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A parametric study on processing of scratch resistant hybrid sol–gel silica coatings on polycarbonate

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ABSTRACT

Scratch resistant silica-based hybrid coatings on polycarbonate substrates were formed by dip-coating of acid-catalyzed tetramethyl orthosilicate (TMOS):diethylenetriamine (DETA):H_2O:2-propanol sols. The sol formulation and dip-coating process parameters on microstructural and performance properties—here optical transmittance and scratch resistance—of the coatings were evaluated. The effect of water quantity, total aqueous component (H_2O + 2-propanol) amount and relative proportion of TMOS:DETA on film formation behavior and on performance properties have been investigated in a systematic way. It was found that an effectively polymerized hybrid coating rich in silica content, as realized for high TMOS or abundant water containing sols, resulted in defective films with microcracking and adhesion problems. High 2-propanol content on the other hand led to incomplete film coverage. It was shown that 5 ± 1 μm-thick, scratch resistant and pristine coatings exhibiting a visible transmittance of 86–88% can be formed with a single deposition process using an optimized sol formulation of TMOS:DETA:H_2O:2-propanol of 30:30:20:20 in wt.%. Meanwhile, the hardness of the PC has increased from an initial value of 13.9 ± 2 to 70 ± 25 (Vickers hardness, HV1) upon coating. A surface hardness approaching to 250 HV1 can be attained by for the thicker coatings (8 ± 1 μm) deposited at higher withdrawal speeds. However, such films suffered from non-uniform coverage and poor surface/optical quality. The transmittance values reduced by a factor of 20–30% for thicker coatings.

1. Introduction

Polycarbonate (PC) has been widely used as a thermoplastic engineering material due to its high optical transparency, impact resistance, thermal stability and lightweight. However, poor scratch and wear resistance limit utilization of PC in many mechanically aggressive conditions/applications. A variety of sophisticated processing techniques have been employed for producing scratch resistant transparent protective coatings on this versatile substrate [1–3]. The main conventional technologies include plasma-enhanced chemical vapor deposition [4–6], hallow cathode activated electron beam evaporation [7], hybrid processes between rf-sputtering and chemical vapor deposition [8,9], and aqueous coating processes [10–12].

There are two approaches for obtaining scratch resistant surface finish on polymeric substrates by aqueous processing routes. The polymer solutions containing homogenously dispersed nanoparticles can be applied as a coating (*ex situ approach*). Coatings containing colloidal silica, zirconia, alumina, metallic and semi-metallic nanoparticles in epoxy or functionalized organic networks were shown to enhance scratch resistance of soft substrates [13–16]. However, the main challenge in this approach is dispersing the nanoparticles in the organic matrix [17–20]. Due to strong attractive forces between nanoparticles, agglomerates or chunks of stiff particles can form in the solution and/or coating which degrades both mechanical and optical performance [21].

Alternatively, scratch resistance coatings can be prepared using hybrid sol–gel approaches by allowing simultaneous hydrolysis/condensation silicon alkoxides and organics (*in situ approach*) [22–25]. Such inorganic–organic hybrid coatings also known as organically modified silicates (Ormosils) have been extensively used for improving intrinsic poor scratch resistance of PC [26–35]. The preparation of silica-based hybrid coatings by the sol–gel process requires careful control of the hydrolysis and condensation of silicon alkoxide. Various parameters such as organic:silicon alkoxide ratio, solvent and water amount can be used to regulate the interactions between the inorganic and organic components affecting the final microstructure and properties as well as reproducibility of the coating process.

The objective of this study was to study the effect of sol formulation-related parameters on scratch resistance and optical properties of an Ormosil coating formed on planar PC. The coating sol mainly consisted of diethylenetriamine (DETA) and tetramethyl orthosilicate (TMOS) as primary organic modifier and silica network former, respectively. A parametric experimental optimization work has been conducted to elucidate the technical/practical processing parameters for realization

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of crack-free and hard large area surface finish on polycarbonate without altering its intrinsic optical quality by employing a single step dip-coating operation. The mechanical properties of the coatings were determined using combination of different analytical techniques including microhardness and abrasion tests. In addition, the influence of dip-coating practice (withdrawal speed) on surface coverage, transmittance, microstructure and performance properties of the coating has been reported.

2. Experimental studies

2.1. Materials

PC discs (30 mm in diameter) processed from Macrolon (Bayer, Germany) granules by injection molding have been used as substrate. Diethylenetriamine ($(NH_2CH_2CH_2)_2NH$ or DETA, 98%) and 3-aminopropyl triethoxysilane ($Si(OC_2H_5)_3$ $(CH_2)_3NH_3$ or APS, 98%) were obtained Merck KGaA (Darmstadt, Germany). 3-triethoxysilyl propyl isocyanate ($(C_2H_5O)_3Si(CH_2)_3NCO$ or ICPTES, 95%), tetramethyl orthosilicate ($Si(OCH_3)_4$, or TMOS, 98%), 2-propanol ($(CH_3)_2CHOH$, 99.5%, anhydrous) and glacial acetic acid (CH_3CO_2H, 100%) were obtained from Sigma-Aldrich (Steinheim, Germany). All chemicals were used without any further purification.

