



Full length article

Sol-gel hybrid coatings containing silica and a perfluoropolyether derivative with high resistance and anti-fouling properties in liquid media



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ABSTRACT

Organic inorganic hybrid coatings were prepared using a commercial triethoxysilane α,ω substituted perfluoropolyether as organic phase in combination with tetraethyl orthosilicate (TEOS) as inorganic phase. The coatings were prepared by sol-gel synthesis of a silica coating in co-presence with the commercial polymer, and deposited on stainless steel substrates by dip-coating procedure. The interactions between the organic and the inorganic components were studied by means of X-ray photoelectron spectroscopy. The synergistic effect of the two opposite phases permitted to obtain hydrophobic coatings (contact angle CA of $\sim 140^\circ$) with high resistance against thermal or mechanical stresses induced in liquid media. The hybrid coatings thus obtained to possess suitable properties for application as anti-fouling coatings in liquid environments. Specific tests performed in particulate fouling conditions confirmed the ability of the hybrid coatings to mitigate CaSO_4 deposits formation, maintaining unaltered the CA value after exposition for 43 days to a flux of a CaSO_4 solution at a flowrate of 0.15 m/s.

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1. Introduction

In the last few decades it has been observed an increasing demand of smart materials able to combine different useful properties, for possible application in the most diverse industrial fields, following the needs of the recent technological breakthroughs. Regarding the field of coatings technology, the organic inorganic hybrid (OIH) coatings represent the multifunctional response for the industrial demand. These materials, in fact, are at the interface of organic and inorganic systems, and they find a compromise between the typical features of organic materials, for example, film forming ability, density, hydrophobia, etc., and the ones of inorganic materials, such as mechanical or thermal stability [1].

Generally, the OIH materials are defined as materials containing organic and inorganic compounds blended at the molecular scale, independently from the existence or not of interactions between

the organic and the inorganic units [2]. Among all the possible OIH systems, the sol-gel derived hybrid coatings had attracted great interest, since the sol-gel synthesis is a low temperature process and permits the combination of inorganic compounds with many organic molecules, comprising polymers, without compromising the integrity and the functionality of the organic unit. The sol-gel derived hybrid coatings can be obtained by many different synthetic techniques [3], but they can be grossly divided in two classes: the first class includes the inorganic-organic matrixes, in which the organic molecules (usually oligomers or polymers) are embedded within an inorganic matrix, and only weak bonds are formed between the organic and the inorganic units. In that case, the inorganic network is formed by hydrolysis and condensation of the inorganic precursor in co-presence with the organic molecules. In the second class are collected all the OIH systems in which the organic and inorganic units are covalently bonded [4].

In this research, we prepared organic-inorganic hybrid coatings interspersing a silica network (obtained by the sol-gel synthesis) with a fluoropolymeric matrix, following the first class synthetic approach, i.e., the hydrolysis and condensation of tetraethylorthosilicate (TEOS, the silica precursor) was made in presence of a α,ω -triethoxysilane perfluoropolyether derivative.

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The organic and the inorganic phases composing these OIH coatings were carefully chosen in view of their specific application, i.e., fouling mitigation. The main feature that we aimed to confer to the anti-fouling coating was the hydrophobicity. It has been in fact demonstrated that low energy surfaces are able to support an air film against the water in which they are immersed; thanks to that, it is possible to reduce the water-wetted area and, consequently, also the probability that biological organism or organic/inorganic particles, present in water, encounter the solid surfaces [5–7].

The perfluoropolyether (PFPE) contributed to impart this property to the coatings. The PFPEs belong to the family of fluoropolymers, hence they are characterized by the presence of the very strong C-F bonds, which confer to the polymer interesting and useful properties, such as low friction coefficient, thermal and chemical stability, low energy surface, and hydrophobicity and oil repellency [8]. A fluoropolymer coating, however, does not possess great mechanical properties. In a previous study [9] we tried to improve the mechanical properties of coatings obtained from α,ω substituted perfluoropolyethers through the combination with inorganic nanoparticles, forming multilayer coatings in which the inorganic and the organic parts did not interact each other from a chemical standpoint. In that way we obtained improvements in mechanical resistance of the hydrophobic coatings, but at the same time we developed very thick and rough coatings, which strongly altered the surface properties of the underlying metal substrates. In this work, the OIH technology was employed with the aim to emphasize the reinforcing effect played by the inorganic compounds in the combination with a α,ω -triethoxysilane-terminated perfluoropolyether (Fluorolink[®]S10), developing a coating of thickness and roughness comparable to one of the simple PFPE coating. As inorganic component in the hybrid coating we used silica (from tetraethylorthosilicate, TEOS); sol-gel silica coatings are in fact well known for their hardness and thermal stability [10]. The possibility to combine Fluorolink[®]S10 with TEOS was already investigated; Taurino et al. [11] demonstrated the superhydrophobic behaviour of TEOS/Fluorolink[®]S10 coatings obtained from a sol-gel process on glass substrates. Similarly, Ferrero and Periolatto [12] employed the same compounds, combined by sol-gel process, to develop hydro/oil-phobic cotton fabrics, while Wongchitphimon et al. [13] used them to alter the surface properties of a fiber membrane. The results of these works prove the effective hydrophobicity of hybrid coating obtained from Fluorolink[®]S10 and TEOS, as we could observe even in this study depositing the coatings on stainless steel surfaces. However, this work explores the ability of TEOS, combined by a sol-gel process with the PFPE, in improving the chemical and mechanical resistance (in particular against shear stresses due to water flowing) of the hybrid coatings.

