

# A study towards improving mechanical properties of sol–gel coatings for polycarbonate

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## Abstract

Scratch-resistant coatings based on 3-glycidoxypolytrimethoxysilane and tetraethylorthosilicate with a cross-linking agent and different amounts of colloidal silica are prepared on polycarbonate substrates by sol–gel technique. The failure mode of this type of coating on soft plastic substrate under pencil scratch test is studied. It is found that the pencil scratch failure contains a gouge failure under the static pressure and a film cracking failure under the sliding of the pencil tip. The gouge failure is due to the early plastic deformation in the substrate, while the film cracking is due to the tensile stress in the film induced by the sliding and friction of the pencil tip. Factors influencing the static gouge failure and sliding cracking failure are investigated. It is found that the cross-linking agent and colloidal silica filler increase the intrinsic cross-linking, hardness, elastic modulus and fracture toughness of the coating material, therefore, reduce the film cracking tendency; whereas the increased layer thickness and multi-layer coating improve the pencil scratch resistance significantly via delayed plastic deformation in the substrate. Based on these analyses, we conclude that the main factors towards improved pencil scratch resistance are: layer thickness, elastic modulus, fracture toughness and intrinsic hardness of the coating material. Pencil hardness is increased from grade 2B to 5H by adjusting these parameters.

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## 1. Introduction

Transparent polymer materials (e.g. polycarbonate, PC) have been used to replace glasses and metals in a wide range of applications, such as display panels for hand-held electronic devices, compact disks, lightweight eyewear lenses and safety windows [1]. Despite their excellent physical and optical properties, the poor scratch and abrasion resistance has hindered their applications [2–5]. A hard and scratch-resistant protective coating is needed in order to improve the surface characteristics while capitalizing on their desirable bulk properties.

Organically modified silicate (also known as Ormosil) coatings have been extensively explored [6–11]. With the increasing applications in coating lenses [1,12], higher scratch resistance and durability on soft plastic for other protective applications (such as protective film for computer monitors) are required. The major

challenge for heavy loading scratch-resistant coatings is the too soft substrate, which deforms and causes coating's early failure even with a very hard thin coating. A good measure for coating's scratch resistance under heavy load is the pencil hardness, which can be tested by the ASTM standard D3363-00 [13] method and well accepted by the industry. With the increasing demands for higher scratch resistance and durable protective coatings for plastics, a good understanding on the pencil scratch failure mode and the major material properties influencing the pencil hardness is essential. The scratching damage of a thin coating on soft substrate under a pencil lead is a complex phenomenon. Boilot et al. [14] classified two categories of scratch behaviour: (1) fine scratches due to very small particles, (2) visible and wide cracks due to bigger particles. The latter is more related to the pencil scratch discussed in this paper. In this case, both substrate and coating properties contribute to the total scratch resistance. The ability of the coating to deform with the substrate is crucial. However, we have found that the failure mode under pencil scratching contains more than one failure mechanism, which needs a special study apart from the classical scratch mechanism.

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This paper aims to analyse the failure mechanism under pencil scratching and study the influence of coating composition, the use of cross-linking agent and silica filler on the material's elastic modulus, fracture toughness, intrinsic hardness and the pencil grade. Although sol–gel coatings containing 3-glycidoxypropyl trimethoxysilane (GLYMO) and tetraethylorthosilicate (TEOS) and fillers have been reported [15–18], no direct analyses on failure mode of pencil scratching and the influencing factors towards pencil scratch resistance have been published.

