

RECOVERING SURFACE CHEMISTRY ON SUPERHYDROPHOBIC COATINGS

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Keywords: Self-healing, Coatings, Superhydrophobic, Bio-inspired

ABSTRACT

During the last decade, bio-inspired coatings with easy-to-clean/self-cleaning, anti-bacteria or anti-fouling properties have been intensively investigated[1] mainly for industrial applications but also out of academic interest. Such advanced properties are strongly related to the coatings surface chemistry. While the challenge to make these functional surfaces has produced a considerable number of new materials and methods[2, 3], it is now important to move one step further and make them robust, durable and easy to manufacture and scale-up[4]. Moreover, since coatings damage can never be totally avoided, introducing self-repairing mechanisms into functional coatings is one way to extend their service life-time and reduce maintenance costs[5, 6].

Previously, our group reported a self-replenishing polymer system which recovers a certain concentration of low-surface-energy groups (e.g. fluorinated-dangling ends), upon surface damage[7] (Fig. 1). Following up, we pursued a dual-approach study (experimental and modelling) to understand in-depth the self-healing mechanism involved and to investigate the influence of several experimental parameters (e.g. polymer network mobility or network constituent's miscibility) on the self-replenishing behaviour. This knowledge is now being used to recover the surface chemistry of other functional coatings.

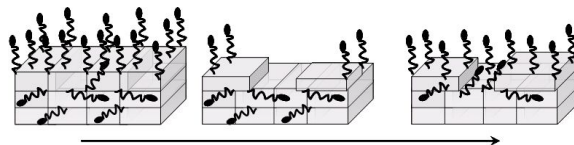


Figure 1: Scheme of the self-replenishing of low-surface-energy groups on polymeric coatings.

In Nature, we can find many examples of structured surfaces which endow peculiar properties to the living organisms, e.g. UV-radiation protection, water absorption, scratch resistance or elements diffusion[8]. Such biological surfaces recover from damage through complex self-healing mechanisms triggered by external-stimuli and transporting material. Following this principle we applied a self-replenishing polymer system[7] to obtain robust and easy processing superhydrophobic coatings, which are able to self-repair their surface chemistry upon damage. These coatings are prepared by simple chemical methods via a one-step procedure, from the initial mixture of the components. By incorporating inorganic nanoparticles in the polymer system, we were able to design surface-structured superhydrophobic coatings (Fig. 2) which will be able to recover their low-surface energy groups, partially responsible for the superhydrophobic behavior, at new surfaces created after damage.

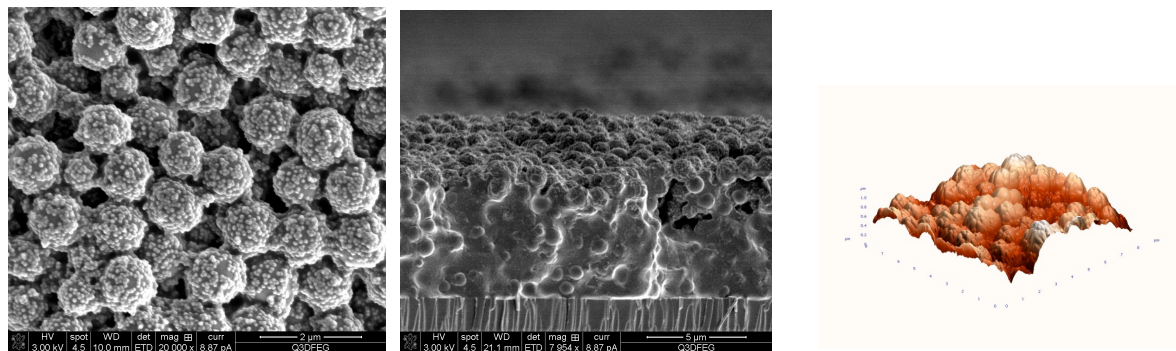


Figure 2: Polymer coating with structured surface: a) air-coating interface, b) cross-section and c) AFM 3D image.

Polymer coatings with structured surfaces were prepared by chemically bonding silica nanoparticles to the polymer network (Fig. 3). Fluoroalkyl-polymeric dangling chains were also inserted in the polymer network through covalent bonds. By this combination, the coatings reach high water contact angles (CA) ($CA_{adv} = 105^\circ$ to 150°). Due to the covalent bonds between the coatings components, these surfaces are extremely robust. After swelling with different solvents and submitting them to sonication, the nanoparticles remain embedded in the polymer network. The solid residue extracted by the solvents is $< 0.1\%$ wt of the initial coating.

A top horizontal layer of a few microns was intentionally removed from these coatings with a Cryo-microtome. The initial water CA was recovered suggesting the occurrence of self-replenishment through reorientation of the fluoroalkyl polymeric chains at the new rough surface.

The current work opens the door to the design of truly smart materials which are able to use intrinsic elements and external triggers (e.g. energy differences or temperature) to repair their surface chemistry and eventually their surface structure upon damage, recovering the associated functional character of the material.

Acknowledgments

The authors thank Ing. M. Hendrix and Ing. N. Lousberg from the Laboratory of Materials and Interface Chemistry at the Chemistry Department of Eindhoven University of Technology (www.chem.tue.nl/smg), for their support with AFM and SEM analyses, respectively.

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