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# Effect of amorphous fluorinated coatings on photocatalytic properties of anodized titanium surfaces

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## ABSTRACT

The photocatalytic activity promoted by anodized titanium surfaces coated with different amorphous perfluoropolymers was evaluated. A copolymer between tetrafluoroethylene and perfluoro-4-trifluoromethoxy-1,3-dioxole and two perfluoropolyethers containing ammonium phosphate and triethoxysilane functionalities, respectively, were tested as coating materials. These coatings revealed good adhesion to the anodized titanium substrate and conferred to it both hydrophobicity and oleophobicity. The photocatalytic activity of the coating on anodized titanium was evaluated by monitoring the degradation of stearic acid via Infrared spectroscopy. The degradation rate of stearic acid was reduced but not set to zero by the presence of the fluorinated coatings, leading to the development of advanced functional coatings. The morphological variations of the coatings as a result of photocatalysis were also determined by atomic force microscopy.

## 1. Introduction

In the last years, titanium has received considerable attention because of its unique characteristics, like exceptional resistance to corrosive environments, high strength-to-weight ratio, high resistance to fatigue and excellent biocompatibility [1–6]. As a consequence, it has been widely applied in several fields of engineering and architecture. Moreover, anodic oxidation can be used to form on the surface of titanium a partially crystalline oxide of titanium dioxide characterized by photocatalytic activity. Different crystal phases of titanium dioxide can be obtained depending on the anodizing procedure, namely, rutile, anatase and brookite: owing to its superior photoactivity, the greater the content of anatase in the titanium dioxide layer, the more effective the photocatalysis [2,3,7–9]. In addition, aesthetically attractive colors, due to interference phenomena between the oxide film and the underlying metal surface, can be conferred to the surface of anodized titanium [6,10]. Titanium dioxide in the anatase phase is a semiconductor photocatalyst, and it offers convenient routes to the decontamination of air and water from gaseous, dissolved or solid compounds, even if present in low concentrations [11,12]. In fact, such materials are able to photocatalyze the complete mineralization of many organic and inorganic compounds, including aromatics, insecticides, pesticides, dyes, surfactants, hormones and halohydrocarbons [3], through a process that can be schematically summarized as follows:

$$\text{Organic pollutant} + O_2 \rightarrow \text{mineralized products} \qquad (1)$$

Further applications of titanium dioxide as photocatalyst are in the fields of solar energy conversion [13–19], electrochromic devices [20], self-cleaning [21] antimicrobial coatings [22] and antitumor treatments [2]. Photocatalytic reactions take place on the surface of the titanium-based photocatalyst, where electron-hole pairs are generated by the exposure to ultra-band gap light. Each electron-hole pair can either recombine or react with species adsorbed on the surface [12,21]. The photogenerated electrons can reduce surface oxygen to water, while the photogenerated holes are able to directly mineralize organic compounds [12,21]. The oxidation process is probably due to the initial oxidation of surface $OH^-$ groups to $OH\cdot$ which subsequently oxidize the adsorbed organic species [2,3,23]. However, one of the major drawbacks of anodized titanium is the easy soiling of this material [24]. In fact, its photocatalytic activity is significantly reduced whenever its surface is in contact with greasy or oily compounds [25]. Thus, the protection with a polymeric coating, which limits the soiling but does not inhibit the photocatalytic properties, can be an important improvement towards a more widespread use of anodized titanium. The polymers that can generate this synergic effect should present some fundamental characteristics: high chemical and thermal resistance to guarantee stability during photocatalysis, high transparency to radiations to allow the photoactivation of the oxide film, high

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permeability to the compounds required for the photocatalytic reactions and low wettability to achieve a self-cleaning effect.

Perfluorinated polymers are characterized by exceptional chemical and thermal stability, low surface energy and low wettability [24–28]. All these properties are strictly related to the presence of highly energetic C–F bonds into their polymeric chains. In addition, amorphous perfluoropolymers are completely transparent to a wide spectrum of radiations and show very low refractive indexes [29–34]. Highly amorphous fluoropolymers also have a good permeability towards elementary gases, such as $O_2$ [35,36] and water vapor [37]. In particular, this property can allow the photocatalytic process to take place even if the organic pollutant is not in direct contact with the surface of the photocatalyst.

Three different coatings were applied on anodized titanium to test their effect on the photocatalytic activity: HYFLON® AD60, a high molecular weight copolymer of tetrafluoroethylene (TFE) and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD) [38,39] and two perfluoropolyethers (PFPEs), FLUOROLINK® F10 and FLUOROLINK® S10, containing ammonium phosphate and triethoxysilane functionalities, respectively. The photocatalytic activity of uncoated anodized titanium and that of the samples coated with fluoropolymers were compared in this study. The photocatalytic activity was assessed by evaluating the photodegradation rate of stearic acid, via the following reaction [40–44]:

$$CH_3(CH_2)_{16}CO_2H + 26\ O_2 \xrightarrow{h\nu \geq E_{\mathrm{band\ gap}}} 18\ CO_2 + 18\ H_2O \qquad (2)$$

Since stearic acid is a solid compound, it can be considered as a molecular model of the solid organic films, which are usually deposited on surfaces such kitchen glasses or light covers in tunnel roads. The photodegradation of stearic acid was evaluated with Fourier transform infrared (FT-IR) analysis by observing specific absorbance peaks: the asymmetric in-plane C–H stretching mode of $CH_3$ group at 2958 $cm^{-1}$ and the asymmetric and symmetric C–H stretching modes of $CH_2$ groups at 2912 $cm^{-1}$ and 2853 $cm^{-1}$ [44,45]. FT-IR analyses for the determination of photodegradation rate were focused on the 2912-$cm^{-1}$ peak because it is more evident and sharp than the others. The morphological changes of fluorinated coatings exposed to UV radiations were also determined by atomic force microscopy (AFM).