## 2. Experimental details

### 2.1. Formulation of coating solutions

A stock solution of GLYMO-TEOS was prepared by hydrolysing them in ethanol (EtOH) and water (H<sub>2</sub>O) in an acidic solution (HIt, Itaconic acid). The molar ratios of the components were: GLYMO:TEOS:EtOH:H<sub>2</sub>O:HIt=1:1.63:2.19:5:0.26. The GLYMO and TEOS were hydrolysed 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), 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: 0.7, 2.08, 4.27 and 5.48. The colloidal silica was first coated with a monolayer of the sol–gel material by adding a small amount of solution A (15 wt.%). This was to stabilize the colloidal particles avoiding flocculation when added to the sol. After measuring the density of the cured un-filled coating (1.3 g/cm<sup>3</sup>), we calculated the volume percent of the filler in coating matrix, so that we have a better understanding of the filler distribution in the final coating layer. The above molar ratios of silica correspond to 6.7, 17.6, 30.5 and 36.0 vol.% in the cured coating matrix. Since the particle size of the silica is about 20 nm, the transparency of the coating was unaffected. Just before the dip coating process, 0.05 wt.% of ethylenediamine (ED) was added to the coating solution as the cross-linking agent of the epoxy ring in GLYMO.

### 2.2. Substrate preparation

Polycarbonate substrates, measured 100 mm × 50 mm × 3 mm, were supplied with a layer of protective film, which was peeled off before oxygen plasma treatment. The treatment was carried out just before the dip coating steps for all specimens used in the current work. The purpose for such a treatment is to remove organic contaminations on the PC surface and activate the surface for better wetting and adhesion between the coating and the substrate [19]. The treatment was done at the following conditions: radio frequency power 400 W; pressure 1.33 × 10<sup>4</sup> Pa; oxygen flow rate 400 cm<sup>3</sup>/min, and treatment time 5 min.

### 2.3. Coating and characterization

The pre-treated PC substrates were dip coated with the above solutions in different withdrawal speeds to study the effect of layer thickness on coating's hardness and scratch resistance. For thicker coatings (> 10 μm), 2 or 3 layers were applied. A curing step and a plasma treatment were carried out before the

subsequent layer was applied. This is to avoid merging of the two layers and cracking upon curing due to too much shrinkage. 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.

The 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 adhesion between coating layer and substrate was assessed using the cross-cut tape test according to ASTM D 3359-02 [20] standard test method. The scratch resistance (termed as pencil hardness thereafter) of the coating was characterized by a commercial pencil hardness tester (Scratch Hardness Tester Model 291, ERICHSEN TESTING EQUIPMENT). The test conforms to ASTM Standard D3360-00 [13], where a vertical force of 7.5 ± 0.1 N was applied at 45° angle to the horizontal film surface as the pencil is moved over the coated specimen. Meanwhile the intrinsic hardness (referred to as nano-indentation hardness thereafter) and Young's modulus of the coatings were measured using a nano-indenter (NanoTest™). A Berkovitch tip (with a three-sided pyramid geometry) was employed. The load was controlled below 0.5 mN and the depth of the indentation was controlled to be less than 1/10 of the coating thickness in order to minimize the effect due to the substrate. The resultant displacement of the indenter into the surface is monitored with a sensitive capacitive transducer and displayed in real time as a function of load. The hardness and elastic modulus are then calculated by the established equations [21] by the software. To measure the film fracture toughness, coatings were applied on a PC thin substrate of 200 μm thick and tested by the controlled buckling test (tension) following our developed methods reported in [22–24]. Critical energy release rate,  $G_{IC}$ , was obtained as the measure of film toughness. The residual stress caused by curing shrinkage was calibrated in the calculation of the film toughness. The method to measure the residual stress is given in Ref. [25]. The chemical bonds in the coating layers were analysed by Fourier Transform Infrared Spectroscopy (FTIR, Bio-Rad Excalibur Series). Infrared absorption spectra of the coatings in the range of 4000–600 nm wavelengths were analysed by FTIR using the attenuated total reflectance (ATR, with Ge crystal) method. An infrared radiation is passed through an infrared transmitting crystal with a high refractive index, allowing the radiation to reflect within the ATR element several times. The absorption of radiation is related to fundamental vibrations of the chemical bonds, therefore, provides information related to the presence or absence of specific functional groups in the coatings.

## 3. Results and discussion

### 3.1. Effect of cross-linking agent

Coating solution B was prepared by adding a few drops (about 0.05 wt.%) of ethylenediamine (ED) to the base solution A (without colloidal silica filler). Ethylenediamine acts as an epoxy-curing agent, which opens the epoxy ring of GLYMO monomers and increases cross-linking density of the coating [6]. Fig. 1

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