



Fluorinated zirconia-based sol-gel hybrid coatings on polycarbonate with high durability and improved scratch resistance



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ARTICLE INFO

Article history:

Received 12 September 2016

Revised 22 December 2016

Accepted in revised form 23 December 2016

Available online 26 December 2016

Keywords:

Sol-gel hybrid coating

Hardness

Durability

AFM indentation

Nanoscratch

Adhesion

ABSTRACT

Hard, scratch-resistant and transparent fluoropolymer-based hybrid coatings are successfully prepared through the sol-gel chemistry and investigated, in the attempt to correlate the chemical, physical and surface properties of these materials with the mechanical properties (i.e. hardness and elastic modulus) measured at the nanoscale by atomic force microscopy (AFM). The organic component of these coatings consists in a hydroxyl-functional fluoropolymer resin, which belongs to the class of chlorotrifluoroethylene-vinylether copolymers and exhibits remarkable properties such as easy handling, great weather resistance, good adhesion and flexibility of coatings. A functionalization of this copolymer is also performed using an isocyanate-functionalized silane in order to assure a covalent cross-linking of organic fluorinated resin with inorganic phases. The combination of the silanized chlorotrifluoroethylene-vinylether copolymer with different sols composed of silica and zirconia is used to obtain high scratch resistance and high durability coatings on polycarbonate. A series of three hybrid coatings with different zirconia/silica molar ratios (0.09/0.48) are developed and analyzed by differential scanning calorimetry (DSC), water contact angle measurements, pencil hardness and adhesion tests. AFM scratch hardness, coating wettability and surface composition measured by Fourier transform infrared spectroscopy (FTIR) are regularly monitored over long-term UV–vis light exposure, to assess the durability of the hybrid coatings. Interestingly, the hybrid fluorinated coatings exhibit an improved scratch resistance and a superior long-term stability when exposed to an accelerated weathering, compared to pristine PC substrates. The mixed silica/zirconia hybrid coatings with a low and intermediate zirconia-to-silica ratio also show excellent mechanical strength, high level of hardness and superior integrity after long-term light exposure.

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1. Introduction

Transparent engineering plastics such as polycarbonate (PC) are recognized as the material-of-choice in an ever-increasing range of applications from photovoltaic devices [1–2] to display panels as well as optical lenses [3], compact disks, safety windows and automotive glazing [4–5]. PC particularly offers the advantage of reducing manufacturing costs and product weight when compared to other inorganic transparent materials such as glass. Despite its good optical properties and high resistance to impact and fracture, PC exhibits some weaknesses, such as poor resistance to scratching and UV exposure. To increase the durability and the surface performances of the final product, transparent hard coatings incorporating UV-absorbing molecules are often used as a solution to counteract these problems [6–8].

Silica-based coatings have usually been investigated and applied onto PC by means of various methods, e.g. physical vapor deposition,

plasma enhanced chemical vapor deposition [9] and atmospheric plasma deposition [10]. However, these deposition approaches require expensive instrumentation in order to be implemented and often show a lack of versatility in terms of size and shape of substrates that can be chosen. In addition to those technologies, sol-gel process has been extensively explored, enabling the significant improvement of PC mechanical performances with the added advantage of low capital costs and easy procedures of implementation [11].

The sol-gel process is a well-known method, initially developed to prepare inorganic materials such as glass and ceramics [12]. Typically starting from a metalloid alkoxide precursor $M(OR)_n$ in a liquid medium, the sol-gel process generates an inorganic network through hydrolysis and condensation reactions [13]. By incorporating polymeric or oligomeric organic species into the inorganic network, organic/inorganic hybrid materials can also be produced by means of sol-gel processes. The introduction of the organic components has the advantage of enhancing flexibility, reducing brittleness of the final material and increasing the adhesion to polymer substrates, while keeping high level of hardness and stiffness generally provided by the inorganic phase [14].

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A great variety of inorganic and organic precursors are available and the bulk and surface properties of the resulting coatings can be tailored by selecting the suitable starting reagents [15–17].

Regarding the inorganic phase, silica alkoxides are usually employed as precursors of inorganic networks, but also metal alkoxides (such as those of aluminum, titanium and zirconium) are frequently used, due to the possibility to obtain hybrid coatings with improved mechanical and optical properties [18–19]. Particularly, zirconia-based hybrid coatings are well-known for their excellent mechanical strength, thermal durability as well as anticorrosion properties compared to other ceramic materials [20–22]. A major hitch of the sol-gel process for the preparation of these multicomponent oxide systems is however the different hydrolysis and condensation rates of the precursors, which can lead to heterogeneous mixtures. In order to control the hydrolysis and condensation kinetics of metallic precursors such as zirconium alkoxides that usually react faster than silica ones, chelating agents of metallic centers i.e. acetic acid, acetylacetone and methacrylic acid are frequently necessary and added [22–23].

To obtain a good interpenetration of organic and inorganic phases, covalent bonding between organic components and inorganic networks is preferred. In light of this, three main approaches have so far been adopted in the choice of organic components: (i) the use of low molecular weight organoalkoxysilanes, such as octyltriethoxysilane or triethoxyphenylsilane that introduce small organic domains within the inorganic network; (ii) the incorporation of a curable organoalkoxysilane $R'Si(OR)_3$ where the R' is a polymerizable group, e.g. 3-(trimethoxysilyl)propylmethacrylate [24] and 3-glycidoxypropyltrimethoxysilane; (iii) the addition of an organic resin (e.g. acrylate or polyurethane resins) [11]. Among these approaches, the use of fluoropolymer resins and fluorinated organically modified silicates has gained attention in the last few years since these types of materials exhibited important properties for a wide variety of applications, including antimicrobial devices [25], self-cleaning superhydrophobic coatings [26], antifouling coatings for heat exchangers and stainless steel components [27–28] as well as nanocomposites for solar cells and optical devices [29].

