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# Scratch resistance of brittle thin films on compliant substrates

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**Abstract**

There has been intensive interest in studying the behavior of hard and brittle thin films on compliant substrates under scratch action. The examples include sol–gel protective coatings on plastic optical lenses, safe windows, and flexible electronic devices and displays. Hard ceramic coatings have been widely used to prolong the life of cutting tools and biomedical implants. In this work, the scratch resistance of sol–gel coatings with different amount of colloidal silica on polycarbonate substrates was tested by the pencil scratch test following the ISO 15184 standard. The scratch failure was found to be tensile trailing cracking in the coating and substrate gouging. The indentation hardness, elasticity modulus and fracture toughness of the coatings were determined and correlated to the observed pencil scratch hardness. Based on the analysis, the main factors to improve the scratch resistance are the elasticity modulus, thickness and fracture toughness of the coatings. General consideration for the improvement of scratch resistance of hard coatings on compliant substrates was also discussed.


*Keywords:* Scratch resistance; Pencil scratch test; Hardness; Cracking; Delamination; Elastic modulus; Fracture toughness; Interfacial fracture toughness

## 1. Introduction

Hard protective coatings on compliant substrates have been widely used in applications such as plastic optical lenses, safety windows, machine tools, biomedical implants, and portable electronic displays. These coatings are often produced by physical vapour deposition [1–4], chemical vapour deposition [4–6], and sol–gel coatings [7–10]. The coating properties can be tailored by controlling the deposition parameters and coating composition according to different functional requirements. A simple and quick assessment of the quality of the coatings is by a scratching test. The test imitates the resistance to accidental damage caused by a sharp object during device usage, and can be used as a general assessment of the coating reliability. However, the disadvantage of such a simple test is that there many factors that may affect the outcome of the test, and due to such a complexity, the current understanding is still limited. Most of the existing work is qualitative in nature; attempt in quantitative analysis is scarce. The aim of the current work is to study the scratch behavior of hard and stiff coatings produced on relatively soft and compliant substrates. Examples used are hybrid sol–gel coatings on polycarbonate substrates. The parametric model generated from the work is semi-quantitative and applicable to other hard coating on compliant substrate systems. Such a model reveals the main factors behind scratch resistance and therefore can provide guidelines for designing scratch resistant hard coatings on compliant substrate.

Scratch is a physical action during which a sharp object is pressed onto, and drawn over the surface of the coating simultaneously. The normal load during the test is either kept constant or progressively increased. Progressively increasing scratch load eventually induces a critical point of damage such as coating delamination, coating cracking (in the case of brittle coatings) or whitening (in the case of polymeric coatings) in a single test. In the constant-load test, multiple tests at increased constant-load levels are needed in order to determine the critical scratch load. In any case, the critical load itself or its derivative (e.g. scratch hardness, defined as the load divided by indented area) is used to compare the performance of different coatings. A number of ASTM and ISO standards are available for the scratch test of coatings. ASTM C 1624 [11] describes a standard test method for hard (Vickers hardness HV $\geq$ 5 GPa) ceramic coatings, while ASTM D 7027 [12] is for the evaluation of polymeric coatings and plastics. Nano-scratch of soft coatings is described by ASTM D

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7187 [13]. For sol–gel coatings on polymeric substrates, pencil scratch test described by ISO 15184 [14], or its counterpart by ASTM D 3363 [15] is popularly used by the industry. Both standards were intended for the film hardness assessment of soft coatings such as paints and varnishes. But practically, they were also used on hard, protective sol–gel coatings for optical lenses, automobile topcoats and other sol–gel coatings on polymer substrates [16–19]. The pencil scratch test is a constant-load scratch test, however, it does not require increased constant-load to reach the critical point of failure. Instead, it uses pencil leads of different hardness grades as the scratch stylus, compared to the diamond stylus usually used in most other test standards. By applying the same normal load with indenters of different hardness, a critical pencil lead grade that does not cause damage to the coating is cited as the pencil hardness of the coating concerned.

