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Application and drying at ambient temperature of thick organic–inorganic hybrid coatings on glass

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ABSTRACT

Organic–inorganic hybrid coatings have achieved success in scientific environments because they can be designed using the sol–gel route to combine the high hardness and chemical stability typical of glass-like or ceramic materials (i.e., the inorganic side) with the toughness and ductility typical of organic materials (i.e., the organic side). Nevertheless, organic–inorganic hybrid coatings are often very brittle, and they can collapse if applied as thick film on rigid substrates because of the shrinkage during the drying/curing process. However, the manufacturing of a thick coating is compulsory, when stringent requirements for scratch performance and wear endurance must be met. In this respect, the present investigation proposes the design of self-drying silicone–epoxy resins and the manufacturing of the corresponding thick coatings (approximately ~120 μm thick) on as-received and micro-corrugated glass using an automatic drawdown applicator. The scratch performance of the coatings was tested using progressive- and constant-mode scratch tests, and the wear resistance was examined using dry sliding linear reciprocating tribological tests. The experimental findings demonstrate how the role of the interface is crucial and how micro-corrugation is extremely beneficial in increasing the threshold of the maximum thickness beyond that at which coating bulging and delamination occur.

1. Introduction

Organic–inorganic hybrid coatings have achieved success in scientific environments because they can be designed via sol–gel route to combine the high hardness and chemical stability typical of glass-like or ceramic materials (i.e., the inorganic side) with the toughness and ductility typical of organic materials (i.e., the organic side) [1,2]. These coatings could be profitably used in several domains where substrate protection and/or functionalization by a tailor-made coating material are pursued [3]. In addition, the potential of these coatings is greatly emphasized because they offer good adhesion to various substrates [3]. Furthermore, some of these coatings can dry/cure at relatively moderate temperature (i.e., ~70–250 °C [4]), making them suitable as topcoats for a large share of substrates, including some thermolable substrates. Nevertheless, organic–inorganic hybrid coatings are often very brittle [5–7] and they can collapse if applied as thick film on rigid substrates due to shrinkage during the drying/curing process [8,9]. Malzbender and de With observed that the shrinkage phenomenon related to the drying/curing process of organic–inorganic hybrid coatings can often induce a large residual stress field inside the coating material, which can lead to an early failure of the coating if applied with a thickness over intrinsic critical values [9]. In particular, when the organic–inorganic hybrid coatings are deposited on non-compliant substrates such as glass substrates, the mismatch at the interface between the shrunk coatings and underlying substrates is strongly emphasized and this mismatch can increase the possibility of a spontaneous collapse of the coating system, which can bulge or even delaminate from the substrate even without the application of an external load.

Thus, preventing the bulging and delamination phenomena of organic–inorganic hybrid coatings synthesized via the sol–gel route is of utmost interest as it would greatly extend applications of this class of materials. In this respect, many efforts have been made by scientists and practitioners to widen the range of coatings that could be designed and manufactured via the sol–gel route. However, the proposed solutions converged toward the implementation of very thin coatings (i.e., typically a few microns) to reduce the onset of the detrimental stress field by material shrinking and toward the adhesion being mainly improved through the combination of two or more organic–inorganic molecules, some with only mere grafting functionality. Such thin coatings have been used in industrial applications such as for optical, decorative or architectural materials. For example, the large-scale dip coating process to prepare reflective and antireflective layers based on Pd containing TiO_2 or SiO_2/TiO_2 systems has become a well-established technology (Irox, Amiran, Calorex, Schott Co.) [10]. Similarly, antireflective coatings suitable as cover sheets for photovoltaic (PV) cells and collectors have been commercially available from nearly a decade, although their preparation involves a relatively high temperature

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(600 °C) firing process [11,12]. Coatings for decorative and architectural purposes were industrialized by including pigments in the sol–gel design with a range of different features [13,14]. In contrast, the manufacturing of a thin coating excludes any possibility of developing surface overlying materials that could meet the industrial standard for anti-scratch or wear resistant barriers. This fact was confirmed by several experimental results reported in the literature [15]. Han et al. attempted to verify the scratch performance of a sol–gel deposited organic–inorganic hybrid coating material based on TEOS, 3-(trimethoxysilyl) propylmethacrylate and urethane acrylate deposited on a float glass by flow coating with a thickness of approximately 3.5 μm. The ultimate critical load was nearly 2 N beyond which the coatings were found to delaminate [15].