2. Material and methods

2.1. Coatings preparation

The hybrid coatings were prepared employing a commercial PFPE, named Fluorolink[®]S10 (Solvay Specialty Polymers). Fluorolink[®]S10 contains inorganic functionalities (Si(OEt)₃ triethoxysilyl groups) at the ends of the polymeric chain, as shown in Fig. 1 [14]. The presence of Si(OEt)₃ groups on the polymer can improve the interaction of the organic phase with the inorganic metal oxide phase. The trialkoxysilyl groups can in fact co-condense during the condensation reaction involved in the sol-gel process, thus leading to the formation of interaction between the organic and the inorganic species [2].

The organic precursor used for the synthesis of silica sol-gel networks was tetraethylorthosilicate (TEOS), purchased from Sigma-Aldrich (99.9% purity). All the other reagents employed

Fluorolink[®]S10

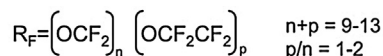
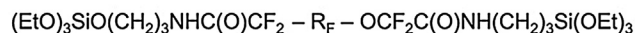


Fig. 1. Molecular structure of the commercial perfluoropolyether Fluorolink[®]S10.

for the coatings preparation were purchased from Sigma-Aldrich (purity >99%) and used without further purification.

The hybrid coatings were prepared by the sol-gel synthesis of a silica coating in the co-presence with the PFPE. A certain amount of PFPE was mixed with TEOS, glacial acetic acid and 2-propanol in a one neck flask. Afterward, a solution made of water and iso-propanol (in the molar ratio 1/167) was added dropwise to the initial mixture, and pH was adjusted (pH ~2) by adding nitric acid. The solution obtained was stirred at room temperature for 24 h; in that time the complete hydrolysis of the silica precursor occurred. Table 1s, presented in supplementary information, lists all the chemicals used for the sol-gel synthesis of the silica network, and the corresponding molar ratios. The amounts of S10 and TEOS used for the coating preparation were calculated in order to have the following weight ratios: 50/50, 70/30, 80/20, respectively for S10 and TEOS. It has been observed that coatings obtained from formulations containing less than 50% in polymeric phase were hydrophilic. On the contrary, a weight amount of TEOS inferior than 20% in the formulation did not impart improvements in the chemical or physical stability of the hybrid coatings in respect to simple Fluorolink[®]S10 coatings.

Following this procedure, the weight percentage of the polymer in respect to the total amount of solvent (2-propanol) in each formulation was the 1.5–2.7%. The coatings presented in this work were named TEOS/S10-50/50, TEOS/S10-30/70 and TEOS/S10-20/80, in respect to the weight percentage of the two main components.

Stainless steel AISI 316 was used as solid substrate for coating deposition. Plain samples of dimensions 30 × 20 mm were employed for the characterization of the coatings and the resistance tests. Tubes samples, of internal diameter 8 mm and length 100 mm were instead used for the particulate fouling tests. Before the coatings deposition, all the stainless steel substrates were washed with water and acetone. The coatings were obtained by a dip-coating procedure, consisting in a prolonged immersion of the samples in the coating formulation (3 h). The samples were then heated in a static oven at 383 K, consequently, the temperature was raised at 473 K, and the samples were kept in the oven for one more hour.

2.2. Characterization techniques

A Krüss Easy Drop instrument was employed for the measurement of the static and dynamic (advancing and receding) contact angles (CA) and the surface free energy of the coatings. The surface free energy (SFE) of coated samples was calculated using the Oss and Good method [15]. According to this method, three pairs of SFE-Theta values were obtained for each analysis by using as test liquids di-iodomethane, distilled water and formamide. For each sample, at least 5 liquid droplets were deposited. Further analyses were performed employing a scanning electron microscope (SEM-LEO ZEISS instrument, model 1430). The X-ray photoelectron spectroscopy (XPS) technique allowed investigating the surface composition of the coatings and the type of interactions generated between the organic and the inorganic phases in the hybrid structure. The instrument (M-Probe apparatus, Surface Science

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