

SURFACE REPAIR: SELF-REPLENISHING FUNCTIONAL POLYMER COATINGS

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ABSTRACT

Previously, we reported a self-replenishing polymer surfaces which recover their low-surface energy (i.e. hydrophobicity), upon surface damage^[1]. Following up, we used a dual experimental-simulation approach to understand in-depth the surface segregation of low surface energy components^[2], the self-healing mechanism involved on the surface recovery and the influence of different parameters (e.g. mobility of the polymer healing components) on the self-replenishing behaviour. Herein we report our further studies on self-replenishing structured-surfaces. The model self-replenishing polymer system was used to develop robust and easy processing hydrophobic surface-structured coatings, which are able to recover the low surface energy groups at new structured surfaces, created after damage.

1. INTRODUCTION

Many efforts have been made towards durable and robust functional surfaces^[3, 4] to face damage and wear, which will always be unavoidable. A rather attracting approach consists in introducing self-repairing mechanisms to prevent early failure or lowering of the materials performance. In the last decade, several strategies have been reported for recovering mechanical properties and bulk damage^[5]. However, little has been done to recover surface properties or functionality^[1], in particular when it depends on the surface structure (topography) as well.

We developed new surface-structured coatings which can self-replenish their surface chemical composition and also self-reproduce the surface structure upon damage. The surface-chemistry repair occurs due to intrinsic elements of the coatings bulk, i.e. low surface energy polymeric dangling chains chemically bonded to a cross-linked polymer matrix^[1]. When damage occurs, the polymeric dangling chains re-orient towards the new air-coating interfaces created, recovering the surface chemical composition. The coatings surface structure is build up by chemically bonding silica nanoparticles to the cross-linked network, which become protuberant at the top-surface. The particles in the bulk allow autonomous reproduction of a new surface roughness every time a surface damage occurs.

2. MATERIALS AND METHODS

The surface-structured coatings were prepared from *all-in-one* dispersions and simple one step chemical methods. The self-replenishing polymer system used was reported before^[1, 2] and consists on Poly(caprolactone)-based precursors with controlled end-functionality and degree of polymerization (DP), which were reacted

with a tri-isocyanate cross-linker, at moderate temperatures and short periods of time. To obtain the low surface energy property, fluorinated dangling chains containing a Poly(caprolactone) spacer with controlled DP and terminal hydroxyl groups, were also inserted in the system, through the reaction with the isocyanate groups of the cross-linker, forming urethane bonds^[1, 2]. To obtain the desired surface structure and chemical composition, several coatings were prepared with SiO₂ nanoparticles, which were synthesized with a specific size, using the well-known Stöber process (\bar{D}_1) (Table 1).

Table 1. Chemical/physical description of the coatings prepared with nanoparticles (DLS average diameter, $\bar{D}_1 = 700$ nm), before intentional surface damage.

Coating with 35 % wt SiO ₂ ^[a]	Overall F content %wt	F/C ratio (XPS)	Advancing Water CA (°) ± 2	Water CA hysteresis (°) ± 2
\bar{D}_1	0	0	83	23
\bar{D}_1	1.5	0.151	135	29
\bar{D}_1	3.0	0.203	147	37

A *all-in-one* mixture containing a small excess of cross-linker (CNO/OH = 1.1) was spread on previously cleaned glass substrates by spin-coating, and finally thermally heated under vacuum, at 80 °C for 30 minutes. Aluminium plates or polymer substrates can also be used for the preparation of these coatings.

3. RESULTS AND DISCUSSION

The surface-morphology of these coatings was investigated by Scanning Electron Microscopy (SEM). In the coatings with 35 % total wt of SiO₂, the nanoparticles were homogeneously distributed through the bulk of the coatings, but also organized on a protuberant layer at the air interface, providing the desired surface roughness (Figure 1a). SEM also showed that the nanoparticles were well embedded in the polymer bulk, the self-healing medium, and that the top particles are covered by a thin polymer layer (Figure 1a). This is an essential requisite for imparting a more hydrophobic character to the coatings surface.

