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Preparation of scratch resistant superhydrophobic hybrid coatings by sol–gel process

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ABSTRACT

Organic–inorganic hybrid coatings on glass substrates with superhydrophobic properties and with improved scratch resistance were obtained by means of applying a multilayer approach including multiple sol–gel processes. The coatings exhibited a water contact angle (WCA) higher than 150°. Ultraviolet (UV)-curable vinyl ester resins and vinyltriethoxysilane (VTEOS) as coupling agent were employed to increase the adhesion between substrate and the inorganic layers. The surfaces were characterized by means of dynamic contact angle and roughness measurements. Indeed, the occurrence of superhydrophobic behavior was observed. The scratch resistance of the hybrid coatings was tested to evaluate the adhesion of the coatings to the glass substrate. The proposed preparation method for scratch resistant, mechanically stable, superhydrophobic coatings is simple and can be applied on large areas of different kinds of substrates.

1. Introduction

The development of easy-to-clean and self-cleaning surfaces is one of the important outcomes of nanotechnology since its early beginnings. The potential applications of self-cleaning surfaces raised enormously since the basic principle has been discovered by Barthlott and co-workers [1–5] showing that the morphological structure of lotus leaves cause their self-cleaning ability. This findings lead to the creation of products with LOTUS® effect. Synonymous names for the LOTUS® effect are self-cleaning, superhydrophobicity and ultrahydrophobicity, respectively. Also other models of self-cleaning structures are available in nature, for instance the surface if insect wings [6,7].

Even though a number of methods have been reported in literature to obtain superhydrophobic surfaces and conditions were recognized that should be met, it has to be noted that many of them are not feasible for large-area applications [8–10]. Large area applications for superhydrophobic surfaces are getting, on the other hand, more and more importance. It can be imagined that usage of superhydrophobic, self-cleaning solar panels can become an important economic factor, to mention just one example [11,12]. Another crucial limitation besides large-area application is the scarce scratch resistance of common superhydrophobic surfaces. Indeed, both a hard as well as scratch-resistant protective coating is needed to really improve surface characteristics of a coating and to extend long-term durability.

The general purpose of a coating is to modify and to protect a decorative, thus enhancing the appearance and durability of the substrate. Consequently, surface properties such as resistance against scratching are critical and have to be enhanced while retaining the basic functions of the specific coating, for example, in automotive coatings, furniture, and domestic appliances, etc.

Generally, scratch resistance is described in terms of abrasion, adhesion and erosion, and evaluated in terms of deformation magnitude [13–15]. Scratch tests are a very useful tool for understanding deformation of materials and removal mechanisms in abrasive wear and it is commonly used for materials surface characterization [16]. However, it has to be pointed out that it is still very complicated to detect the reasons for scratches and to find relationships between coating structure, coating properties, scratch resistance and scratch conditions. This topic is also one of the main aims of this study.

Several reports focused on improving the scratch resistance and mechanical strength of sol–gel derived polymeric films: PMMA hard coatings with enhanced scratch resistance have been developed by using a sol–gel method with silatrane in the presence of 3-glycidoxy-propyltrimethoxysilane [17]. Hybrid coatings with good scratch resistance were obtained employing resins for dual-curing processes combining the advantages of both [18–20].

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However, also in these cases the long-term stability of the coating is not sufficient.

In this work, results about the preparation of superhydrophobic coatings on glass substrates by means of applying a multilayer approach including multiple sol–gel processes are reported, while in former work [21] the superhydrophobic coating developed was more simply composed. The coating reported here comprises (a) an organic binder having free –OH groups as sub-layer directly on the glass, (b) an organosilane modifier having groups that can co-react in the sol–gel process, (c) inorganic precursors and network formers which during the curing process form an inorganic hybrid network, and (d) a perfluoropolyether (PFPE) top-layer as low surface free energy top-coating. The principal structure of the multilayer film developed for superhydrophobic, scratch resistant glass coatings is illustrated in Fig. 1.

The sub-layer was applied directly on glass and contained a UV-curable vinylester resin. Due to the high polarity of the resin a better adhesion between glass and inorganic layers was intended to achieve. The additional use of a photoinitiator opened the possibility to cross-link the resin at ambient temperature by UV-irradiation. On that layer VTEOS was deposited to increase the adhesion to following inorganic layers. The use of mixtures of several liquid metal alkoxides as precursors for metal dioxide networks and α,ω-trialkoxysilane-terminated PFPE as low surface free energy coating allowed to obtain superhydrophobic coatings with advancing contact angles with water of about 150° [21]. The same mixture as in [21] was employed in the present study. Only the solvent for the precursor mixture used had to be changed from tetrahydrofurane (THF) to ethyl acetate because the vinylester is soluble in THF and thus, THF would damage the sub-layer.