2.2. Preparation of polycarbonate substrates

PC discs were cut in half and the chips were cleaned by air-blowing. Then, PC substrates were washed with 2-propanol five times and dried at 25 ± 1 °C. In order to improve the adhesion of hybrid coatings on PC substrates silanization treatment was applied. Silanization solution was prepared by dissolving 1 g APS in 100 mL 2-propanol. PC substrates were coated with APS/2-propanol solution using a dip-coater (Bungard RDC-15, Germany) with a withdrawal speed of 3.0 mm/s. The silanized substrates were dried at 25 ± 1 °C and kept in vacuum desiccators prior to hybrid coating application.

2.3. Preparation of hybrid coating sol

The organic component of the hybrid coating was prepared by chemical modification of DETA with triethoxysilyl groups, via urea linkages. Such functionalization with hydrolyzable triethoxysilyl groups enables integration between organic groups and hydrated methoxy groups of TMOS during polymerization leading to hybridization of silica network. This modification was achieved by mixing 8.6 g DETA and 33 g 2-propanol in the jacketed round bottom flask cooled to 1 °C with the help of a water bath. Mixing operation was done by magnetic stirrer for 30 min and stirring speed was 850 rpm. Then, 66 g of ICPTES was added drop-wise into DETA/2-propanol solution with an automatic syringe pump with dropping speed of 30 mL/h. After the addition of 3-ICPTES, the jacketed round bottom flask was sealed and solution was mixed with magnetic stirrer at a rate of 900 rpm for 10 h. Then, hybrid (Ormosil) coating sol was prepared by mixing functionalized-DETA, TMOS, 2-propanol, de-ionized (DI) water and acetic acid. The formulations of all hybrid coating are given in Table 1. For preparation of final hybrid coating sol, first the required amount of functionalized-DETA, TMOS and 2-propanol were mixed in a 50 mL beaker and continuously stirred. Then, acetic acid solution (0.14 M) was added into the sol to attain a final approximate pH value of 5. Slightly acidic sol condition was chosen to avoid fast condensation and thereby obtain stable sols for coating application. The coating sols were typically aged for 4 h in ambient atmosphere prior to coating process.

Table 1
Formulations of organic–inorganic hybrid coating sols.

Sol formulation	DETA (wt.%)	TMOS (wt.%)	2-Propanol (wt.%)	H_2O (wt.%)
R1	30	30	30	10
R2	30	30	20	20
R3	30	30	10	30
R4	15	15	35	35
R5	40	10	25	25
R6	10	40	25	25

2.4. Preparation of hybrid coatings

The silanized PC substrates were dip-coated with hybrid coating sols using a Bungard (RDC-1 Model Germany) with a typical withdrawal speed of 3 mm/s. In addition, selected hybrid sol formulation (R2 of Table 1) was also deposited using various dip-coating withdrawal speeds, at 0.6, 1, 2, 3, 4, 5 and 6 mm/s. After dip-coating finished samples were dried at 25 ± 1 °C to remove residual solvents and then pre-cured in air at 60 °C for 30 min, and finally cured at 135 °C for 4 h.

2.5. Characterization

The optical performance of the bare (uncoated) and coated PC samples was performed by diffuse reflectance ultraviolet–visible (UV-Vis) spectroscopy (using Varian-Cary 100 Bio) in the wavelength range of 375 to 800 nm at room temperature. Ambient air measurements were used for background correction.

The morphology of the coatings was investigated using an Olympus PMEU-F200 model optical microscopy. Micropublisher 3.3 RTV camera was used to capture microstructural images of the hybrid coatings. Further microstructural examination was performed on a FEI Quanta 400F model field emission scanning electron microscopy (FESEM). The samples employed in SEM investigations were coated with 10 nm thick gold layer prior to examination.

The hardness (in Vickers, HV1) of the coatings was measured by a Shimadzu HMV microhardness tester, at a standard load of 9.81 g and 10 s loading time. Multiple (five) indentation size measurements were accomplished and imaging of the indents was performed using optical microscope.

The scratch resistance of the coatings was evaluated using severe brass abrasion tester (Eraser Test) according to MIL-E-12397B standard. The eraser part (scratcher) of the testing equipment was a high grade composite rubber containing abrasive fillers (50 vol.%). The abrasion test was conducted by applying a constant load (1134 g) to the eraser when it is in contact with the sample surface. Then, the eraser was rubbed to the sample surface and ten different 3-cm long straight strokes were applied. All the strokes were made along the full path (3 cm) without any interruption. Finally, tested samples were washed with DI-water, dried by air-blowing and scratch marks were examined with optical microscopy.

Veeco Dektak M6 profilometer was employed for coating thickness measurements. Scan distance of the stylus was 10 mm, a span length enabling track of a step between a bare and coated region of partially coated PC substrates which were specifically produced for thickness measurements. The average film thickness values were determined after three measurements at a scan speed of 50 s.

The gelation of hybrid sols was monitored by visual examination. The complete gelation was considered as the physical state, where the gelling product reached an observed viscosity preserving its shape and remaining firm without any distortion when tilted 45° angle. The sol samples in test tubes practically enabled such examination.

3. Results

The gelation time for all sol formulations is listed in Table 2 together with the thicknesses of the coatings produced from the respective sols. The withdrawal speed was 3 mm/s for all coating operations. The gelation times vary in the range of 6–30 h, and coating thickness was in the order of 3–20 μm, approaching to only several microns for some