The surface chemical composition of these coatings was investigated by X-Ray Photoelectron Spectroscopy (XPS). For all the coatings, atomic O1s (532.7 eV), C1s (284.8 eV) Si2p (103.3 eV) and F1s (689.1 eV) were present at the surface^[6]. The two last elements identify the presence of silica nanoparticles and fluorinated dangling chains at the top 10 nm layer of the coating, respectively.

These results provide confirmation of the presence of the Fluoroalkyl-dangling chains at the coatings surface, on the thin polymer layer covering the nanoparticles (a take-off angle of 0° was used to probe the surface with a penetration depth of ~ 10 nm). Upon increasing the overall Fluorine (F) concentration up to 3.0 % wt an increase in the F/C ratio was observed (Table 1). All the coatings prepared had a well-aligned layer of protuberant particles at the surface, which was further confirmed by Atomic Force Microscopy (AFM) (Figure 1 b).

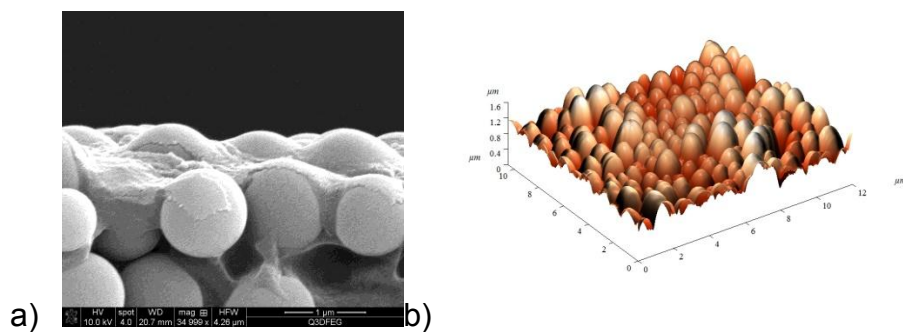


Figure 1. Characterization of the original (non-damaged) surface-structured coatings (with 35% wt of nanoparticles): a) SEM image of the air-interface and b) 3D AFM-height image.

All the advancing water contact angles (θ_{adv}) measured for the structured-coatings (with fluorinated dangling chains) exhibited a $\theta_{adv} > 120^\circ$ (Table 1), which is nearly the max. value that can be achieved on a flat surface with full coverage of low surface energy groups^[7]. As the overall F concentration was increased up to 3.0 wt % the water θ_{adv} increased considerably, up to 147° , which is even close to the superhydrophobic range.

Self-replenishing behaviour

In practical applications these coatings will be inevitably damaged by accidental scratches, sand or dirt rubbing, contact with water, chemicals or animals. To study the self-replenishing effect we tried to inflict a controlled damage at the surface of these coatings, without introducing too many “artifacts”, *e.g.* knife marks, extra roughness, smearing or contamination. A (cryo)microtoming technique was used to cut horizontal slices, plane parallel to the surface, while introducing a minimum of surface cutting effects and knife-originated-roughness. A home-made support was designed to cut plane-parallel slices of 10-30 μm at the top surface. After cut, the coatings were allowed to return to ambient temperature and their morphology was re-analyzed by SEM and AFM (Figure 3).

