



One-step, self-assembled highly oleophobic nanocomposite coatings

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ABSTRACT

In a previous work, hybrid polymer/NP (nanoparticle) coatings with a homogeneous dispersion of NPs were realized by grafting amine-functionalized silica NPs onto associative thickening perfluorinated copolymers (HASE-F). Due to the presence of acid groups on the HASE-F copolymers, the grafting led to the formation of HASE-F/Si derivatives that will swell in water at neutral pH. Here, we report the post-grafting with perfluorinated acids RFn (C_4F_9 , C_6F_{13} and C_8F_{17}) in one step on the residual amine functionalities present on the NPs to afford HASE-F/Si/RFn derivatives. It was found that HASE-F/Si/RFn is well dispersible in water at pH 7, and this suspension can be deposited by spraying and spreading techniques on a glass substrate. The new coatings display high oleophobic properties with olive oil contact angles up to 120° , which is due to a spontaneous self-organization in nanosheets.

1. Introduction

The design and properties of nanostructured surfaces are growing research topic because they are used for applications in multiple domains and rapidly expanding fields with advanced and functional materials, nano-decorated surfaces, (nano)optics and (nano)biotechnologies being among the most prominent examples. Despite recent advances and significant progress in these areas, the development of novel nanostructured surfaces that can be used for specific nano-optics and bio-sensing applications remains an important challenge, especially with regards to the specific surface design and overall wettability [1–4].

Fluorocarbon chains are known to induce special organization at the surface of materials due to their amphiphobic character as revealed in SAMs organizations [5,6] or in electropolymerized surface coatings [3,4,7–9]. Additionally, the highly oleophobic properties caused by fluorocarbon skeletons are extremely important for many applications in textiles, aerospace, filtration, wood substrates, and paints. Amongst the current methods used to achieve these surface properties, the combination of fluorinated polymers and inorganic nanoparticles (NPs) is an efficient way to also ensure high mechanical and thermal stability [10–14].

Associative polymers, such as hydrophobically modified alkali-soluble emulsions (HASE), have the ability to form three-dimensional network gels in water at neutral pH [15–17]. The substitution of their hydrocarbon moieties into fluorinated ones leads to very low surface tension copolymers (HASE-F), with a thickening effect equivalent to the hydrocarbon HASE [18–22]. Silica NPs functionalized with amine

groups can be covalently attached to the carboxylic functionalities of the HASE-F co-polymer as demonstrated previously [23] to form NPs networks (HASE-F/Si) in water with a high stability and a homogeneous dispersion of NPs, which is preserved when the suspension is deposited on a glass support.

Here, in order to enhance the oleophobicity and self organization properties of these networks as a deposited surface, while also conserving their dispersion ability in water, we have grafted perfluorinated acids of different lengths (from C_4F_9 (RF4) to C_8F_{17} (RF8)) onto the free amine residual functionalities of NPs in HASE-F/Si derivative, to obtain HASE-F/Si/RFn nanocomposites (see Fig. 1 for RF8 post-grafting). Water dispersion as well as coating behavior, surface organization and wettability of these derivatives are studied and a surprising, spontaneous organization into nanosheets structures at the surface of the spread or sprayed coatings is observed.

2. Experimental details

2.1. Instrumentation

IR spectra (Perkin Elmer (United States of America) Spectrum 100 FT-IR spectrometer, KBr pellet method), SEM (JEOL 6700F microscope (Japan) at the accelerating voltage of 3 keV), zeta potential (Zetasizer Nano ZS from Malvern Instruments (United Kingdom)), static contact angle of olive oil ($\gamma_L=32$ mN/m) (4.9 μ L droplet, KRUS goniometer (Germany), average value of 3 measures), elemental analysis (C, N and F content) were performed to characterize the compounds.

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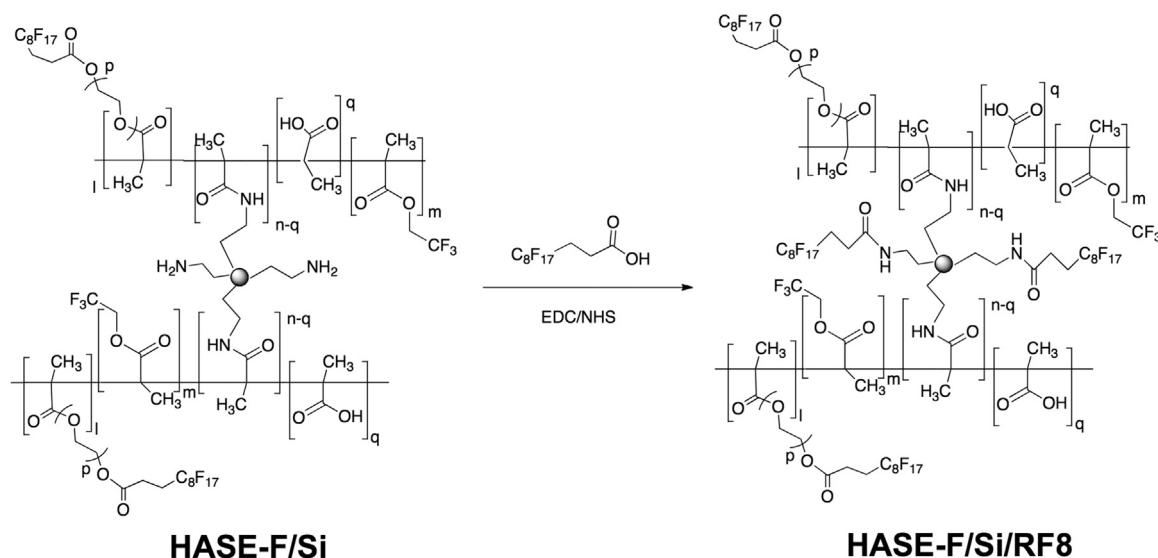


Fig. 1. Synthesis of the organic/inorganic polymeric network HASE-F/Si/RF8 starting from HASE-F/Si.