## 2. Experimental details

A stock solution of 3-glycidoxypropyl trimethoxysilane (GLYMO) and tetraethylorthosilicate (TEOS) was prepared by hydrolyzing them in ethanol (EtOH) and water ($H_2O$) in an acidic solution (HIt, itaconic acid). The molar ratios of the components were: GLYMO:TEOS:EtOH:$H_2O$:HIt = 1.0:1.63:2.19:5.0:0.26. The GLYMO and TEOS were hydrolyzed separately and then mixed together. The mixture solution was stirred for 24 h and used as the base solution for coatings. To this base solution, a colloidal silica solution (Ludox AS-40) was first acidified by HIt to pH 3, and then added as hard filler in different molar ratios of 0.70, 2.08, 4.27, and 5.48. The colloidal silica was first coated with a monolayer of the sol–gel by adding 15 wt.% of the base solution. The purpose was to stabilize the colloidal particles to avoid flocculation when added to the sol. The adsorption of GLYMO onto colloidal silica has been studied by Daniels and Francis [20]. It was found that the maximum adsorption was limited to 2.2 monomer units/$nm^2$. The 15 wt.% used in this study was calculated based on the maximum adsorption on the silica colloidal surface. The prevention of flocculation was observed by us during the preparation of sol–gel solution. Without the addition of GLYMO into the colloidal, the sol–gel solution turned white and never turned back to clear.

The density of the cured un-filled coating was measured to be 1.3 g/$cm^3$, and the volume percentage of the fillers in coating matrix was calculated to be 6.7, 17.6, 30.5 and 36.0 vol.% in the cured coatings, corresponding to the different molar addition of the colloidal silica fillers. The particle size of the silica is about 20 nm, so that the coatings remained transparent after curing. Before dip coating, 0.05 wt.% of ethylenediamine (ED) was added to the coating solution as the cross-linking agent of the epoxy ring in GLYMO.

Polycarbonate (PC) substrates, measured 100 mm × 50 mm × 3 mm, were treated by oxygen plasma (MARCH PX-1000) before coating was applied. The purpose of the plasma treatment was to remove organic contaminations on the PC surface and activate the surface for better wetting and adhesion between the coating and the substrate [21]. The treatment was done at the following conditions: RF power 400 W, pressure 130 mbar, oxygen flow rate 400 sccm, and treatment time 5 min. The pre-treated PC substrates were dip coated with the above solutions in different withdrawal speeds so that the effect of layer thickness on coating's hardness and scratch resistance could be studied. Preliminary calibration found that the coating thickness increased with the withdrawal speeds, as shown in Table 1. With increased silica concentration, the same withdrawal speed gave rise to thicker coatings. This is understandable since the viscosity increases with the filler addition.

After the dip coating, specimens were placed in a bench top furnace for drying and curing. The drying was done at 80 °C for 40 min and curing at 110 °C for 90 min. To achieve thicker coatings (>5–8 μm, depending on the colloidal concentration as shown in Table 1), varying the coating speed proved to be inadequate. Thus multiple coatings were applied. After each coating and curing step, a plasma treatment was carried out before the subsequent layer was applied. This is to avoid mixing of the two layers and to eliminate potential risk of cracking upon curing.

The final thickness of the coating was measured using a profilometer (Talysurf Series 2 Stylus Profilometer) across the uncoated and coated areas on the same specimen. The scratch resistance of the coating was characterized by a commercial pencil hardness tester (Scratch Hardness Tester Model 291, Erichsen Testing Equipment, Germany). The test conformed to the ISO standard 15184 [14], where a vertical force of 7.5 ± 0.1 N was applied at tip of the pencil. The pencil was fixed at 45° angle to the horizontal coating surface as the pencil was moved over the coated specimen. The pencil lead was flattened before the test as specified in the standard. From soft to hard (9B to 9H), the hardest pencil grade that does not cause damage to the coated specimen was termed as the pencil hardness of the coating. We have added a measurement of the tangential force during the pencil scratch test. Effective friction coefficient was given as quotient of the steady-state tangential force over the vertical force. The term "effective friction coefficient" was used to take into account the change of the film surface condition during the test. Therefore it was expected that film damage (e.g. cracking, delamination) would cause an increase in the effective friction coefficient. On the other hand, by the conventional definition, the friction coefficient between a pencil/film friction pair should have a fixed value.

The intrinsic hardness (referred to as indentation hardness thereafter) and Young's modulus of the coatings were measured using a nano-indenter (NanoTest™, Micro Materials Limited, Wrexham, United Kingdom). The nano-indentation was carried in the depth-controlled mode, with depth of the indentation controlled at around 850 nm for all cases. To measure the film fracture toughness, coatings were applied on thinner PC substrates of 200-μm thick and tested by the controlled buckling test method, which was described elsewhere [22–24]. 8–10 samples were tested for each type of coatings. The residual stress caused by curing shrinkage was measured by the curvature method [25] and was taken into consideration in the fracture toughness calculation.