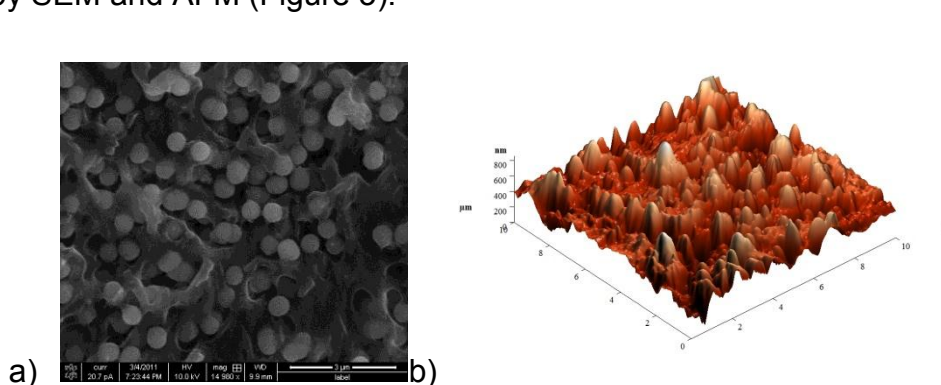


Figure 3. Characterization of a coating with 35 wt % of nanoparticles, after controlled damage (through Cryo-microtoming): a) SEM image of the air-interface and b) 3D AFM-height image.

For all of the damaged coatings, SEM revealed a new layer of protuberant particles at the new top surface (Figure 3a). This new surface structure results from the SiO_2

nanoparticles, initially homogeneously distributed and chemically bonded in the bulk polymer network. Furthermore, the polymer layer which contains the low surface-energy groups is also present at the new surface providing a recovery of the surface chemical composition (confirmed by the F/C ratio determined by XPS). AFM analyses of the new coatings surface have also shown a newly-reproduced topography created by the nanoparticles, previously buried in the polymer bulk (Figure 3b).

The water θ_{adv} measured on the new surfaces (after damage) were comparable with the original coatings (non-damaged), e.g. for a structured-coating with an initial $\theta_{adv} = 104^\circ \pm 2^\circ$ a final $\theta_{adv} = 106^\circ \pm 2^\circ$ was measured on the microtomed surface. These results clearly confirm the self-healing ability of the coatings prepared, which can recover their surface chemical composition and reproduce a new surface structure upon damage.

4. CONCLUSION

Surface-structured coatings which can replenish their surface chemical composition on a rough surface are reported^[8]. The chemical composition recovery is provided by the self-replenishing polymer system used^[1], which embeds the roughness inducing components, i.e. silica nanoparticles. The surface structure reproduction is inherent to the surface damage, via the nanoparticles homogeneously distributed and chemically bonded to the cross-linked polymer bulk.

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REFERENCES

- [1] T. Dikic, W. Ming, R. A. T. M. van Benthem, A. C. C. Esteves, G. de With, Self-replenishing surfaces, *Adv. Mater.*, 24 (2012) 3701.
- [2] A. C. C. Esteves, K. Lyakhova, L. G. J. van der Ven, R. A. T. M. van Benthem, G. de With, Surface segregation of low surface energy polymeric dangling chains in a cross-linked polymer network investigated by a combined experimental–simulation approach, *Macromolecules*, 46 (2013) 1993.
- [3] L. Boinovich, A. M. Emelyanenko, A. S. Pashinin, Analysis of long-term durability of superhydrophobic properties under continuous contact with water, *Appl. Mater. Interf.*, 2 (2010) 1754.
- [4] Y. Yu, Z.-H. Zhao, Q.-S. Zheng, Mechanical and superhydrophobic stabilities of two scale surfacial structure of Lotus leaves, *Langmuir*, 23 (2007) 8212.
- [5] D. Y. Wu, S. Meure, D. Solomon, Self-healing materials: a review of recent developments, *Prog. Polym. Sci.*, 33 (2008) 479.
- [6] J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Minesota, USA
- [7] R. E. Johnson, R. H. Dettre, *Contact angle, wettability and adhesion*, Vol. 43, *Advances in Chemistry Series*, ACS, Washington DC, (1964).
- [8] A. C. C. Esteves, K. Lyakhova, L. G. J. van der Ven, R. A. T. M. van Benthem, G. de With, Self-replenishing of structured-surfaces revealed by a combined experimental-simulation approach, (2013) *in preparation*.