## 2. Materials and methods

### 2.1. Materials

Commercially pure titanium (ASTM Grade 2) was employed as metallic substrate and amorphous perfluoropolymers HYFLON® AD60, FLUOROLINK® F10 and FLUOROLINK® S10 (from now on briefly indicated as AD60, F10 and S10, respectively) were used as protective coatings (Fig. 1).

These fluoropolymers are produced and commercialized by Solvay Specialty Polymers. HYFLON® AD60 is a random copolymer of tetrafluoroethylene (TFE) and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD), characterized by a low refractive index (equal to 1,327) and $T_g$ of 130 °C [29,30]. FLUOROLINK® F10 is an α,ω-ammonium phosphate terminated PFPE (AMW 2700 g/mol) [10,46] in which perfluoroether units $–OCF_2–$ and $–OCF_2CF_2–$ are randomly distributed along the perfluorinated polymeric backbone ($R_F$) and the ending phosphate moieties are able to establish polar interactions with the underlying titanium dioxide surface, increasing the adhesion of the coating [10]. FLUOROLINK® S10 is an α,ω-terminated triethoxysilane PFPE derivative (AMW 1800 g/mol); the triethoxysilane groups at the chain-ending positions are exploited to develop chemical bonds between coating and substrate, through the reaction with the OH groups located on the anodized titanium surface [47]. This polymer cross-links at 150 °C, in presence of acetic acid [48]. Moreover, GALDEN® HT110 (Solvay Specialty Polymers) was used as solvent for AD60. It is a PFPE-based solvent with boiling point of 110 °C and formula as follow: $CF_3O(CF_2CF(CF_3)O)_p(CF_2O)_nCF_3$ ($p + n = 2 - 3$; $p/n = 20 - 50$) [30]. Stearic acid (>97%, Merck-Schuchardt), 2-propanol (99.8%, Sigma-Aldrich), acetic acid (99.9%, Carlo Erba Reagents) and hexane (95%, Sigma-Aldrich) were also used in the formulations of the coatings or in the photocatalysis tests.

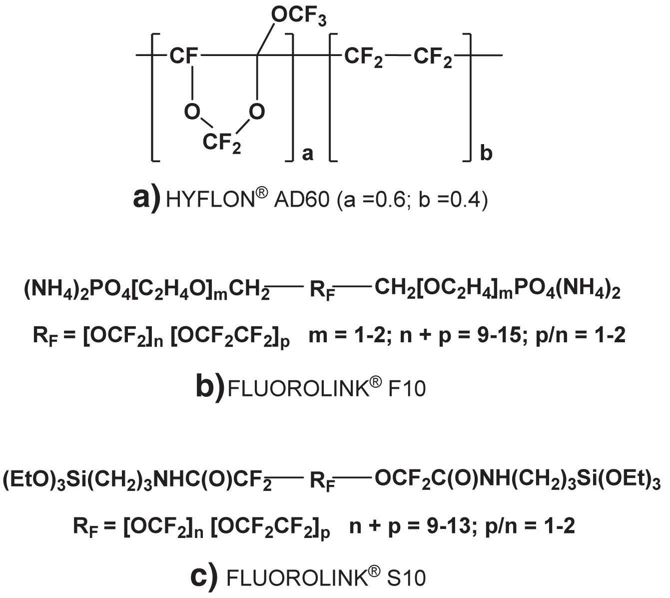

**Fig. 1.** Molecular structure of the employed amorphous perfluoropolymers: (a) HYFLON® AD60, (b) FLUOROLINK® F10 and (c) FLUOROLINK® S10.

### 2.2. Photocatalysis

Titanium plates (sizes: 15 mm width, 270 mm height, 1.5 mm thickness) were anodized following a procedure previously reported [6,10]. The characteristic hue assumed by anodized titanium adopting different anodizing parameters is caused by interference phenomena, regulated by the thickness of the surface $TiO_2$ layer [6,7]. Anodized titanium plates were separately coated with AD60, F10 and S10 fluoropolymers as described in a previous work [24]. After the deposition of the coatings, samples were annealed at temperatures higher than the $T_g$ of the deposited fluoropolymers in order to unbend the polymeric chains and to homogenize the layer.

A saturated solution of stearic acid was prepared, dissolving 0.5 g of acid in 50 mL in hexane. Differently coated plates and one bare anodized titanium sample were weighted then immersed into the solution of stearic acid; due to its high volatility, hexane evaporated immediately after removing samples from the solution, allowing to obtain a layer of stearic acid crystals on the surface of the plates. The treated samples were weighted again to check the effective quantity of deposited acid. Subsequently, the coated anodized titanium plates were placed simultaneously into a circular UV Rayonet reactor (diameter = 30 cm) equipped with eight 8 W mercury lamps emitting UV light (λ = 300 nm) arranged along the reactor inner wall; the light intensity of each lamp, equal to $1.0 \cdot 10^{-3}$ $W/m^2$, was measured with a Delta Ohm HD 2102.2 radiometer positioned in the middle of the UV reactor. Each sample was accurately positioned with the coated part exposed to UV light. The reactor was equipped with a ventilation system that maintained the temperature at 30 ± 5 °C and assured a constant relative humidity around 80% (monitored by a Fluke 971 Temperature Humidity Meter), for the whole duration of the photocatalytic test, which lasted 10 h. Samples were characterized by FT-IR spectroscopy before and after the irradiation at