning of organo-tin composites, and in view of an imminent ban of the less-toxic copper composites, more eco-friendly alternatives have emerged [2].

In particular, protein-release coatings based on PEG-ilate substances [3–7], or hydrophilic substances [8,9], as well as fouling release coatings based on PDMS with low superficial free energy, have been developed. Such strategies are mainly based on the thermodynamic of the surfaces. In PDMS systems the formation of weak bounds between the marine organism and the low-energy surfaces promotes the release of the biofilm during navigation [10]. Moreover, the absorption of water on PEG-ilate surfaces is thermodynamically favoured over the adhesion of gluing protein substances [6]. In some cases, the introduction of fluorinate components, as linear [3], or hyper branched [5], molecules enhances the foul release effect of low energy systems resulting from furtherly lower free energy of the surface. In addition, the low-modulus of PDMS systems easily deforms releasing the stiff organisms attached (e.g. Barnacles) through a peel-off mechanism [11]. Among the various solutions amphiphilic coatings are particularly interesting. They are able to combine, in a single product, the protein-release effect of the hydrophilic surfaces and the inhibition of strong bounds, typical of a low energy, hydrophobic surface [3]. At the same time, the mosaic organization of the different domains further inhibits the structural rearrangement of hydrophilic/hydrophobic protein substances adopted by several organisms to adapt to the support surfaces [3].

As reported by [2] and other authors [11], only few of these strategies effectively resulted in a proper commercially available product. Mainly, commercial products exploit the AF/FR and low-modulus properties of PDMS coatings (e.g. Intersleek 700, International; Silic One, Hempel) acting as foul-release paints. On the other hand, to the

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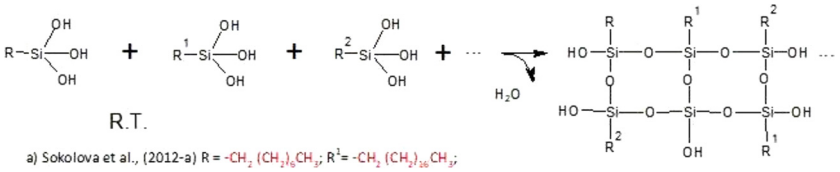
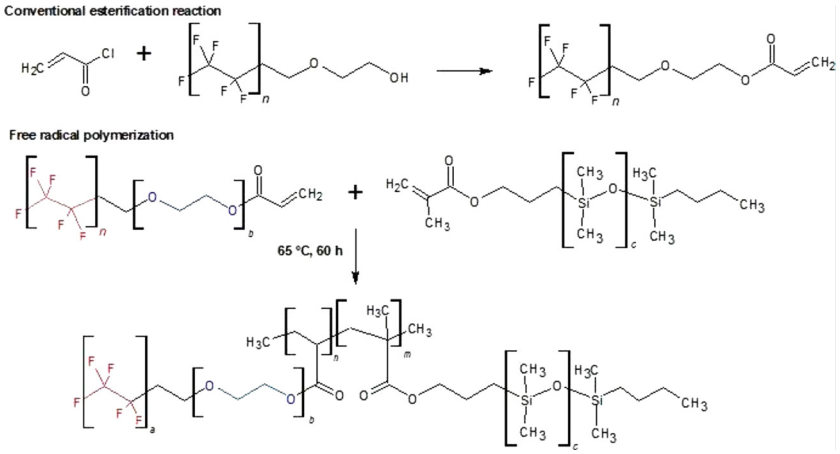
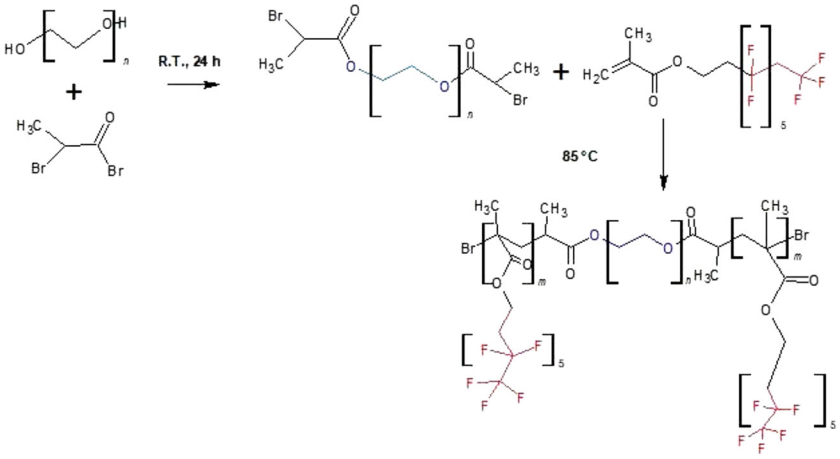
Table 1
Reaction routes applied for the manufacturing of amphiphilic polymers discussed in the introduction. Highly hydrophilic and highly hydrophobic domains are indicated in the schemes with blue and red colours, respectively. Medium polarity moieties are also used in the design of amphiphilic patterning ad they are evidenced by the green colour.

Strategy	*Manufacturing reaction*
amphiphilic coatings from sol-gel chemistry	 a) Sokolova et al., (2012-a) R = $-CH_2(CH_2)_6CH_3$; R^1= $-CH_2(CH_2)_{16}CH_3$; R^2=$-CH_2CH_2(CF_2)_5CF_3$; R^3=-OH b) Sokolova et al., (2012-b); c) Gunari et al., (2011) R= $-(CH_2)_3N(CH_3)_2$; R^1=-OH; or R = $-CH_2(CH_2)_6CH_3$; R^1= $-CH_2(CH_2)_{16}CH_3$; R^2=-OH; R^3=$-CH_2CH_2(CF_2)_5CF_3$ d) Finlay et al., (2010) R = -OH; R1= $-(CH_2)_3N(H)CH_3$ or $-(CH_2)_3N^+(CH_3)_3I$ or $-(CH_2)_3NH_2$ or -Ph or $-CH_2CH_2CH_3$ or $-CH_2(CH_2)_6CH_3$ e) Bennet et al., (2010) R= -OH; R1= $-CH_2(CH_2)_{16}CH_3$ or $-CH_2(CH_2)_6CH_3$ or -Ph or $-CH_2CH_2CH_3$ or $-CH_2CH_2CF_3$ or $-(CH_2)_3NH_2$ or $-(CH_2)_3N(H)CH_3$ or $-(CH_2)_3N(CH_3)_2$ or $-(CH_2)_3N^+(CH_3)_3I$; R^2=$-CH_2(CH_2)_6CH_3$ or -Ph f) Tang et al., (2005) R= -OH; R1= $-CH_2CH_2CH_3$ or $-CH_2(CH_2)_6CH_3$ or $-(CH_2)_3NHCH_2CH_2NH(CH_2)_3$-
Amphiphilic polymeric additive from free radical polymerization. Martinelli et al. [15]	
Amphiphilic polymer from atom-tranfer radicalic polymerization. Hussain et al. [18]; Hussain et al. [17]	

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