Despite the significant efforts made to produce versatile and industrially sustainable organic–inorganic hybrid coating materials, there are only a handful of practical applications in which these materials are effectively in service. Thus, the present investigation proposes an alternative approach to controlling the shrinkage during post-drying at ambient temperature of thick organic–inorganic hybrid coatings on already “in service” glass. This approach would be extremely beneficial as it would increase the threshold of the maximum thickness beyond which coating bulging and delamination would occur, thus expanding the applicability of organic–inorganic hybrid coatings in industrial domains in which their combined high micro-mechanical performance and wear endurance cannot be ignored. The alternative approach consists of the development of a highly transparent organic–inorganic hybrid material, whose structure is designed on a silicone skeleton with lateral chains consisting of epoxy groups that are cross-linkable with amine-based organofunctional silane hardeners. After cross-linking, the hardener confers both high mechanical and tribological resistance to the coating material. Proper formulations of silicone–epoxy resins were designed and applied with a high thickness (approximately 120 μm) using an automatic drawdown applicator on as-received and sandblasted glass substrates. The process was followed by spontaneous drying to ensure the consolidation of the coatings. Sandblasting was thought to generate a high specific contact area at the coating–substrate interface through the onset of widespread micro-asperities on the glass surface. Such micro-asperities were believed to act as obstacles to the stress field generated by the strong shrinkage phenomenon during the drying/cross-linking of the thick overlaying layer of the silicone–epoxy resin, thus avoiding or delaying the coating failure by bulging or delamination. Characterization of the morphology, visual appearance, micro-mechanical and tribological performance of the coatings was thus performed. The experimental findings revealed that the silicone–epoxy coatings deposited on the sandblasted glass substrate were extremely suitable for protecting the overlying layer from early failure due to scratches or wear phenomena. Accordingly, the coating demonstrated high potential to preserve the initial efficiency of the underlying glass substrate over a long period.

2. Experimental

2.1. Materials

Flat substrates, 3.8 mm thick, 25 × 100 mm^2 wide and cut from a 2 m^2 tempered glass sheet, were coated with a high-solid two-pack silicone–epoxy resin (SILIKOPON EF, Evonik, Essen, Germany) dilutable (1:1) by esters, ketones and glycol ethers and cross-linked with bis (trimethoxysilylpropyl) amine (amine H-equivalent, 335 g/mol) supplied by Evonik (Ameo, Essen, Germany). Thickeners (Tego Viscoplus 3030, Evonik, Essen, Germany) and flow promoters (Tego Flow 370, Evonik, Essen, Germany) were added to the formulation to obtain a homogenous coating thickness through strict control of the mixture rheology.

2.2. Manufacturing process

As received glass substrates were degreased by sonication in 95% EtOH for 30 min. Half of the specimens were sandblasted (6 bar, fine glass beads, sandblasting equipment, 0580, Fervi Srl, Modena, Italy) to coarsen the starting morphology and favor coating adhesion. To remove all glass residuals from the previous process, the substrates were rinsed thoroughly by sonication in demineralized water. The silicone–epoxy formulation was then deposited after dilution (1:1) in acetone on both the as-received and sandblasted glass substrates using an automatic drawdown bar applicator (Automatic Film Applicator L, BYK-Gardner, Geretsried, Germany) equipped with a doctor blade. The resulting coatings were left to cure at ambient temperature for 24 h. After curing, the coating thicknesses were measured using a digital Palmer caliber (293-816, Mitutoyo, Kawasaki, Japan) with a resolution of ±0.001 μm. All coatings with thicknesses falling outside the prescribed range of 120 ± 20 μm were discarded.

2.3. Characterization of the coatings

The morphology of the coatings was recorded using a contact inductive gauge of a CLI profiler (TalySurf CLI 2000, Taylor Hobson, Leicester, UK). An area of 4 × 4 mm^2 was analyzed, and 2000 profiles were stored with a resolution of 1 μm. The data were elaborated using TalyMap 3.1 software (Taylor Hobson, Leicester, UK) to extrapolate the roughness parameters and corresponding 3D maps. The scratch resistance of the hybrid coating was evaluated by constant-load scratch tests (Micro-Combi, CSM Instruments, Peseaux, Switzerland) using two different Rounded Conical Rockwell C diamond indenters with tip radii of 800 and 200 μm and an applied load of 20 N along the 2 mm scratch

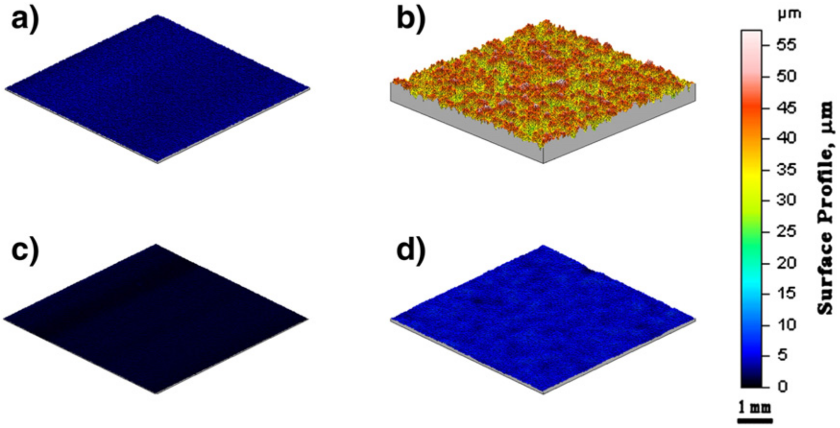

Fig. 1. 3D maps of the as-received and coated glasses: (a) as-received glass, (b) sandblasted glass, (c) as-received coated glass, and (d) sandblasted coated glass.