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Protein antifouling and fouling-release in perfluoropolyether surfaces

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ABSTRACT

Perfluoropolyether polymers have been described as high performance fouling-release materials for marine coatings. Moreover, they have a good potential to be exploited in the biomedical field too. In this article several perfuoropolyether photopolymers were characterized in terms of surface and mechanical properties outlining the relationship between these properties and the polymer molecular structure. In particular the anti-fouling and fouling-release performances, evaluated using Bovine Serum Albumin as testing protein, was correlated to other material properties, like a parameter considering both surface tension components γ and elastic modulus E. A good correlation between the anti-fouling/fouling-release of perfluoropolyethers and $(E^*\gamma_{polar})^{1/2}$ can actually be established. Our results show that perfluoropolyether photopolymers are good protein anti-fouling/fouling-release materials.

1. Introduction

Anti-fouling materials have attracted a significant interest, especially as marine coatings and in biotechnology. In the former case they are used to prevent biofouling adhesion on ship hulls [1], thus reducing hydrodynamic drag and fuel consumption, while in biochemistry and biotechnology anti-fouling surfaces allow for the design and realization of protein resistant devices and components [2]. Anti-fouling and fouling-release are two different concepts. The former means preventing the adhesion of fouling organisms or proteins in static conditions, while the latter involves the possibility of removing them dynamically by the hydrodynamic forces exerted through a fluid flow.

A well-known protein anti-fouling polymer largely applied in biomedical and biological research is poly(ethylene glycol) (PEG) [2,3]. Ostuni et al. [4] studied a variety of self-assembled monolayers (SAMs) with different functional groups to explain the protein binding resistance of PEG. They showed that the interaction of surface with water and PEG charge neutrality are fundamental issues for anti-fouling properties.

On the other hand, atoxic fouling-release industrial coatings have been proposed as sustainable products for applications in marine environments [5]. To avoid the use of toxic chemicals [6] like tin salts, atoxic release coatings based on silicones and fluoropolymers have been developed. In particular, perfluoropolyether (PFPE) functional oligomers, largely used as building blocks [7,8,9] for high performance protective coatings and water/oil repellant surface treatments, are promising for this application [10,11].

The increasing diffusion of microfluidic devices for biomedical uses has led toward the development of fouling-release materials also for their fabrication [12,13]. Actually, UV curable perfluoropolyether-dimethacrylates (PFPE-DMA) have been used for device microfabrication [13] and more recently amphiphilic structures containing both hydrophilic and hydrophobic moieties have been proposed as potential fouling-release coatings. De Simone et al. [14] described also blends of photocurable perfluoropolyether-dimethacrylate/polyethylene glycol-methacrylate polymeric (PFPE/PEG blend), and studied the effect of the PEG chain molecular weight on fouling-release properties against spores. Other works in the literature have tested the effectiveness of other perfluoropolyether polymers as protein-adhesion resistant substrate [15]. In contrast to the available information concerning biofouling release properties of perfluoropolyether coatings, very little is known about the mechanism of molecular interaction of perfluoropolyether surfaces and proteins.

The main topic of our work is to study the behavior of perfluoropolyether polymers as protein adhesion resistant substrates, which can be applied in the realization of microfluidic

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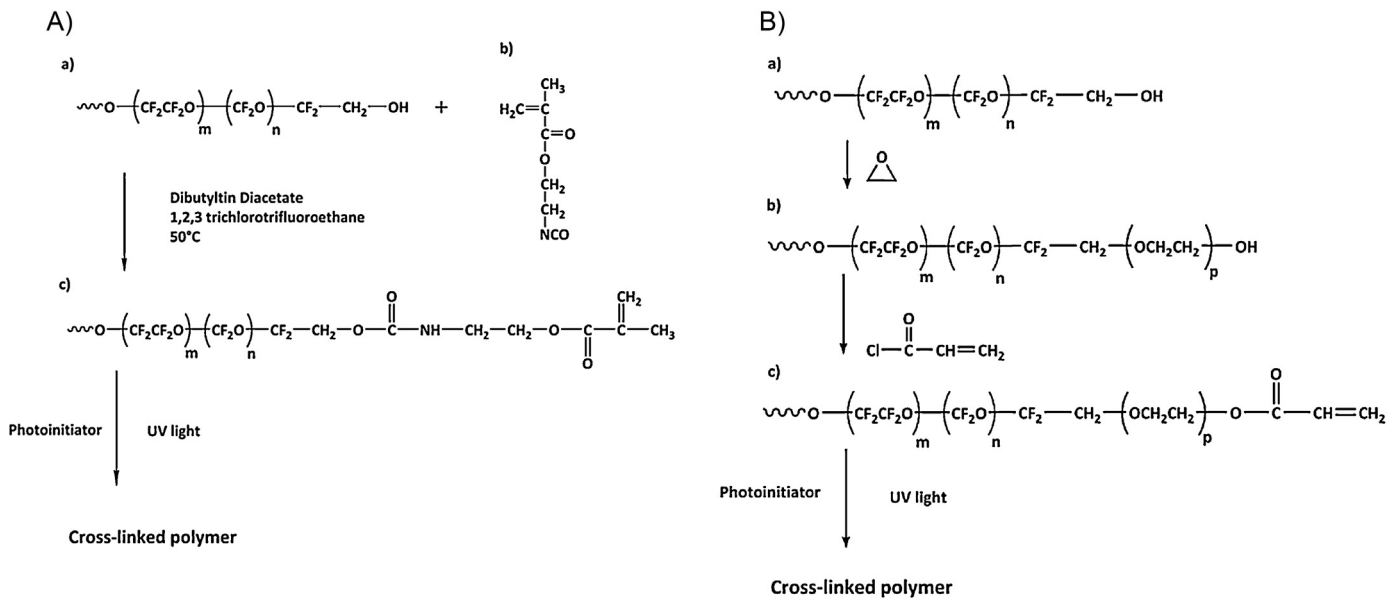