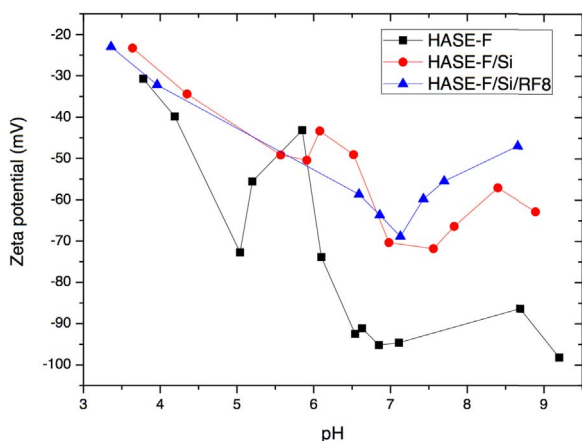


Fig. 2. Silica NPs aggregation characterized by zeta potential as a function of pH for HASE-F (black curve), HASE-F/Si (red curve) and HASE-F/Si/RF8 compounds (blue curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

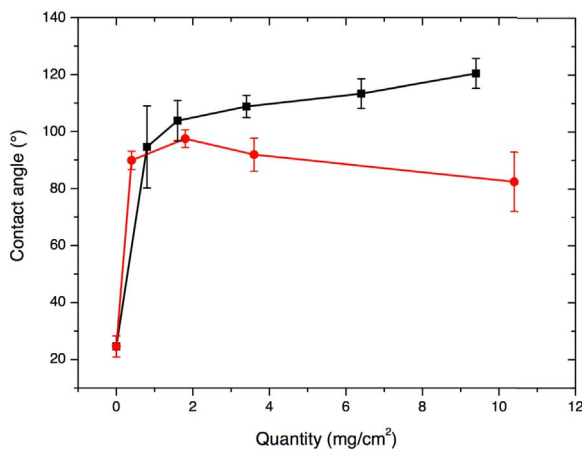


Fig. 3. Surfaces wettability with oil for HASE-F/Si (red curve) and HASE-F/Si/RF8 (black curve) as a function of spreaded amount on glass plate per square centimetre (mg/cm^2). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Coupling fluorinated compound to silica NPs/polymeric compounds

N-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC.HCl) (378.6 mg) and *N*-hydroxy succinimide (NHS) (454.4 mg) was added to a solution of RFn (972.3 mg) in water (85 mL, pH=4.83) and stirred during 2 h at 28 °C. A water solution (45 mL, pH=8.46) of HASE-F/Si compound (787.3 mg) was then added and react five days at 28 °C to obtain HASE-F/Si/RFn. The product was then dialyzed (MWCO: 4000–6000 Da).

2.3. Coating methods

HASE-F/Si and HASE-F/Si/RFn aqueous solutions (2–10.7 wt%) were spread on microscope slides (25 mm×75 mm) cut into 20 mm×25 mm pieces (i.e. 0 to 10 mg/cm^2) or sprayed layer-by-layer with an air brush (nozzle diameter of 0.3/0.5 mm) and at 10 cm from the substrate at 3 mg/cm^2 .

3. Results and discussion

First, amino-functionalized silica NPs were covalently grafted to the HASE-F copolymer as previously described elsewhere to afford HASE-F/Si [23]. Once the NP network is formed, there remains some free amine functionalities, which can be grafted again. This is demonstrated by comparing the zeta potential of HASE-F/Si to HASE-F as a function of pH, presented Fig. 2. At acidic pH, the presence of ionized $-\text{NH}_2$ groups was revealed by a higher zeta potential -22 mV against -30 mV for the initial HASE-F copolymer. Then, when increasing pH, suspension zeta potential is slightly higher for the grafted polymer and the stabilization pH is reached at 7 against 6.5 for HASE-F. This corresponds to the ionization of the $-\text{COOH}$ groups into $-\text{COO}^-$ groups and to the transformation of $-\text{NH}_3^+$ into $-\text{NH}_2$ groups.

RFn compounds were previously separately activated with EDC and NHS in water and then reacted with hybrid HASE-F/Si. After completion of the reaction, the fluorine percentage is significantly higher: for HASE-F/Si/RF8 (F: 12,84%) compared to HASE-F/Si (F: 9,20%) which provides further evidence of the grafting between RF8 acid carboxylic groups and residual amine functions of the NPs.

As seen Fig. 2, at acidic pH, the zeta potential is near -30 mV due to the protonation of the amino groups for HASE-F/Si and is slightly lower for HASE-F/Si/RF8.

This slight difference demonstrated a decrease in the number of

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