The preparation method chosen here was spray-coating which was carried out carefully layer-by-layer. Using a very thin vinylester resin sub-layer then would allow modification of the glass surface without cost-effective surface pre-treatment of the glass, for instance by acidic or basic procedures.

The preparation process described in this paper is very time saving, and easy-to-handle compared to the previously described procedures [22–25]. Spray and spin coating were employed because of the advantages for preparing coatings with minimum wastage of precursor solution.

2. Experimental

2.1. Materials

α,ω-Triethoxysilane-terminated perfluoropolyether (PFPE, FLKS10) having a molecular weight of 2000 g mol^{-1} was kindly supplied by Solvay-Solexis (Italy). Tetraethyl orthotitanate (TEOT), tetra-n-propyl zirconate (TPOZ), vinyltriethoxysilane (VTEOS), ethyl acetate, and vinylester resin (VERM® 411-350) were purchased from Sigma–Aldrich (Milan, Italy) and used without further purification. Tetrahydrofuran (THF) and ethyl acetate as solvents was purchased from Carlo Erba.2-Hydroxy-2-methyl-1-phenyl propan-1-one (Additol HDMAP) was used as photoinitiator and it was kindly supplied by CYTEC Surface Specialties (Italy). All reagents were used as received without further purification.

2.2. Preparation of organic–inorganic hybrid coatings

Microscope slides (2.5 cm × 7.6 cm) were used as substrates and were cleaned by washing with a standard RCA1 solution (NH_4OH:H_2O_2:H_2O = 1:1:5 vol:vol:vol) at 70 °C for 10 min and then rinsed several times in bi-distilled water.

The subsequent formulations were applied by spin-coating with a Laurell WS-400B-NPP-Lite spincoater (UK) at 3000 rpm for 40 s.

Multilayer samples were prepared by deposition of the subsequent intermediate layers starting with a first resin layer by spin-coating followed by a second layer which was a mixture of the vinylester resin and VTEOS. The first layer was prepared by dissolving the resin in ethyl acetate (20 wt.%). The formulation for the second layer was prepared by adding VTEOS (50 wt.%) to the vinylester resin. HDMAP (2 wt.%) as photoinitiator was added to both vinylester mixtures.

The photochemical curing was performed by using a spot light sources LC8 Lightningeure (Hamamatsu Photonics KK, Shizuoka, Japan) for a time of 60 s, with radiation intensity on the surface of the sample of 10 mW/cm^2.

Later on, several inorganic layers and a top-fluorinated monolayer were deposited on the UV-cured resin layers in the direction already shown in Fig. 1.

The inorganic multilayers deposited onto the thermoset resin were prepared by depositing via air-brushing a solution of TEOT, TPOZ in ethyl acetate (5 wt.%) corresponding to a calculated weight ratio of TiO_2/ZrO_2 = 60/40 wt/wt in the final metal oxide layers.

At the end of the procedure, the PFPE was applied by spin-coating. The solution was prepared as described in the previous work [21] by dissolving TEOT, TPOZ and FLKS10 in THF (corresponding to a calculated weight ratio of PFPE/TiO_2/ZrO_2/SiO_2 = 84/4/6/6 wt/wt/wt in the final layer).

The subsequent hydrolysis and condensation reactions necessary to allow the sol–gel-process and formation of the metal oxide networks were performed by storing the photocured films in an oven at 100 °C for 2 h.

The composition and layer number of the coatings prepared and investigated in this study are summarized in Table 1.

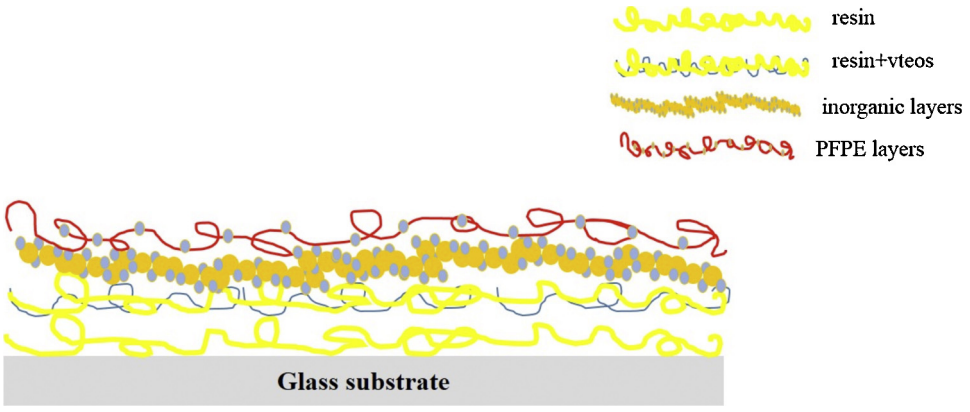

Fig. 1. Model of the formation of superhydrophobic, scratch-resistant glass coatings via a multilayer approach.

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