Acrylate-based UV-cured self-replenishing hydrophobic coatings for further industrial applications

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ABSTRACT

Self-healing functional polymer surfaces, designed with an intrinsic and spontaneous mechanism which replenishes the damaged surfaces with the original chemical functionalities, are of great interest to maintain a high performance of the functionality and extend the lifetime of materials.

We report self-replenishing UV-cured hydrophobic polymer coatings prepared through the incorporation of methacrylate-terminated perfluorinated-dangling chains into poly(ethylene glycol diacrylate) (PEGDA)-based networks. The coatings are able to spontaneously and fully self-replenish the surface hydrophobicity, multiple times, upon consecutive intentional damages. The rate of recovery was found to be dependent on the glass transition temperature (T_g) of the networks, which directly correlates to the PEG block length in the PEGDA oligomer used. This study demonstrates that an intrinsic self-replenishing mechanism can be implemented in new network architectures, created rapidly and efficiently by free radical UV-polymerization, which allows preparing self-healing functional polymer coatings in a faster and eco-friendlier way.

1. INTRODUCTION

The recovery of surface chemical groups is crucial for extending the service-life of hydrophobic polymeric coatings. One way to achieve this is to introduce a self-healing mechanism which can replenish the low surface energy groups at the surface after the damage. The proof-of-principle was previously reported for a "model" self-replenishing system based on a Poly(urethane) thermally cross-linked soft (low-T_g) network with a small amount of fluorinated dangling chains[1]. In these systems the low surface energy dangling groups can re-orient towards the new air/coating interfaces created upon damaged[2,3]. Nowadays, photo-curable polymeric materials are attracting a renewed industrial and academic interest in the field of polymer

coatings due to its fast curing, eco-friendliness and excellent performance characteristics. Hence, using UV-curing instead of thermal curing to obtain self-healing/self-replenishing polymer coatings could improve significantly the curing speed and readily allow exploring systems with better thermal and mechanical properties by tuning the network architecture.

2. MATERIALS

The methacrylate-terminated dangling chain (R_{f8}-PCL$_{16}$-MA) was synthesized via a synthesis route, as shown in Figure 1. PEGDA of different molecular weights (M_n = 200, 400 and 600 g/mol, denoted as PEG200DA, PEG400DA and PEG600DA, respectively) were used to build the cross-linked bulk matrix by UV-initiated radical polymerization. The components were then mixed into solutions (Table 1) and casted on glass substrates by a doctor blade applicator (with an approximate wet thickness of 120 µm) and then cured for 30 seconds under UV irradiation, inside a N_2-filled quartz chamber.
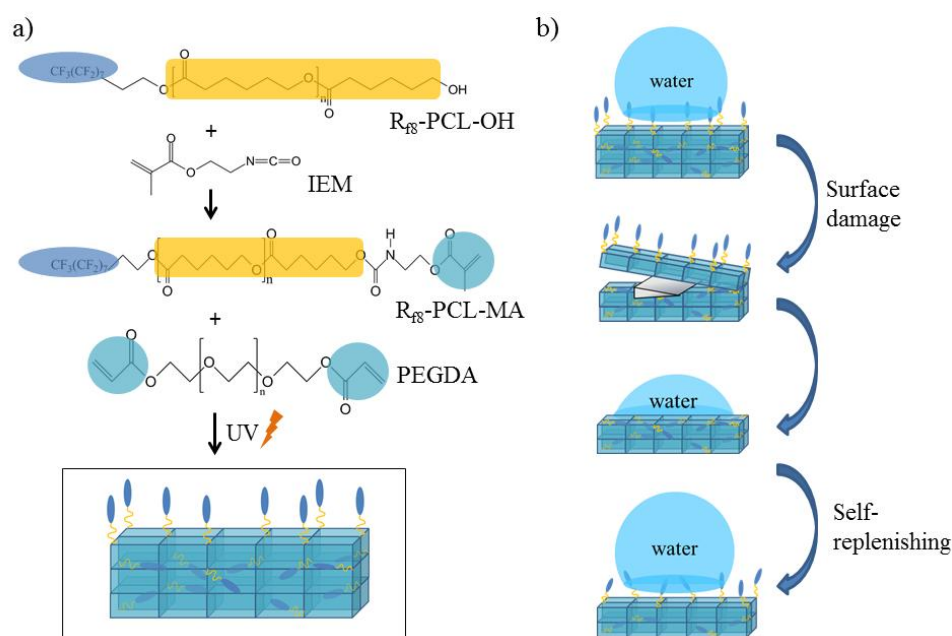

Figure 1. *a)* Schematic of the chemical synthesis route of the methacrylate-terminated dangling chains (R_{f8}-PCL$_{16}$-MA) and of the UV-cured polymer network with dangling chains. *b)* Schematic of the self-replenishing mechanism *via* the re-orientation of dangling chains towards the new air-coating interfaces created upon the surface damage.

3. METHODS

The characterization of the cross-linked coatings was carried out by Differential Scanning Calorimetry (DSC). Their surface was characterized by X-Ray Photoelectron Spectroscopy (XPS) and dynamic water Contact Angle (CA) measurements. Microtoming was utilized to perform intentional damages parallel to the air-coating interface.

4. RESULTS

The successful chemical synthesis of the methacrylate-terminated dangling chain was proved by H-NMR, GPC, FT-IR and Maldi-ToF. After UV-curing, all of the studied coatings showed nearly 100% chemical conversion for the vinyl bonds by Confocal Raman Microscopy and no oxygen inhibition effect was observed. The less than 1 wt% of extractable in chloroform further confirmed that the methacrylate-terminated dangling chains were covalently bonded to the networks.