Fig. 1. (A) Perfluoropolyether dimethacrylates (c) obtained from the reaction of a perfluoropolyether macrodiol (a) with an isocyanate ethyl methacrylate (b); (B) perfluoropolyether poly(ethylene glycol) diacrylates obtained from a perfluoropolyether diol (a) by the sequential addition of a poly(ethylene glycol) chain (b) and finally of acrylic end chain groups (c).

biomedical devices. Different UV curable perfluoropolyether polymers, copolymers and blends are described, fully characterized, and their protein antifouling and fouling-release behavior is investigated. The main structural parameters [16,17] affecting their functional behavior are highlighted, giving useful information for the design and selection of high performance, protein resistant PFPE surfaces.

2. Experimental

2.1. Perfluoropolyether materials

One PFPE urethane dimethacrylate oligomer (commercial name: Fluorolink^{TM} MD700) was provided by Solvay Specialty Polymers (Bollate, Italy), and will be indicated as PFPE-DMA 2000 in the following. The main properties are M_n = 1980 g/mol; density = 1.66 g/ml. A higher molecular weight version of the PFPE urethane dimethacrylate was synthesized in our laboratory starting from a perfluoropolyether macrodiol (Fluorolink^{TM} D4000, Solvay Specialty Polymers) with M_n = 4000 g/mol, following the experimental procedure reported by Priola et al. [18] using isocyanatoethylmethacrylate (IEM, Alfa Aesar) for the functionalization reaction. PFPE-PEG-DAs were kindly provided by Solvay Specialty Polymers; here the PFPE macromer is chain-extended by two PEG segments and endcapped by acrylic groups through ester bond. In particular, two PFPE-PEG-DA grades that differ for the number of repeating PEG units were characterized in terms of surface and anti-fouling/fouling-release properties. The former PFPE-PEG-DA sample has a M_n = 2030 g/mol and is characterized by an average of 4.6 ethylene glycol (EG) repeating units in the backbone; the latter with M_n = 2206 g/mol, is made of 8 EG repeating units. The chemical structures of PFPE oligomers are shown in Fig. 1. PFPE surfaces were prepared by adding 4% (w/w) of photoinitiator (Darocur 1173, Ciba) with the exception of PFPE-DMA 4000 that was prepared by adding 1% of 2,2-dimethoxy-2-diphenylacetophenone (Sigma–Aldrich). All surfaces were exposed to UV light for crosslinking. UV irradiation was made with a bromograph (MF 1030, Nuova Delta Elettronica, Italy) under vacuum. The bromograph contained 4 UV-A lamps of 15 W each, with an emitted power density of 4 mW/cm^2.

2.2. Contact angle measurement

Samples for contact angle measurements were prepared by spin coating (750 rpm, 1 min) (ws400 6npp lite, Laurell Technologies Corp.) on well cleaned glass panels. The contact angle measurements were performed using an optical video contact angle system (OCA-15-plus, Dataphysics, Germany). The static contact angle was measured using the sessile drop method with dedicated software (SCA 2.0) determining the contact angle based on the Young–Laplace fitting. A 1 μl droplet of water (Chromasolv water for HPLC, Sigma–Aldrich) was dispensed on the sample using the electronic syringe unit of the instrument equipped with a 500 μl Hamilton syringe. The measurement was repeated several times on different areas on the substrate. The same procedure was followed using diiodomethane (Sigma–Aldrich), because at least two liquids are necessary to compute surface tension. Surface tension was obtained by applying the harmonic mean equation [19] to find both the dispersive and the polar components. Dynamic measurements were done by increasing the drop volume in the wetting process (advancing contact angle) and then decreasing it in the de-wetting phase (receding contact angle). The syringe needle remained in the drop during the whole process. In the first wetting phase a 3 μl drop was created on the solid surface and then slowly increased in volume. In the second phase the surface was de-wetted and the drop size reduced. The whole cycle was repeated 5 times at 1 μl/s, with a delay time of 1 s between each cycle. Advancing and receding angles are computed by the tangent at the three-phase contact line.

2.3. Dynamic mechanical analysis

Samples for dynamic-mechanical analysis were prepared by casting 0.5–1.0 g of oligomer in a rounded cap having diameter of 24 mm. A silicone rubber layer was placed on the top, and the sample was exposed to UV-light for 10 min. After complete cross-linking PFPE films were punched to obtain disks having

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