Here, we report the simple preparation of a new type of sol-gel hybrid coatings based on a mixed oxide system composed of silica and zirconia with enhanced scratch hardness and elastic modulus for outdoor applications as protective coatings on PC substrates. A chlorotrifluoroethylene-vinylether copolymer with hydroxyl functional groups was selected as the organic component for this work, aiming for excellent outdoor durability, good transparency and solvent resistance. High weather resistance can be guaranteed by the fluorinated segments, while vinyl ether comonomers provide the polymer with various properties such as solubility in organic solvents, flexibility and transparency [30]. Moreover, the presence of hydroxyl groups in the fluorinated resin enabled us to functionalize the polymer with an isocyanate alkoxysilane in order to obtain an organic network crosslinked with the inorganic components. Silica hybrid coatings obtained with this functionalized copolymer and a high content of a silica-based sol has already proven to provide the coating with very good mechanical properties [31]. In a previous study by our group, a mixed silica-titania system was also evaluated to investigate the effect of Ti-O-Si and Ti-O-Ti network on the mechanical properties [32]. However, a decrease in the scratch resistance and comparable values of elastic moduli were observed in that mixed oxide system when compared to the single oxide coating with a similar inorganic content.

In contrast to the previous work, sol-gel hybrids containing a mixture of silica and zirconia were formulated in the present study with the aim of improving the durability and performance of the hybrid coatings. The effect of different zirconia-to-silica ratios on the chemical, physical and nano-mechanical properties of the developed materials was investigated in this work on compositions having a constant inorganic-to-organic weight ratio. These sol-gel hybrid materials were successfully applied on PC substrates by spin-casting sols containing a

silicized fluoropolymer and silica and zirconia precursors. By tuning the chemical composition of the sol gel precursors, their reaction kinetics were successfully controlled and transparent coatings could be obtained, thus preventing any sol destabilization. Moreover, the fluorinated hybrid coatings showed good transparency and adhesion to PC surfaces as well as excellent scratch resistance. To the best of our knowledge, this is the first example of zirconia-based fluorinated hybrid coatings on polymer substrates with high mechanical properties and superior outdoor durability. This work provides a novel and straightforward approach for the development of high performance protective coatings that may find direct application in several technological fields including optical elements, touch-screen devices, automotive components and solar cells.

2. Materials and methods

2.1. Materials

Tetraethylorthosilicate (TEOS), zirconium propoxide 70 wt.% in 1-propanol (ZrP), 3-(triethoxysilyl) propyl isocyanate (IPTES), dibutyltin dilaurate (DBTDL), 2-butanone (MEK), 2-propanol (IPA), methanol (MeOH) and ethanol (EtOH) were supplied by Sigma Aldrich. Glacial acetic acid was purchased by J.T. Baker Chemicals. The fluorocarbon resin Lumiflon LF-910 LM is a chlorotrifluoroethylene-vinylether copolymer (CTFE-VE, for brevity) provided by Asahi Glass Company Ltd (Japan) [33]. It was used as a starting fluoropolymer resin for the following functionalization steps described in the next section. All the products were used without any further purification.

2.2. Functionalization of fluorocarbon resin

The CTFE-VE resin was functionalized according to the procedure reported in a previous paper [32] with minor modifications as briefly described in the following. In a 250 mL three-necked round-bottomed flask equipped with a reflux condenser and a nitrogen gas inlet system, 40 g of CTFE-VE were mixed with 3.88 g of IPTES using a ratio of NCO/OH equivalent ratio of 1/3. This ratio was selected based on a preliminary assessment of the stability of the formulation as it was found to guarantee compatibility with the inorganic phase while maintaining an acceptable shelf-life for the functionalized resin FEVEsil. The hydroxyl equivalents in the Lumiflon resin are provided by the supplier and expressed as mass of potassium hydroxide necessary to neutralize 1 g of resin (for brevity, OH number = 100 mg of KOH per gram of resin). It is important to underline that CTFE-VE resin was supplied as a 66 wt.% solution in xylene and therefore the dry polymer content was only considered for stoichiometric calculations. The initial amount of Lumiflon resin added to the flask was 40 g, which thus corresponded to a dry polymer content of 26.4 g. Taking into account that the OH number, i.e. mg of KOH per gram of polymer, was 100, the equivalent moles of OH in the dry CTFE-VE resin were 0.0471 mol and can be calculated as follows:

$$\begin{aligned} \text{eqOH} &= g_{\text{polymer}} \cdot \text{OHnumber} \cdot \frac{1}{\text{MW}_{\text{KOH}}} \\ &= 26.4 \text{ g} \cdot \frac{0.1 \text{ g KOH}}{g_{\text{polymer}}} \cdot \frac{1}{56.1 \frac{\text{g}}{\text{mol}}} = 0.0471 \text{ mol} \end{aligned} \quad (1)$$

The selected NCO/OH equivalent ratio was 1/3 and therefore 0.0157 mol of NCO were added to the fluoropolymer that corresponded to 3.88 g of IPTES.

Then, the reaction was catalyzed by using DBTDL with a concentration of 0.3 wt.% with respect to the polymer mass. The catalyst was added to the flask as a 1 wt.% solution in ethyl acetate (e.g. 7.92 g of this solution containing 79.2 mg of DBTDL). The reaction was carried out in an inert nitrogen atmosphere at 75 °C under constant stirring

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