Table 1. Chemical components used in the UV-cured coatings (unit: wt%).

	Nomenclature	R_{f8}-PCL_{16}-MA	Binder	Photoinitiator	Dioxane	Overall F content
1	PEG200DA-F	7.8	71.2	1	20	1.5
2	PEG400DA-F	7.8	71.2	1	20	1.5
3	PEG600DA-F	7.8	71.2	1	20	1.5

Table 2: Dynamic water CA measured on polymer coatings, on the original surfaces and on surfaces created after intentional damage (by microtoming), 4 hours and 48 hours of recovery (at room temperature and inside a desiccator)[4].

	T_g (°C)	Initial		4 h of recovery		48 h of recovery	
		CA_{adv} (°)	CA_{rec} (°)	CA_{adv} (°)	CA_{rec} (°)	CA_{adv} (°)	CA_{rec} (°)
PEG200DA-F	+ 18	118 ± 2	76 ± 4	60 ± 2	11 ± 4	118 ± 1	47 ± 4
PEG400DA-F	- 23	116 ± 3	87 ± 3	120 ± 1	61 ± 1	121 ± 1	59 ± 3
PEG600DA-F	- 43	114 ± 2	76 ± 6	119 ± 1	44 ± 3	121 ± 1	46 ± 2

The self-replenishing ability was demonstrated by comparing the surface hydrophobicity and fluorine surface concentration before and after damaging. Within a short recovery time (4 h), the PEG400DA-F and PEG600DA-F films exhibited a high CA_{adv} of ~120°, similar to the levels of the original surfaces. However, in the same conditions the PEG200DA-F film clearly exhibited a CA_{adv} of 60°. Surprisingly, when allowed to recover for 48 hours, the PEG200DA-F film also exhibited a rather high hydrophobicity, closer to value of the original surface, while the PEG400DA-F and PEG600DA-F stayed at the same high CA_{adv} as before. The XPS results after 48 h of recovery support this observation in the term of surface Fluorine concentration. At 48 h after damaging, the F/C atomic ratio for all the films and at all cutting depths were significantly higher than the "theoretical bulk average". Furthermore, these values were maintained, within the error margins, at the same level of the respective original surfaces. For PEG200DA-F in particular, the fluorine content was observed to increase gradually from 4h to 48 h of recovery time by XPS. Considering the higher T_g of PEG200DA-F is higher (18°C) than the other two, this could explain why the re-orientation of the dangling chains towards the new surfaces created upon damage, takes a longer time to achieve a self-replenishing level of nearly 100%. For all the three UV-cured coatings, these results clearly show that surface hydrophobicity can be reestablished to a large extent, albeit with different recovery time.
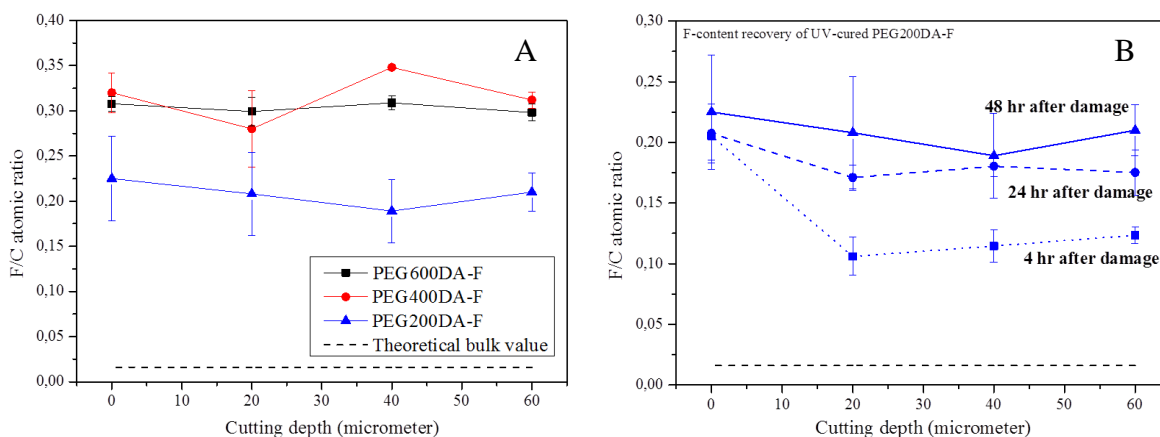
Figure 2: Fluorine/Carbon (F/C) atomic ratio, determined from XPS at different cutting depths for A) UV-cured coatings containing dangling chains, at 48 hours after damaging and B) for the UV-cured PEG200DA-F film, at different times of recovery after the damage. Cutting depth = 0 µm corresponds to the original, non-damaged surfaces. The black dashed lines correspond to the "theoretical bulk value", which is the expected F/C ratio, if there is no dangling chains surface segregation[4].

5. CONCLUSIONS

Low surface energy polymeric dangling chains consisting of perfluoroalkyl-end capped linear polymeric spacers (PCL-based) with a terminal methacrylate group were successfully synthesized. These dangling chains were incorporated into PEGDA-based cross-linked polymer networks via UV-initiated radical polymerization. After the intentional damaging, the rate of hydrophobicity recovery was found to be dependent on the networks properties (such as T_g), which is associated with the PEG segment length of the PEGDA oligomers used. All the UV-cured polymer coatings exhibit a clear, multiple self-replenishing ability, and recovered the initial chemical composition and hydrophobicity, at air-polymer interfaces created after surface damages. These new self-replenishing acrylate-based systems, cured by a faster and more eco-friendly process, are one step closer to the application of hydrophobic polymer coatings with a surface functionality self-repairing ability, in areas like automotive or aerospace engineering, where functionalities like self-cleaning/easy-to-clean are highly desired.

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